Abstract:
The present invention is related to a method for producing a olefin polymerization catalyst component, which method comprises the steps of (a) halogenating a magnesium compound of the formula MgR²⁺ wherein R²⁺ is an alkoxide or aryloxide group and wherein R²⁺ is an alkoxide or aryloxide group or halogen, with a tetravalent titanium halide in the presence of a halohydrocarbon and an activator; to form a first intermediate product; (b) contacting the intermediate product with a mixture of a tetravalent titanium halide and an internal electron donor; wherein step (b) comprises two sub steps (b1) and (b2); (b1) contacting the first intermediate product with a mixture of a tetravalent titanium halide and an internal electron donor; to obtain a second intermediate product; and (b2) contacting the second intermediate product with a tetravalent titanium halide to obtain a third intermediate product; and (c) washing the third intermediate product with an inert hydrocarbon liquid. With this novel and inventive method the properties of the polymer that is observed with the resulting procatalyst may be tuned.
PROCESS FOR PREPARING A PROCATALYST FOR POLYMERIZATION OF OLEFINS

The present invention is related to a method for producing a olefin polymerization catalyst component, which method comprises the steps of halogenating a magnesium compound of the formula MgR'R" wherein R' is an alkoxide or arylxide group and wherein R" is an alkoxide or arylxide group or halogen, with a tetravalent titanium halide in the presence of a halohydrocarbon and an internal electron donor. Such catalyst systems are generally referred to as "Ziegler-Natta" catalysts comprising a transition metal-containing solid catalyst compound (also typically referred to as a procatalyst); an organometallic compound (also typically referred to as a co-catalyst) and optionally one or more electron donor compounds (e.g. external electron donors).

Such a process is for example known from US 4,414,132 and US 4,535,068 wherein a magnesium compound, such as magnesium diethoxide is reacted with a titanium halide compound in the presence of a halohydrocarbon and e.g. ethyl benzoate or p-methyl toluate as internal donor and moreover an acid halide, such as benzyol chloride. A disadvantage of said methods is that benzyol chloride is a toxic compound and should be avoided. Moreover, said method does not sufficiently allow the tuning of the procatalyst in such a manner that the properties of the resulting product may be tuned.

It is an object of the present invention to provide a novel method that leads to phthalate free procatalyst. It is another object of the present invention to provide a novel method that is relatively easy. It is another object of the present invention to provide a novel method that leads to procatalyst that has a high productivity. It is another object of the present invention to provide a novel method that provides an increased control of MWD, XS, and/or hydrogen response by means of tuning the process parameters.

**Summary of the present invention**

The present invention relates to a method for producing an olefin polymerization catalyst component, which method comprises the steps of: (a) halogenating a magnesium compound of the formula MgR'R" wherein R' is an alkoxide or arylxide group and wherein R" is an alkoxide or arylxide group or halogen, with a tetravalent titanium halide in the presence of a halohydrocarbon and an activator; to form a first intermediate product; (b)
contacting the first intermediate product with a mixture of a tetravalent titanium halide and an internal electron donor, wherein step (b) comprises two sub steps (b1) and (b2):

(b1) contacting the first intermediate product with a mixture of a tetravalent titanium halide and an internal electron donor; to obtain a second intermediate product; and

(b2) contacting the second intermediate product with a tetravalent titanium halide; to obtain a third intermediate product; and (c) washing the third intermediate product with an inert hydrocarbon liquid to obtain a catalyst component;

wherein the internal donor is preferably represented by a compound according to formula A:

![Formula A](image)

wherein each R^8 group is independently a linear, branched or cyclic hydrocarbyl group selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 30 carbon atoms; R^1, R^2, R^3, R^4, R^5, and R^6 are each independently selected from hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; R^7 is a hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, alkoxycarbonyl or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; N is nitrogen atom; O is oxygen atom; and C is carbon atom; or

wherein the internal donor is preferably represented by a compound according to formula B:
wherein each $R^{80}$ group is independently a linear, branched or cyclic hydrocarbyl group selected from alkyl, alkenyl, aryl, aralkyi, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 30 carbon atoms; $R^{81}, R^{82}, R^{83}, R^{84}, R^{85}$, and $R^{86}$ are each independently selected from hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyi, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; $R^{87}$ is a hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyi, alkoxy carbonyl or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; $N$ is nitrogen atom; $O$ is oxygen atom; and $C$ is carbon atom.

In the present invention, step (b) comprises two sub steps (b1) and (b2): (b1) contacting the first intermediate product with a mixture of a tetravalent titanium halide and an internal electron donor; to obtain a second intermediate product; and (b2) contacting the second intermediate product with a tetravalent titanium halide to obtain a third intermediate product; and wherein step (c) is: (c) washing the third intermediate product with an inert hydrocarbon liquid to obtain a procatalyst.

In an embodiment, the activator is a monoester, preferably a benzoate ester, more preferably ethylbenzoate.

In an embodiment, the internal donor is represented by a compound according to the formula A:
Formula A

\[
\text{O} \quad \text{C} \quad \text{O} \quad R_8 \quad \text{R}_3 \quad \text{R}_4
\]

\[
\text{R}_1 \quad \text{R}_2 \quad \text{R}_5 \quad \text{R}_6
\]

\[
\text{N} \quad \text{R}_7 \quad \text{C} \quad \text{O} \quad \text{R}_3
\]

wherein each \( R^8 \) group is independently a linear, branched or cyclic hydrocarbyl group selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 30 carbon atoms; \( R^1 \), \( R^2 \), \( R^3 \), \( R^4 \), \( R^5 \), and \( R^6 \) are each independently selected from hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \( R^7 \) is a hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, alkoxy carbonyl or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \( N \) is nitrogen atom; \( O \) is oxygen atom; and \( C \) is carbon atom; most preferably wherein said compound according to Formula A is

![Chemical structure](attachment:image.png)

4-[benzoyl(methyl)amino]pentan-2-yl benzoate (AB).

In this embodiment, in the compound according to Formula A \( R^7 \) is a hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, alkoxy carbonyl or alkylaryl groups, and one or more combinations thereof. In a preferred embodiment, \( R^7 \) is a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, alkoxy carbonyl or alkylaryl groups, and one or more combinations thereof. In other words, in a preferred embodiment \( R^7 \) is not hydrogen.
In an embodiment, the internal donor is represented by a compound according to the formula B:

\[
\begin{align*}
\text{Formula B} \\
\end{align*}
\]

wherein each \(R^{80}\) group is independently a linear, branched or cyclic hydrocarbyl group selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 30 carbon atoms; \(R^{81}, R^{82}, R^{83}, R^{84}, R^{85}\), and \(R^{86}\) are each independently selected from hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \(R^{87}\) is a hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, alkoxy carbonyl or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \(N\) is nitrogen atom; \(O\) is oxygen atom; and \(C\) is carbon atom; most preferably

\[
\begin{align*}
\end{align*}
\]

wherein said compound according to Formula B is

\[
\text{ethyl (4-((ethoxycarbonyl)oxy)pentan-2-yl)(methyl)carbamate (AB-OEt).}
\]

In an embodiment, the magnesium compound is a dialkoxy magnesium compound, preferably diethoxymagnesium.

In an embodiment, the tetravalent titanium compound is a titanium tetrahalide, preferably \(\text{TiCl}_4\) and/or wherein the same tetravalent titanium compound is used in each of the steps.
In an embodiment, the halohydrocarbon is chlorobenzene. In an embodiment, the inert hydrocarbon liquid is an alkane, preferably isopentane or n-heptane.

In an embodiment, the activator is ethylbenzoate, wherein the internal donor is 4-[benzoyl(methyl)amino]pentan-2-yl benzoate (AB), wherein the magnesium compound is diethoxymagnesium, wherein the tetravalent titanium compound for each step is TiCU, wherein the halohydrocarbon is chlorobenzene, wherein the inert hydrocarbon liquid is an alkane.

In an embodiment, the activator is ethylbenzoate, wherein the internal donor is ethyl (4-((ethoxycarbonyl)oxy)pentan-2-yl)(methyl)carbamate (AB-OEt), wherein the magnesium compound is diethoxymagnesium, wherein the tetravalent titanium compound for each step is TiCU, wherein the halohydrocarbon is chlorobenzene, wherein the inert hydrocarbon liquid is an alkane.

Definitions
The following definitions are used in the present description and claims to define the stated subject matter. Other terms not cited below are meant to have the generally accepted meaning in the field.

"internal donor" or "internal electron donor" or "ID" as used in the present description means: an electron-donating compound containing one or more atoms of oxygen (O) and/or nitrogen (N). This ID is used as a reactant in the preparation of a solid procatalyst.

"activator" as used in the present description means: an electron-donating compound containing one or more atoms of oxygen (O) and/or nitrogen (N) which is used to during the synthesis of the procatalyst prior to or simultaneous with the addition of an internal donor.

"external donor" or "external electron donor" or "ED" as used in the present description means: an electron-donating compound used as a reactant in the polymerisation of olefins. An ED is a compound added independent of the procatalyst.
"procatalyst" as used in the present description have the same meaning: a component of
a catalyst composition (also called "catalyst component" in this description) generally
comprising a solid support, a transition metal-containing catalytic species and optionally
one or more internal donor.

"halide" as used in the present description means: an ion selected from the group of: fluoride
(F-), chloride (Cl-), bromide (Br-) or iodide (I-).

"alkoxide" or "alkoxy" as used in the present description means: a functional group or side-
chain obtained from a alkyl alcohol. It consist of an alkyl bonded to a negatively charged
oxygen atom, "alkyl" as used in the present description means: an alkyl group being a
functional group or side-chain consisting of carbon and hydrogen atoms having only single
bonds. An alkyl group may be straight or branched and may be un-substituted or
substituted. An alkyl group may also comprise alkenyl or alkylaryl groups.

"aryloxe" or "aryloxy" or "phenoxy" as used in the present description means: a functional
group or side-chain obtained from an aryl alcohol. It consist of an aryl bonded to a negatively
charged oxygen atom, "aryl" as used in the present description means: an aryl group being a
functional group or side-chain derived from an aromatic ring. An aryl group and may be
un-substituted or substituted with straight or branched hydrocarbyl groups. An aryl group
also encloses alkaryl groups wherein one or more hydrogen atoms on the aromatic ring
have been replaced by alkyl groups.

"MWD" or "Molecular weight distribution" as used in the present description means: the
same as "PDI" or "polydispersity index". It is the ratio of the weight-average molecular weight
(Mw) to the number average molecular weight (Mn), viz. Mw/Mn, and is used as a measure
of the broadness of molecular weight distribution of a polymer. Mw and Mn are determined
by GPC using a Waters 150 °C gel permeation chromatograph (GPC) combined with a
Viscotek 100 differential viscosimeter; the chromatograms were run at 140 °C using 1,2,4-
trichlorobenzene as a solvent; the refractive index detector was used to collect the signal
for molecular weights.
"XS" or "xylene soluble fraction" or "CXS" or "cold soluble xylene fraction" as used in the present description means: the weight percentage (wt.%) of soluble xylene in the isolated polymer, measured according to ASTM D 5492-10.

"d50" as used in the present description means: the Particle Size Distribution D50 or median diameter or medium value of the particle size distribution and is measured using Malvern SCIROCOCO 2000 laser scattering detector according to ASTM D 4464-15.

"production rate" or "yield" as used in the present description means: the amount of kilograms of polymer produced per gram of procatalyst consumed in the polymerization reactor per hour, unless stated otherwise.

Unless stated otherwise, when it is stated that any R group is "independently selected from" this means that when several of the same R groups are present in a molecule they may have the same meaning of they may not have the same meaning. For example, for the compound $R_2M$, wherein $R$ is independently selected from ethyl or methyl, both R groups may be ethyl, both R groups may be methyl or one R group may be ethyl and the other R group may be methyl.

**Detailed description of the present invention**

As discussed above the present invention relates to a method which comprises the steps of:

(a) halogenating a magnesium compound of the formula Mg'R'R" wherein R' is an alkoxide or aryloxide group and wherein R" is an alkoxide or aryloxide group or halogen, with a tetravalent titanium halide in the presence of a halohydrocarbon and an activator; to form a first intermediate product;

(b) contacting the first intermediate product with a mixture of a tetravalent titanium halide and an internal electron donor; wherein step (b) comprises two sub steps (b1) and (b2):

(b1) contacting the first intermediate product with a mixture of a tetravalent titanium halide and an internal electron donor; to obtain a second intermediate product; and

(b2) contacting the second intermediate product with a tetravalent titanium halide to obtain a third intermediate product; and
(c) washing the third intermediate product with an inert hydrocarbon liquid to obtain a catalyst component;

wherein the internal donor is preferably represented by a compound according to formula A:

\[
OCOR_8
\]

\[
R_3\quad R_4
\]

\[
R_1\quad R_2
\]

\[
R_5\quad R_6
\]

\[
NR_7COR_3
\]

Formula A

wherein each \(R^8\) group is independently a linear, branched or cyclic hydrocarbyl group selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 30 carbon atoms; \(R^1, R^2, R^3, R^4, R^5,\) and \(R^6\) are each independently selected from hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \(R^7\) is a hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, alkoxy carbonyl or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \(N\) is nitrogen atom; \(O\) is oxygen atom; and \(C\) is carbon atom; or

wherein the internal donor is preferably represented by a compound according to formula B:

\[
OR_{80}
\]

\[
R_{83}\quad R_{84}
\]

\[
R_{81}\quad R_{82}
\]

\[
R_{85}\quad R_{86}
\]

\[
NR_{87}OR_{80}
\]

Formula B
wherein each \( R^8 \) group is independently a linear, branched or cyclic hydrocarbyl group selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 30 carbon atoms; \( R^1, R^2, R^3, R^4, R^5, \) and \( R^6 \) are each independently selected from hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \( R^7 \) is a hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, alkoxy carbonyl or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \( N \) is nitrogen atom; \( O \) is oxygen atom; and \( C \) is carbon atom.

The present inventors have observed that the use of the combination of an activator (preferably a monoester activator) and internal donor (preferably according to Formula A or B) in the process, an activator during step (a) and an internal donor during step (b) eliminates the need to add an acid halide, such as benzoyl chloride, during step (b) thereby making the process more environmentally friendly and more safe and allows the process to be carried out on a larger scale. Each of the steps of the process is discussed in more detail below.

**STEP (a)**

Step (a) relates to halogenating a magnesium compound of the formula \( \text{MgR}'R'' \) wherein \( R' \) is an alkoxide or aryloxide group and wherein \( R'' \) is an alkoxide or aryloxide group or halogen, with a tetravalent titanium halide in the presence of a halohydrocarbon and an activator; to form a first intermediate product.

Examples of suitable magnesium compounds of the formula \( \text{MgR}'R'' \) wherein \( R' \) is an alkoxide or aryloxide group and wherein \( R'' \) is an alkoxide or aryloxide group or halogen are disclosed in US 4,535,068, column 4, lines 11-34 and in US 4,414,132 column 2, lines 33-50 which sections are incorporated by reference.

In an embodiment, the magnesium compound is according to \( \text{MgR}'R'' \) wherein \( R' \) is an alkoxide or aryloxide group and \( R'' \) is an alkoxide or aryloxide group, most preferably \( R'=R'' \).

In an embodiment, the magnesium compound is a dialkoxy magnesium compound wherein, in the formula of \( \text{MgR}'R'' \), \( R' \) is an alkoxide and \( R'' \) is an alkoxide, most preferably \( R'=R'' \). In
an embodiment, the magnesium compound is diethoxymagnesium, wherein \( R' = R'' \) = ethoxide (viz. -OCH\(_2\)CH\(_3\)). In an embodiment, \( R' \) may comprise between 1 and 20 carbon atoms. In an embodiment, \( R'' \) may comprise between 1 and 20 carbon atoms.

Suitable examples of tetravalent titanium compounds are disclosed in US 4,535,068, column 4, lines 53-58 and in US 4,414,132 column 3, lines 3-8 which sections are incorporated by reference. Examples are: dialkoxy-titanium dihalides, alkoxy-titanium trihalides, phenoxy-titanium trihalides and titanium tetrahalides. In an embodiment, the tetravalent titanium compound is a titanium tetrahalide, preferably TiCU.

Suitable examples of the halohydrocarbon are disclosed in US 4,535,068, column 4, line 59 - column 5, line 9 and in US 4,414,132 column 3, lines 10-25 which sections are incorporated by reference. In an embodiment, the halohydrocarbon is an aromatic halohydrocarbon, such as (di)chlorobenzene. In an embodiment, the halohydrocarbon is chlorobenzene. In addition to said halohydrocarbon an inert diluent or solvent may also be present. The same inert solvents as used in step (c) may also be used here.

The ratio between the amount of titanium compound and halohydrocarbon may for example between 25:75 and 75:25, such as between 60:40 and 40:60 or even 50:50 (all in v/v).

During step (a) the halogenation of magnesium is preferably carried out in such a manner that magnesium halide is formed in which the atomic ratio of halogen to magnesium is at least 1.2, preferably at least 1.5. The molar ratio of the magnesium compound and the titanium compound during step (a) are in an embodiment between 0.005 : 1 and 2 : 1, preferably between 0.01 : 1 to 1 : 1.

In an embodiment, the activator is a monoester, preferably a benzoate ester, more preferably ethylbenzoate. More monoesters are discussed in WO 2014/18164, page 7, line 28 to page 8 lines 26, which section is incorporated by reference. The amount of the activator may be such that the content of the activator in the procatalyst is between 1 and 7 wt.%, such as between 2 and 5 wt.% based on the procatalyst weight.
The molar ratio of activator to magnesium compound during step (a) may for example between 0.05: 1 and 0.5 : 1, preferably between 0.1 : 1 and 0.3 : 1, more preferably between 0.1 : 1 and 0.3 : 1.

Step (a) may be carried out at temperatures ranging e.g. between 60 °C to 140 °C, preferably between 80 °C to 120 °C, more preferably between 100 °C to 120 °C, such as 110 °C. In an embodiment, the starting compounds are first mixed at room temperature, e.g. 25 °C, and subsequently heated.

Step (a) may be carried out for a duration of between 0.1 and 6 hours, preferably between 0.5 and 3.5 hours, such as between 0.5 and 1.0 hour.

After step (a) preferably an additional step is carried out, being step (a'): step (a') filtrating the reaction mixture obtained in step (a) to obtain a solid product, being the first intermediate reaction product. The retentate is the first intermediate reaction product. The filtrate may be discarded. Instead of filtrating step (a') may also involve decanting.

**STEP (b)**

Step (b) relates to contacting the first intermediate product with a tetravalent titanium halide and an internal electron donor. There are several embodiments to this step that will be discussed below.

Suitable examples of tetravalent titanium compounds are disclosed in US 4,535,068, column 4, lines 53-58 and in US 4,414,132 column 3, lines 3-8 which sections are incorporated by reference.

In an embodiment, the same tetravalent titanium compound is used in each of the steps (a) and (b). Examples are: dialkoxy-titanium dihalides, alkoxy-titanium trihalides, phenoxy-titanium trihalides and titanium tetrahalides. In an embodiment, the tetravalent titanium compound is a titanium tetrahalide, preferably TiCU. In an embodiment, TiCU is used in each of the steps (a) and (b).
Suitable examples of the halohydrocarbon are disclosed in US 4,535,068, column 4, line 59 - column 5, line 9 and in US 4,414,132 column 3, lines 10-25 which sections are incorporated by reference. In an embodiment, the halohydrocarbon is an aromatic halohydrocarbon, such as (di)chlorobenzene. In an embodiment, the halohydrocarbon is chlorobenzene.

The ratio between the amount of titanium compound and halohydrocarbon may for example between 25:75 and 75:25, such as between 60:40 and 40:60 or even 50:50 (all in v/v).

The titanation treatments increase the content of titanium in the solid catalyst. Preferably, the final molar ratio of tetravalent titanium to magnesium in the procatalyst obtained is between 0.005 to 3.0, preferably from 0.02 to 1.0.

In an embodiment, the final tetravalent titanium content is between 1.5 and 5.5 wt.%, preferably between 2.0 and 4.5 wt.% based on the procatalyst weight.

Step (b) may be carried out at temperatures ranging e.g. between 60 °C to 140 °C, preferably between 80 °C to 120 °C, more preferably between 100 °C to 120 °C, such as 110 °C.

Steps (b), or (b1) or (b2) may be carried out for a duration of between 0.1 and 6 hours, preferably between 0.25 and 2 hours, for example 0.3 to 1.0 hour, such as 0.5 hours.

After step (b) (or after both of steps (b1) and (b2) preferably an additional step is carried out, being respectively step (b')/(b1')/(b2'):

- step (b') filtrating the reaction mixture obtained in step (b) to obtain a solid product, being the second intermediate reaction product. The retentate is the second intermediate reaction product. The filtrate may be discarded.
- step (b1') filtrating the reaction mixture obtained in step (b1) to obtain a solid product, being the second intermediate reaction product. The retentate is the second intermediate reaction product. The filtrate may be discarded.
- step (b2') filtrating the reaction mixture obtained in step (b2) to obtain a solid product, being the third intermediate reaction product. The retentate is the third intermediate reaction product. The filtrate may be discarded.

Instead of a filtrating step, this step may also involve decanting.

In an embodiment, no acyl halide, preferably no benzoyl chloride is used during step b).

In an embodiment, the internal donor is represented by a compound according to formula A wherein each \( R^8 \) group is independently a linear, branched or cyclic hydrocarbyl group selected from alkyl, alkenyl, aryl, aralkyi, or alkyaryl groups, and one or more combinations thereof, preferably having from 1 to 30 carbon atoms; \( R^1, R^2, R^3, R^4, R^5, \) and \( R^6 \) are each independently selected from hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyi, or alkyaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \( R^7 \) is a hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyi, alkoxy carbonyl or alkyaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \( N \) is nitrogen atom; \( O \) is oxygen atom; and \( C \) is carbon atom. In an embodiment, said compound according to Formula A is 4-[benzoyl(methyl)amino]pentan-2-yl benzoate (AB).

More compounds according to Formula A that are suitable, and more information about the preferred embodiments are discussed in WO 2014/1 18164, page 8, line 28 to page 10 line 8, which section is incorporated by reference. It should be noted that Formula I of WO 2014/1 18164 corresponds to Formula A according to the present invention.

In an embodiment, the internal donor is represented by a compound according to formula B wherein each \( R^{80} \) group is independently a linear, branched or cyclic hydrocarbyl group selected from alkyl, alkenyl, aryl, aralkyi, or alkyaryl groups, and one or more combinations thereof, preferably having from 1 to 30 carbon atoms; \( R^{81}, R^{82}, R^{83}, R^{84}, R^{85}, \) and \( R^{86} \) are each independently selected from hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyi, or alkyaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \( R^{87} \) is a hydrogen or a linear, branched
or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyi, alkoxycarbonyl or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; N is nitrogen atom; O is oxygen atom; and C is carbon atom; most preferably wherein said compound according to Formula B is ethyl (4-((ethoxycarbonyl)oxy)pentan-2-yl)(methyl)carbamate (AB-OEt).

In an embodiment, R81, R82, R83, R84, R85, and R86 of Formula B are independently selected from a group consisting of hydrogen, C1-C10 straight and branched alkyl; C3-C10 cycloalkyl; C6-C10 aryl; and C7-C10 alkaryl and aralkyi group. In a further embodiment, R81 and R82 are each a hydrogen atom and R83, R84, R85, and R86 are independently selected from a group consisting of C1-C10 straight and branched alkyl; C3-C10 cycloalkyl; C6-C10 aryl; and C7-C10 alkaryl and aralkyi group, preferably from C1-C10 straight and branched alkyl and more preferably from methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, phenyl group. In a further embodiment, when one of R83 and R84 and one of R85 and R86 has at least one carbon atom, then the other one of R83 and R84 and of R85 and R86 is each a hydrogen atom. In a further embodiment, R87 is selected from a group consisting of methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, phenyl, benzyl, substituted benzyl and halophenyl group. In a further embodiment, R80 is a aliphatic hydrocarbyl group or an aromatic hydrocarbyl group. R80 may be substituted on unsubstituted. In case R80 is an aliphatic hydrocarbyl group, it may be selected from the group consisting of aliphatic substituted and unsubstituted hydrocarbyls having 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, more preferably 1 to 6 carbon atoms. More preferably, R80 is selected from the group consisting of methyl, ethyl, n-propyl, i-propyl, n-butyl, 2-butyl, t-butyl, pentyl or hexyl. Most preferably, R80 is ethyl. In case R80 is an aromatic hydrocarbyl group, it may be phenyl or substituted phenyl or any other aromatic group having from 6 to 20 carbon atoms.

Two preferred examples compounds according to formula B are:

![Chemical structure](image)

ethyl (4-((ethoxycarbonyl)oxy)pentan-2-yl)(methyl)carbamate
Step (b) comprises two sub steps (b1) and (b2): (b1) contacting the first intermediate product with a mixture of a tetravalent titanium halide and an internal electron donor; to obtain a second intermediate product; and (b2) contacting the second intermediate product with a tetravalent titanium halide to obtain a third intermediate product. The internal donor is added in a single addition during step (b1). This invention comprises in step (a) halogenation of magnesium, the addition of an activator and a 1st titanation, in step (b1) the addition of an ID and a 2nd titanation and in step (b2) a 3rd titanation. Step (c) relates to the work up. A procatalyst prepared according to this invention produces a polymer having a regular molecular weight distribution and a relatively low value for xylene solubles.

**STEP (c)**

Step (c) relates to washing the intermediate product obtained with an inert hydrocarbon liquid.

The washing of step (c) may be carried out with one or more washing cycles. During each washing cycle the solid intermediate product is contacted with an amount of internal hydrocarbon liquid and mixed. For example, two, three, four, five, six or seven washing cycles may be carried out. The amount of liquid added during each washing cycle may be determined by the person skilled in the art. The liquid may be different or the same during each washing cycle, preferably the same. The amount of liquid may be different or the same during each washing cycle, preferably the same.

In an embodiment, step (c) may be carried out at a temperature of between room temperature and 100 °C, preferably between room temperature and 60 °C. The temperature during step (c) may be constant or may be decreased, e.g. from 60 °C to 25 °C, in several steps. For example when 5 washing cycles are carried out, the temperature may be
decreased with each cycle. The temperature may be determined by the temperature of the liquid to be added or by external cooling or heating.

In an embodiment, the inert hydrocarbon liquid is an alkane, such as n-pentane, isopentane, n-hexane, n-heptane, iso-octane, preferably isopentane. However, toluene may also be used. This inert hydrocarbon liquid is used to wash the solid intermediate product obtained. During this washing any unreacted material, including physically absorbed halohydrocarbon may be removed.

After step (c) preferably an additional step is carried out, being step (c'): step (c') filtrating the reaction mixture obtained in step (c) to obtain a solid product, being the procatalyst. The retentate is the procatalyst. The filtrate may be discarded. Instead of a filtrating step, this step may also involve decanting.

The procatalyst can be used as such wetted by the solvent or suspended in solvent or it can be first dried, preferably partly dried, for storage. After step (c') preferably an additional step is carried out, being step (c''): step (c'') drying the solid product obtained in step (c'). This step may for example be carried out by conventional dryings means, such as a flow of an inert gas, e.g. dry nitrogen, during a certain period of time, e.g. between 0.5 and 10 hours, e.g. between 1 and 3 hours, such as 2 hours. Drying can e.g. be carried out by low pressure nitrogen flow for several hours preferably at temperature from 10 to 100°C depending on the boiling point of the solvent used, preferably from 15 to 70 °C. The procatalyst obtained can be used as dried or suspended in mineral oil for storage.

Several embodiments of the present invention are shown below.

The present invention relates to a method for producing an olefin polymerization procatalyst, which method comprises the following steps:

(a) halogenating a magnesium compound of the formula MgR'R" wherein R' is an alkoxide or aryloxide group and wherein R" is an alkoxide or aryloxide group or halogen, with a tetravalent titanium halide in the presence of a halohydrocarbon and an activator; to form a first intermediate product;
In an embodiment, the present invention relates to a method for producing an olefin polymerization procatalyst, which method comprises the following steps:

(a) halogenating a dialkoxymagnesium, preferably diethoxymagnesium, with a titanium tetrahalide, preferably TiCU, in the presence of a halohydrocarbon, preferably chlorobenzene, and an activator, preferably ethylbenzoate; to form a first intermediate product;

(b1 ) contacting the first intermediate product with a mixture of a titanium tetrahalide, preferably TiCU, and an internal electron donor, preferably AB or AB-OEt; to obtain a second intermediate product; and

(b2) contacting the second intermediate product with a titanium tetrahalide, preferably TiCU, to obtain a third intermediate product; and

(c) washing the third intermediate product with an inert hydrocarbon liquid, preferably an alkane, to obtain a procatalyst.

In an embodiment, the present invention relates to a method for producing an olefin polymerization procatalyst, which method comprises the following steps: (a) halogenating diethoxymagnesium with TiCU in the presence of chlorobenzene, and ethylbenzoate; to form a first intermediate product; (b1 ) contacting the first intermediate product with a mixture of TiCU and AB to obtain a second intermediate product; and (b2) contacting the second intermediate product with TiCU to obtain a third intermediate product; and (c) washing the third intermediate product with an alkane, such as n-heptane or isopentane, to obtain a procatalyst.

In an embodiment, the present invention relates to a method for producing an olefin polymerization procatalyst, which method comprises the following steps: (a) halogenating diethoxymagnesium with TiCU in the presence of chlorobenzene, and ethylbenzoate; to
form a first intermediate product; (b1) contacting the first intermediate product with a mixture of TiCl₄ and AB-OEt to obtain a second intermediate product; and (b2) contacting the second intermediate product with TiCU to obtain a third intermediate product; and (c) washing the third intermediate product with an alkane, such as n-heptane or isopentane, to obtain a procatalyst.

A procatalyst prepared according to this first embodiment produces a polymer having a regular molecular weight distribution and a relatively low value for xylene solubles.

The present invention is further elucidated based on the Examples below which are illustrative only and not considered limiting to the present invention.

**Examples**

Several different procatalysts were synthesized according to the Synthesis Examples below. The specifications of these procatalysts are provided in Table 1. Synthesis examples 1 and 5 are prepared according to the present invention, having a single addition of the internal donor. Synthesis Examples 2 and 6 are prepared according to a method according to the clauses (see below) not according to the present claims, having a dual (50%/50%) addition of the internal donor. In Synthesis Example 3 the temperature of the process is reduced from 110 °C to 96 °C. In Synthesis Example 4 the ratio of titanium tetrachloride to chlorobenzene is amended from 40:60 v/v to 50:50 v/v. Comparative Synthesis Example 8 is according to a prior art method wherein only one electron donor is used.

Table 1 shows in the first column the number of the synthesis example, in the second column the designation of the procatalyst, in the third column the activator as well as the amount thereof (between brackets), in the fourth column the reaction temperature in first three steps, in the fifth column the internal donor as well as the amount thereof (between brackets), in the sixth column the d50 value in microns of the procatalyst particles obtained, in the seventh through the eleventh column the percentage of respectively magnesium, titanium, the internal donor, the activator and the alkoxide of the magnesium alkoxide starting product are shown.
These different procatalysts were used in the polymerization of propylene. The details thereof are discussed in Polymerization Examples below and Table 2. Table 2 shows in the first column the number of the polymerization example, in the second column the designation of the procatalyst, in the third column productivity for the production of PP (in kilogram per gram catalyst), in the fourth column the bulk density (in kilogram per cubic meter), in the fifth column the weight average molecular weight ($M_w$), (in grams per mole), in the sixth column the number average molecular weight ($M_n$), (in grams per mole), in the seventh column molecular weight distribution ($M_w/M_n$), in the eighth column the percentage of xylene solubles, in the ninth and tenth column the melting temperature ($T_m$) and crystallization temperature ($T_c$) respectively (in degrees Celsius) and in the eleventh column the crystallinity percentage.

**Synthesis Example 1: Preparation of Procatalyst A**

**Step a: halogenation of magnesium and 1st titanation**

An amount of 4.5 g of magnesium ethoxide (with an average particle size of 538 microns) was placed in a 300 ml reaction-filtration flask under a nitrogen atmosphere. Then, 100 mL of a mixture of TiCU and chlorobenzene (CB) (40:60 v/v) was added to the flask at a temperature of 25 °C. Then, a solution of 0.8 mL ethylbenzoate (EB) in 3 mL CB was added to the flask at a temperature of 25 °C. The resulting reaction mixture was heated to a temperature of 110 °C and stirred at that temperature for a period of 40 minutes. After the stirring was stopped, the reaction mixture obtained was filtered at 110 °C.

**Step b1: addition of ID and 2nd titanation**

The filtrate was discarded and the solid was retained in the flask and subsequently, 100 mL of a mixture of TiCU and CB (40:60 v/v) was added to the flask at a temperature of 25 °C. Next, a solution of 1058 mg of internal donor ethyl (4-((ethoxycarbonyl)oxy)pentan-2-yl)(methyl)carbamate (AB-OEt) in 2 mL of CB was added to the flask. The resulting reaction mixture was heated to a temperature of 110 °C and stirred at that temperature for a period of 30 minutes. After the stirring was stopped, the reaction mixture obtained was filtered.

**Step b2: 3rd titanation**

The filtrate was discarded and the solid was retained in the flask and subsequently, 100 mL of a mixture of TiCU and chlorobenzene (40:60 v/v) was added to the flask. The resulting reaction mixture was heated to 110 °C and stirred at that temperature for a period of 30 minutes. After the stirring was stopped, the reaction mixture obtained was filtered.
Step c: work up
The filtrate was discarded and the solid was retained in the flask and subsequently, the contents of the flask were washed 5 times with 100 mL of heptane starting at a temperature of 60 °C. The solid product was stirred for 5 minutes per wash prior to filtration in which the filtrate was discarded and the solid was retained in the flask. The temperature was gradually reduced from 60 °C to 25 °C during the washings. Finally, the solid product obtained was dried using a nitrogen purge at a temperature of 25°C for a period of 2 hours. The specifications of this procatalyst are provided in Table 1.

Synthesis Example 2**: Preparation of Procatalyst B** [according to a method in the clauses (below) - not according to the claims!]

Step a: *halogenation of magnesium and 1*st titanation in presence of an activator
An amount of 4.5 g of magnesium ethoxide (with an average particle size of 538 microns) was placed in a 300 mL reaction-filtration flask under a nitrogen atmosphere. Then, 100 mL of a mixture of TiCu and chlorobenzene (CB) (40:60 v/v) was added to the flask at a temperature of 25 °C. Then, a solution of 0.8 mL ethylbenzoate (EB) in 3 mL CB was added to the flask at a temperature of 25 °C. The resulting reaction mixture was heated to a temperature of 110 °C and stirred at that temperature for a period of 40 minutes. After the stirring was stopped, the reaction mixture obtained was filtered at 110 °C.

Step b1: 1*st addition of internal donor and 2*nd titanation
The filtrate was discarded and the solid was retained in the flask and subsequently, 100 mL of a mixture of TiCu and CB (40:60 v/v) was added to the flask at a temperature of 25 °C. Next, a solution of 529 mg of internal donor AB-OEt in 2 mL of CB was added to the flask. The resulting reaction mixture was heated to a temperature of 110 °C and stirred at that temperature for a period of 30 minutes (1*st ID addition). After the stirring was stopped, the reaction mixture obtained was filtered.

Step b2: 2*nd addition of internal donor and 3*rd titanation
The filtrate was discarded and the solid was retained in the flask and subsequently, 100 mL of a mixture of TiCu and chlorobenzene (40:60 v/v) was added to the flask. Next, a solution of 529 mg of internal donor AB-OEt in 2 mL of CB was added to the flask. The resulting reaction mixture was heated to 110 °C and stirred at that temperature for a period of 30 minutes. After the stirring was stopped, the reaction mixture obtained was filtered.

Step c: work up
The filtrate was discarded and the solid was retained in the flask and subsequently, the contents of the flask were washed 5 times with 100 mL of heptane starting at a temperature of 60 °C. The solid product was stirred for 5 minutes per wash prior to filtration in which the filtrate was discarded and the solid was retained in the flask. The temperature was gradually reduced from 60 °C to 25 °C during the washings. Finally, the solid product obtained was dried using a nitrogen purge at a temperature of 25°C for a period of 2 hours. The specifications of this procatalyst are provided in Table 1.

Synthesis Example 3: Preparation of Procatalyst C

Synthesis Example 3 was carried out in the same way as Synthesis Example 1, except the reaction temperature was maintained at a temperature of 96 °C instead of a temperature of 110 °C for each of the steps 1), 2), 3) and 4). The specifications of this procatalyst are provided in Table 1.

Synthesis Example 4: Preparation of Procatalyst D

Synthesis Example 4 was carried out in the same way as Synthesis Example 1, except that the ratio of the mixture of TiCl₄ and chlorobenzene was 50:50 by volume instead of 40:60 by volume. The specifications of this procatalyst are provided in Table 1.

Synthesis Example 5: Preparation of Procatalyst E

Synthesis Example 5 was carried out in the same way as Synthesis Example 1, except that during step 2 a solution of 1318 mg of internal donor 4-[benzoyl(methyl)amino]pentan-2-yl benzoate (AB) in 2 mL of CB was used instead of a solution of 1058 mg of internal donor ethyl (4-((ethoxycarbonyl)oxy)pentan-2-yl)(methyl) carbamate (AB-OEt) in 2 mL of CB.

Synthesis Example 6*: Preparation of Procatalyst F* [according to a method in the clauses (below) - not according to the claims]

Synthesis Example 6 was carried out in the same way as Synthesis Example 2, except that during step 2 and step 3 a solution of 659 mg of internal donor 4-[benzoyl(methyl)amino]pentan-2-yl benzoate (AB) in 2 mL of CB was used instead of a solution of 529 mg of internal donor ethyl (4-((ethoxycarbonyl)oxy)pentan-2-yl)(methyl)carbamate (AB-OEt) in 2 mL of CB.
Synthesis Example 7*: Preparation of Procatalyst G [according to a method in the clauses (below) - not according to the claims!]

Synthesis Example 7 was carried out in the same way as Synthesis Example 2, except that during step 2 and step 3 a solution of 1058 mg of internal donor 4-(benzoyl(methyl)amino)pentan-2-yl benzoate (AB) in 2 mL of CB was used instead of a solution of 1058 mg of internal donor ethyl (4-((ethoxycarbonyl)oxy)pentan-2-yl)(methyl)carbamate (AB-OEt) in 2 mL of CB.

Synthesis Example 8*: Preparation of Procatalyst H* [comparative example according to the prior art!]

Step 1') halogenation of magnesium and 1st titanation in presence of activator
An amount of 5.7 g of magnesium ethoxide (with an average particle size of 538 microns) was placed in a 300 mL reaction-filtration flask under a nitrogen atmosphere. Then, 150 mL of a mixture of TiCU and chlorobenzene (CB) (50:50 v/v) was added to the flask at a temperature of 25 °C. Then, a solution of 2.4 mL ethylbenzoate (EB) in 3 mL CB was added to the flask at a temperature of 25 °C. The resulting reaction mixture was heated to a temperature of 110 °C and stirred at that temperature for a period of 60 minutes. After the stirring was stopped, the reaction mixture obtained was filtered at 110 °C.

Step 2') 2nd titanation
The filtrate was discarded and the solid was retained in the flask and subsequently, 150 mL of a mixture of TiCU and CB (50:50 v/v) was added to the flask at a temperature of 25 °C. The resulting reaction mixture was heated to a temperature of 110 °C and stirred at that temperature for a period of 30 minutes. After the stirring was stopped, the reaction mixture obtained was filtered.

Step 3') activation with acid chloride and 3rd titanation
The filtrate was discarded and the solid was retained in the flask and subsequently, 150 mL of a mixture of TiCU and chlorobenzene (50:50 v/v) was added to the flask. Next, 0.4 mL of benzoyl chloride was added to the flask. The resulting reaction mixture was heated to 110 °C and stirred at that temperature for a period of 30 minutes. After the stirring was stopped, the reaction mixture obtained was filtered.

Step 4') work up
The filtrate was discarded and the solid was retained in the flask and subsequently, the contents of the flask were washed 6 times with 150 mL of isopentane at a temperature of
25 °C. The solid product was stirred for 5 minutes per wash prior to filtration in which the filtrate was discarded and the solid was retained in the flask. Finally, the solid product obtained was dried using a nitrogen purge at a temperature of 40°C for a period of 90 minutes. The specifications of this procatalyst are provided in Table 1.

Polymerization Example 1: Using Procatalyst A

Liquid pool propylene polymerization was carried out in a one gallon bench scale reactor. The method of polymerization involved baking the polymerization reactor at a temperature of 110°C for a period of 60 minutes, then applying three high pressure (15 bar) nitrogen purges at a temperature 110°C, then lowering the reactor temperature to 30°C whilst purging the reactor with nitrogen. Then the reactor was purged three times with 50 g of propylene for each purge. Then 1.375 kg of liquid propylene was introduced to the reactor followed by the addition of 200 psig hydrogen to the reactor from an 75 mL stainless steel cylinder. The reactor temperature was then raised to 62°C with a stirring speed of 500 rpm and 0.25 mmol of the external electron donor, cyclohexylmethyldimethoxysilane, was injected into the reactor. Then, 2.0 mmol of a co-catalyst, triethylaluminium was injected in the reactor. Then the procatalyst, corresponding to 0.01 mmol Ti, was injected into the reactor. The reactor temperature was then raised to 67°C and the stirring speed increased to 1500 rpm and polymerization was carried out for a period of 1 hour. After this period had expired, the propylene in the reactor was vented and product polypropylene was collected. The yield was determined after allowing the product to dry. Polymerization and product analysis results are given in Table 2.

Polymerization Example 2*: Using Procatalyst B*

Polymerization Example 1 was repeated except that procatalyst B was used in the process. Polymerization and product analysis results are given in Table 2.

Polymerization Example 3: Using Procatalyst C

Polymerization Example 1 was repeated except that procatalyst C was used in the process. Polymerization and product analysis results are given in Table 2.

Polymerization Example 4: Using Procatalyst D
Polymerization Example 1 was repeated except that procatalyst D was used in the process. Polymerization and product analysis results are given in Table 2.

**Polymerization Example 5**: Using Procatalyst E

Polymerization Example 1 was repeated except that procatalyst E was used in the process. Polymerization and product analysis results are given in Table 2.

**Polymerization Example 6**: Using Procatalyst F

Polymerization Example 1 was repeated except that procatalyst F was used in the process. Polymerization and product analysis results are given in Table 2.

**Polymerization Example 7**: Using Procatalyst G

Polymerization Example 1 was repeated except that procatalyst G was used in the process. Polymerization and product analysis results are given in Table 2.

**Polymerization Example 8**: Using Procatalyst H

Polymerization Example 1 was repeated except that procatalyst H was used in the process. Polymerization and product analysis results are given in Table 2.

Table 1:

<table>
<thead>
<tr>
<th>S.E.#</th>
<th>Procat.</th>
<th>ACT (mL)</th>
<th>Temp [°C]</th>
<th>ID (mg/l)</th>
<th>d50 [μm]</th>
<th>Mg [%]</th>
<th>Ti [%]</th>
<th>ID [%]</th>
<th>ACT [%]</th>
<th>RO [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>EB (0.8)</td>
<td>110</td>
<td>AB-OEt (1058)</td>
<td>67.00</td>
<td>18.04</td>
<td>2.81</td>
<td>3.20</td>
<td>3.33</td>
<td>2.78</td>
</tr>
<tr>
<td>2#</td>
<td>B#</td>
<td>EB (0.8)</td>
<td>110</td>
<td>AB-OEt (529/529)</td>
<td>75.76</td>
<td>17.92</td>
<td>2.47</td>
<td>4.15</td>
<td>3.38</td>
<td>3.33</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>EB (0.8)</td>
<td>96</td>
<td>AB-OEt (1058)</td>
<td>61.00</td>
<td>17.54</td>
<td>2.80</td>
<td>5.51</td>
<td>3.05</td>
<td>2.47</td>
</tr>
<tr>
<td>4</td>
<td>D*</td>
<td>EB (0.8)</td>
<td>110</td>
<td>AB-OEt (1058)</td>
<td>77.00</td>
<td>17.24</td>
<td>2.79</td>
<td>3.76</td>
<td>2.53</td>
<td>1.54</td>
</tr>
<tr>
<td>5</td>
<td>E</td>
<td>EB (0.8)</td>
<td>110</td>
<td>AB (1318)</td>
<td>86.63</td>
<td>16.50</td>
<td>3.57</td>
<td>16.14</td>
<td>2.89</td>
<td>0.58</td>
</tr>
<tr>
<td>6#</td>
<td>F#</td>
<td>EB (0.8)</td>
<td>110</td>
<td>AB (858/859)</td>
<td>80.13</td>
<td>18.78</td>
<td>3.43</td>
<td>16.88</td>
<td>2.00</td>
<td>0.31</td>
</tr>
<tr>
<td>7#</td>
<td>G#</td>
<td>EB (0.8)</td>
<td>110</td>
<td>AB (1058)</td>
<td>83.17</td>
<td>18.60</td>
<td>3.63</td>
<td>16.88</td>
<td>2.96</td>
<td>0.67</td>
</tr>
<tr>
<td>8*</td>
<td>H*</td>
<td>EB(2.4)</td>
<td>110</td>
<td>BC (0.4 mL)</td>
<td>84.00</td>
<td>17.98</td>
<td>2.87</td>
<td>-</td>
<td>9.00</td>
<td>0.25</td>
</tr>
</tbody>
</table>
From this Table is clear that when a procatalyst according to the prior art (procatalyst H*) is compared to a procatalyst according to the present invention (procatalyst A) it can be observed that the productivity almost doubles (from 17.5 to 33.7), the molecular weight sharply increases with a very similar bulk density and MWD. The XS also decreases (from 4.56 to 2.27), this is with a decrease in the amount of activator. This is also observable from the comparison of procatalyst H* with procatalyst E showing that the productivity increases (from 17.5 to 26.2), the molecular weight (both Mw and Mn) increases as well as the MWD (from 6.97 to 8.00). The XS decreases (from 4.56 to 2.19). In other words, the present invention allows for a procatalyst providing a lower XS and higher productivity with a broad MWD. Hence the method according to the present invention is effective.

Hence, one or more objects of the present invention are obtained using the present inventive method.

**Clauses**

The following clauses define several aspects and embodiments of the invention.

1. A method for producing a olefin polymerization catalyst component, which method comprises the steps of:
   (a) halogenating a magnesium compound of the formula MgR'' wherein R'' is an alkoxide or aryloxide group and wherein R' is an alkoxide or aryloxide group or halogen, with a tetravalent titanium halide in the presence of a halohydrocarbon and an activator; to form a first intermediate product;
(b) contacting the first intermediate product with a mixture of a tetravalent titanium halide and an internal electron donor; to obtain a second intermediate product; and
(c) washing the second intermediate product with an inert hydrocarbon liquid.

2. A method according to clause 1, wherein step (b) comprises two sub steps (b1) and (b2):
   (b1) contacting the first intermediate product with a mixture of a tetravalent titanium halide and an internal electron donor; to obtain a second intermediate product; and
   (b2) contacting the second intermediate product with a tetravalent titanium halide to obtain a third intermediate product; and wherein step (c) is:
   (c) washing the third intermediate product with an inert hydrocarbon liquid to obtain a procatalyst.

3. A method according to clause 1, wherein step (b) comprises two sub steps (b1) and (b2):
   (b1) contacting the first intermediate product with a mixture of a tetravalent titanium halide and a first portion of an internal electron donor; to obtain a second intermediate product; and
   (b2) contacting the second intermediate product with a mixture of a tetravalent titanium halide and a second portion of an internal electron donor; to obtain a third intermediate product; and wherein step (c) is:
   (c) washing the third intermediate product with an inert hydrocarbon liquid to obtain a procatalyst.

4. A method according to any one of the preceding clauses, wherein the activator is a monoester, preferably a benzoate ester, more preferably ethylbenzoate.

5. A method according to any one of the clauses 1-4, wherein the internal donor is represented by a compound according to formula A:
wherein each R₈ group is independently a linear, branched or cyclic hydrocarbyl group selected from alkyl, alkenyl, aryl, aralkyl, or alkyaryl groups, and one or more combinations thereof, preferably having from 1 to 30 carbon atoms; R₁, R₂, R₃, R₄, R₅, and R₆ are each independently selected from hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, or alkyaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; R⁷ is a hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, alkoxy carbonyl or alkyaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; N is nitrogen atom; O is oxygen atom; and C is carbon atom; most preferably wherein said compound according to Formula A is

4-[benzoyl(methyl)amino]pentan-2-yl benzoate (AB).

6. A method according to any one of the clauses 1-4, wherein the internal donor is represented by a compound according to formula A:
Formula A
wherein each $R^8$ group is independently a linear, branched or cyclic hydrocarbyl group selected from alkyl, alkenyl, aryl, aralkyi, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 30 carbon atoms; $R^1$, $R^2$, $R^3$, $R^4$, $R^5$, and $R^6$ are each independently selected from hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyi, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; $R^7$ is a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyi, alkoxy carbonyl or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; $N$ is nitrogen atom; $O$ is oxygen atom; and $C$ is carbon atom; most preferably wherein said compound according to Formula A is

![Chemical Structure](attachment:structure.png)

4-[benzoyl(methyl)amino]pentan-2-yl benzoate (AB).

7. A method according to any one of the clauses 1-4, wherein the internal donor is represented by a compound according to formula B:

![Chemical Structure](attachment:structure2.png)

wherein each $R^{80}$ group is independently a linear, branched or cyclic hydrocarbyl group selected from alkyl, alkenyl, aryl, aralkyi, or alkylaryl groups, and one or more combinations
thereof, preferably having from 1 to 30 carbon atoms; \( R^8 \), \( R^{82} \), \( R^{83} \), \( R^{84} \), \( R^{85} \), and \( R^{86} \) are each independently selected from hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \( R^{87} \) is a hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, alkoxy carbonyl or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \( N \) is nitrogen atom; \( O \) is oxygen atom; and \( C \) is carbon atom; most preferably:

\[
\begin{align*}
\text{O} & \quad \text{O} & \quad \text{N} & \quad \text{O} \\
\end{align*}
\]

wherein said compound according to Formula B is ethyl (4-((ethoxycarbonyl)oxy)pentan-2-yl)(methyl)carbamate (AB-OEt).

8. A method according to any one of the preceding clauses, wherein the magnesium compound is a dialkoxymagnesium compound, preferably diethoxymagnesium.

9. A method according to any one of the preceding clauses, wherein the tetravalent titanium compound is a titanium tetrahalide, preferably TiCU and/or wherein the same tetravalent titanium compound is used in each of the steps.

10. A method according to any one of the preceding clauses, wherein the halohydrocarbon is chlorobenzene.

11. A method according to any one of the preceding clauses, wherein the inert hydrocarbon liquid is an alkane, preferably n-heptane or isopentane.

12. A method according to clause 2, wherein the activator is ethylbenzoate, wherein the internal donor is 4-[benzoyl(methyl)amino]pentan-2-yl benzoate (AB), wherein the magnesium compound is diethoxymagnesium, wherein the tetravalent titanium compound for each step is TiCU, wherein the halohydrocarbon is chlorobenzene, wherein the inert hydrocarbon liquid is an alkane.
13. A method according to clause 2, wherein the activator is ethylbenzoate, wherein the internal donor is ethyl (4-((ethoxycarbonyl)oxy)pentan-2-yl)(methyl)carbamate (AB-OEt), wherein the magnesium compound is diethoxymagnesium, wherein the tetravalent titanium compound for each step is TiCU, wherein the halohydrocarbon is chlorobenzene, wherein the inert hydrocarbon liquid is an alkane.

14. A method according to clause 3, wherein the activator is ethylbenzoate, wherein the internal donor is 4-[benzoyl(methyl)amino]pentan-2-yl benzoate (AB) and wherein the first portion and the second portion are each half (50%/50%) of the total amount of internal donor added, wherein the magnesium compound is diethoxymagnesium, wherein the tetravalent titanium compound for each step is TiCU, wherein the halohydrocarbon is chlorobenzene, wherein the inert hydrocarbon liquid is an alkane.

15. A method according to clause 3, wherein the activator is ethylbenzoate, wherein the internal donor is ethyl (4-((ethoxycarbonyl)oxy)pentan-2-yl)(methyl)carbamate (AB-OEt) and wherein the first portion and the second portion are each half (50%/50%) of the total amount of internal donor added, wherein the magnesium compound is diethoxymagnesium, wherein the tetravalent titanium compound for each step is TiCU, wherein the halohydrocarbon is chlorobenzene, wherein the inert hydrocarbon liquid is an alkane.

16. A method according to any one of the preceding clauses wherein no acyl halide, preferably no benzoyl chloride, is used.
Claims

1. A method for producing a olefin polymerization catalyst component, which method comprises the steps of:

   (a) halogenating a magnesium compound of the formula \( \text{MgR'R''} \) wherein \( \text{R'} \) is an alkoxide or aryloxide group and wherein \( \text{R''} \) is an alkoxide or aryloxide group or halogen, with a tetravalent titanium halide in the presence of a halohydrocarbon and an activator preferably being a monoester; to form a first intermediate product;

   (b) contacting the first intermediate product with a mixture of a tetravalent titanium halide and an internal electron donor; wherein step (b) comprises two sub steps (b1) and (b2):

       (b1) contacting the first intermediate product with a mixture of a tetravalent titanium halide and an internal electron donor; to obtain a second intermediate product; and

       (b2) contacting the second intermediate product with a tetravalent titanium halide to obtain a third intermediate product; and

   (c) washing the third intermediate product with an inert hydrocarbon liquid to obtain a catalyst component;

   wherein the internal donor is preferably represented by a compound according to formula A:

   \[
   \begin{align*}
   \text{OCOR}_8 \\
   \text{R}_3 \text{R}_4 \\
   \text{R}_1 \text{R}_2 \\
   \text{R}_5 \text{R}_6 \\
   \text{NR}_7 \text{COR}_8
   \end{align*}
   \]

   Formula A

   wherein each \( \text{R}_8 \) group is independently a linear, branched or cyclic hydrocarbyl group selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 30 carbon atoms; \( \text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^6 \), and \( \text{R}^8 \) are each independently selected from hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20 carbon atoms; \( \text{R}^7 \) is a hydrogen or a linear, branched or cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, alkoxy carbonyl or...
alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20
carbon atoms; N is nitrogen atom; O is oxygen atom; and C is carbon atom; or

wherein the internal donor is preferably represented by a compound according to
formula B:

\[
\begin{align*}
&\text{Formula B} \\
&\text{wherein each } R^{80} \text{ group is independently a linear, branched or cyclic hydrocarbyl group}
\end{align*}
\]

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selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations
thereof, preferably having from 1 to 30 carbon atoms; \( R^{81}, R^{82}, R^{83}, R^{84}, R^{85}, \text{and } R^{86} \) are each

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independently selected from hydrogen or a linear, branched or cyclic hydrocarbyl group,

selected from alkyl, alkenyl, aryl, aralkyl, or alkylaryl groups, and one or more combinations
thereof, preferably having from 1 to 20 carbon atoms; \( R^{87} \) is a hydrogen or a linear, branched

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cyclic hydrocarbyl group, selected from alkyl, alkenyl, aryl, aralkyl, alkoxycarbonyl or

alkylaryl groups, and one or more combinations thereof, preferably having from 1 to 20

carbon atoms; N is nitrogen atom; O is oxygen atom; and C is carbon atom.

2. A method according to claim 1, wherein the activator is a benzoate ester, preferably

ethylbenzoate.

3. A method according to any one of the claims 1-2, wherein the internal donor is a

compound according to Formula A being
4. A method according to any one of the claims 1-2, wherein the internal donor is a compound according to Formula B being

\[
\begin{align*}
\text{C}_6\text{H}_{15} & \quad \text{O} \\
\text{N} & \quad \text{C}_6\text{H}_{15}
\end{align*}
\]

ethyl (4-((ethoxycarbonyl)oxy)pentan-2-yl)(methyl)carbamate (AB-OEt).

5. A method according to any one of the preceding claims, wherein the magnesium compound is a dialkoxy magnesium compound, preferably diethoxymagnesium.

6. A method according to any one of the preceding claims, wherein the tetravalent titanium compound is a titanium tetrahalide, preferably TiCl and/or wherein the same tetravalent titanium compound is used in each of the steps.

7. A method according to any one of the preceding claims, wherein the halohydrocarbon is chlorobenzene.

8. A method according to any one of the preceding claims, wherein the inert hydrocarbon liquid is an alkane, preferably n-heptane or isopentane.

9. A method according to any one of the preceding claims, wherein the activator is ethylbenzoate, wherein the internal donor is 4-[benzoyl(methyl)amino]pentan-2-yl benzoate (AB), wherein the magnesium compound is diethoxymagnesium, wherein the tetravalent
titanium compound for each step is TiCU, wherein the halohydrocarbon is chlorobenzene, wherein the inert hydrocarbon liquid is an alkane.

10. A method according to any one of the preceding claims, wherein the activator is ethylbenzoate, wherein the internal donor is ethyl (4-((ethoxycarbonyl)oxy)pentan-2-yl)(methyl)carbamate (AB-OEt), wherein the magnesium compound is diethoxymagnesium, wherein the tetravalent titanium compound for each step is TiCU, wherein the halohydrocarbon is chlorobenzene, wherein the inert hydrocarbon liquid is an alkane.

11. A method according to any one of the preceding claims wherein no acyl halide, preferably no benzoyl chloride, is used.
**INTERNATIONAL SEARCH REPORT**

**PCT/EP2016/078769**

### A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F4/651 C08F10/06 C08F110/06

**ADD.**

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

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F

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

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

EPO-Internal, WPI Data, CHEM ABS Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of the actual completion of the international search 11 January 2017

Date of mailing of the international search report 19/01/2017

Name and mailing address of the ISA/

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Fax: (+31-70) 340-3016

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Ni kol ai, Joachim
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