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**WO 2006/010599**

(54) Title: PROCESS FOR PREPARING A POLY-1-OLEFIN IN THE PRESENCE OF A ZIEGLER CATALYST

(57) Abstract: The invention relates to a process for preparing a poly-1-olefin by polymerization of a 1-olefin of the formula  $R^4\text{CH}=\text{CH}_2$ , where  $R^4$  is hydrogen or an alkyl radical having from 1 to 10 carbon atoms, in suspension, in solution or in the gas phase, at a temperature of from 20 to 200°C and a pressure of from 0.5 to 50 bar, in the presence of a catalyst which comprises the reaction product of a magnesium alkoxide with a transition metal compound (= component a) and an organometallic compound (= component b) and whose component a has been prepared in a manner having the feature that a magnesium alkoxide powder having a mean particle size, expressed as the  $d_{50}$ , in the range from 100 to 1000  $\mu\text{m}$  is firstly processed by dry milling in a mill under inert conditions to produce magnesium alkoxide powder having a mean particle size, expressed as the  $d_{50}$ , of less than 15  $\mu\text{m}$ , then suspended in an inert hydrocarbon in which the magnesium alkoxide is insoluble, and is reacted immediately without further pretreatment with a transition metal compound of titanium, zirconium, vanadium or chromium.

## Process for preparing a poly-1-olefin in the presence of a Ziegler catalyst

The invention relates to a process for preparing a poly-1-olefin in the presence of a Ziegler catalyst, one of whose components has been prepared from a magnesium alkoxide suspension and a transition metal compound.

Magnesium alkoxides  $Mg(OR^1)(OR^2)$  or "complex" magnesium alkoxides can be reacted with compounds of titanium, zirconium, vanadium or chromium to produce solids which together with organometallic compounds of group 1, 2 or 13 of the Periodic Table (the groups are cited as printed, for example, in *Handbook of Chemistry and Physics*, 76<sup>th</sup> edition (1995 - 1996)) give excellent catalysts for olefin polymerization.

A process for the polymerization of  $\alpha$ -olefins in the presence of a mixed catalyst whose component a has been prepared by reacting magnesium alkoxides with tetravalent, halogen-containing titanium compounds is known (cf. US-A 3,644,318). The magnesium alkoxides are used in the commercially available form. The polymers obtainable by this known process have a narrow molar mass distribution.

Also known is a process for preparing a Ziegler catalyst, in which a dissolved magnesium alkoxide is reacted with a halogen-containing Ti or V compound and a transition metal alkoxide (cf. EP-A 319 173). The catalyst particles formed are spherical and have a mean particle size of from 10 to 70  $\mu m$ .

Finally, the use of a product of the reaction of a tetravalent, halogen-containing titanium compound with a magnesium alkoxide in which at least 40% by weight of the particles have a diameter of less than 63  $\mu m$  as transition metal component is known (cf. EP-A 223 011). A magnesium alkoxide having this particle size is obtained, *inter alia*, by

milling a commercial product in a ball mill. The magnesium alkoxide is used as a suspension in an inert hydrocarbon.

Furthermore, it has been stated in EP-A 532 551 that Ziegler catalysts having a high to

5 very high activity which are able to control the particle size distribution of the polymer are obtained when the magnesium alkoxide is used as a gel-like dispersion. This gel-like dispersion is obtained by suspending the commercial magnesium alkoxide in an inert hydrocarbon and dispersing this suspension under protective gas (Ar, N<sub>2</sub>) in a dispersing unit by means of a high-shear mixer (e.g. <sup>®</sup>Ultra-Turrax or <sup>®</sup>Dispax, IKA-  
- 10 Maschinenbau Janke & Kunkel GmbH) for a period of a number of hours or days with strong cooling.

WO 01/38405 describes a further process for reacting a gel-like dispersion of magnesium alkoxide with a transition metal compound to produce a Ziegler catalyst, in

15 which the magnesium alkoxide is firstly milled dry to a particular mean particle size in a mill under inert conditions and is only then suspended in a suspension medium and converted into the gel-like dispersion by stirring or shearing with a high-speed mixer.

A further method of producing the gel-like dispersion of magnesium alkoxide is

20 described in WO 03/99882, according to which the suspension of magnesium alkoxide in a suspension medium is firstly subjected to heat treatment beyond a particular period of time and is then converted into the gel-like dispersion by stirring or shearing with a high-speed mixer.

25 All known catalyst formulations are not completely satisfactory in that, as in the case of the magnesium alkoxide dispersion, the energy and time required for the preparation is unsatisfactorily high and should be reduced by means of suitable measures. In the case of the disclosed catalysts based on an Mg(OEt)<sub>2</sub> suspension, the polyolefin prepared by means of the catalyst has an unsatisfactorily broad particle size distribution with a high  
30 proportion of coarse material.

It was therefore an object of the present invention to find a process for preparing polyolefins in the presence of a Ziegler catalyst, one of whose components is the reaction product of a magnesium alkoxide with a transition metal compound, with the suspended magnesium alkoxide no longer requiring any pretreatment prior to the 5 reaction. In this simpler and more economical preparation, the catalyst should nevertheless display a very high polymerization activity over a long time, and the polymer prepared by means of the catalyst should have a particle size distribution which is just as narrow as polymer prepared in the presence of catalysts which are the result of complicated dispersion processes.

10

This object is achieved by a process for preparing a poly-1-olefin by polymerization of a 1-olefin of the formula  $R^4CH=CH_2$ , where  $R^4$  is hydrogen or an alkyl radical having from 1 to 10 carbon atoms, in suspension, in solution or in the gas phase, at a temperature of from 20 to 200°C and a pressure of from 0.5 to 50 bar, in the presence of a catalyst 15 which comprises the reaction product of a magnesium alkoxide with a transition metal compound (= component a) and an organometallic compound (= component b) and whose component a has been prepared in a manner having the feature that a magnesium alkoxide powder having a mean particle size, expressed as the  $d_{50}$ , in the range from 100 to 1000  $\mu m$ , preferably from 200 to 800  $\mu m$ , is firstly processed by dry 20 milling in a mill under inert conditions to produce magnesium alkoxide powder having a mean particle size, expressed as the  $d_{50}$ , of less than 15  $\mu m$ , then suspended in an inert hydrocarbon in which the magnesium alkoxide is insoluble, and is reacted immediately without further pretreatment with a transition metal compound of titanium, zirconium, vanadium or chromium.

25

The invention further relates to the catalyst obtainable by this process.

To prepare the component a, a commercially available magnesium alkoxide is used. This magnesium alkoxide can be a "simple" magnesium alkoxide of the formula 30  $Mg(OR^1)(OR^2)$ , where  $R^1$  and  $R^2$  are identical or different and are each an alkyl radical having from 1 to 6 carbon atoms. Examples are  $Mg(OC_2H_5)_2$ ,  $Mg(OiC_3H_7)_2$ ,

$Mg(OnC_4H_9)_2$ ,  $Mg(OCH_3)(OC_2H_5)$ ,  $Mg(OC_2H_5)(OnC_3H_7)$ . It is also possible to use a "simple" magnesium alkoxide of the formula  $Mg(OR)_nX_m$ , where  $X$  = halogen,  $(SO_4)_{1/2}$ ,  $OH$ ,  $(CO_3)_{1/2}$ ,  $(PO_4)_{1/3}$ ,  $Cl$ ,  $R$  is defined as for  $R^1$  or  $R^2$  and  $n + m = 2$ .

5 However, a "complex" magnesium alkoxide can also be used. For the purposes of the present invention, a "complex" magnesium alkoxide is a magnesium alkoxide comprising magnesium together with at least one metal of group 1, 2, 13 or 14 of the Periodic Table. Examples of such a complex magnesium alkoxide are:

10  $[Mg(OiC_3H_7)_4]Li_2$ ;  $[Al_2(OiC_3H_7)_8]Mg$ ;  $[Si(OC_2H_5)_6]Mg$ ;  $[Mg(OC_2H_5)_3]Na$ ;  $[Al_2(OiC_4H_9)_8]Mg$ ;  $[Al_2(O-secC_4H_9)_6(OC_2H_5)_2]Mg$ .

The complex magnesium alkoxides (alkoxo salts) are prepared by known methods.

15 Preference is given to using the simple magnesium alkoxides, in particular  $Mg(OC_2H_5)_2$ ,  $Mg(OnC_3H_7)_2$  or  $Mg(OiC_3H_7)_2$ . The magnesium alkoxide is used in pure form.

Commercial  $Mg(OC_2H_5)_2$  generally has the following specification:

20	Mg content	21 – 22% by weight
	$MgCO_3$	$\leq 1\%$ by weight
	$C_2H_5OH$ content	< 0.3% by weight

25 The mean particle diameter is in the range from 600 to 700  $\mu m$ , with at least 90% of the particles having a particle diameter in the range from 200 to 1400  $\mu m$ .

The commercial magnesium alkoxide having a mean particle diameter of from about 600 to 700  $\mu m$  is, according to the invention, milled in the dry state in a mill under inert conditions until the milled material has a mean particle diameter, expressed as the  $d_{50}$ , of less than 15  $\mu m$ .

For the purposes of the invention, a mill is considered to be under inert conditions when the proportion of gasses from the atmospheric environment in the total space of the milling apparatus which comes into contact with the magnesium alkoxide during milling has been reduced to less than 1% by volume by displacement by inert gases. For the 5 purposes of the present invention, inert gases are, in particular, nitrogen, hydrogen and argon.

Mills which are particularly suitable for the purposes of the present invention are, for example, ball mills, impact mills, opposed jet mills, spiral jet mills or air separation mills 10 of the Ultra Rotor type. A particularly useful mill is an opposed jet mill as is described in the company brochure "Mechanische Verfahrenstechnik, Trocken- and Nassprozesse" No. 017/10 297.2d from Hosakawa Alpine AG, Augsburg/Germany, and can also be procured from this company.

15 The milled magnesium alkoxide having a mean particle diameter of less than  $15 \mu\text{m}$  is, according to the invention, brought into suspension, i.e. uniformly distributed by stirring, in a vessel under inert conditions.

For the purposes of the invention, a vessel is considered to be under inert conditions 20 when the proportion of gases from the atmospheric environment in the total space of the vessel which comes into contact with the magnesium alkoxide during stirring has been reduced to less than 1% by volume by displacement by inert gases.

Inert hydrocarbons which are suitable for the purposes of the invention are aliphatic or 25 cycloaliphatic hydrocarbons such as butane, pentane, hexane, heptane, iso-octane, cyclohexane, methylcyclohexane, and also aromatic hydrocarbons such as toluene, xylene; it is also possible to use hydrogenated diesel oil fractions or petroleum spirit fractions which have carefully been freed of oxygen, sulfur compounds and moisture.

The suspension is then immediately reacted in one stage or in a plurality of stages with a Ti compound (TiCl<sub>4</sub>, Ti(OR)<sub>4</sub> etc.), a Zr compound (Zr(OR)<sub>4</sub> etc.), a V compound (VCl<sub>4</sub>, VOCl<sub>3</sub> etc.) or a chromium compound (CrO<sub>2</sub>Cl<sub>2</sub> etc.).

5 For this purpose, the magnesium alkoxide suspension is reacted with the transition metal compound at a temperature in the range from 20 to 100°C, preferably from 60 to 90°C, in the presence of an inert hydrocarbon while stirring at a stirrer speed corresponding to requirements. From 0.05 to 5 mol of transition metal compound, preferably from 0.1 to 3.5 mol, are used per 1 mol of magnesium alkoxide. The reaction 10 time is from 0.5 to 8 hours, preferably from 2 to 6 hours.

A solid which is insoluble in hydrocarbons and comprises magnesium and transition metal, which for the purposes of the invention is referred to as component a, is obtained. The component a forms a suspension with the hydrocarbon (solid/liquid).

15 The polymerization catalyst to be used according to the invention is prepared by combining the component a and an organometallic compound of a metal of group 1, 2 or 13 of the Periodic Table (component b). The component a can be reacted directly as a suspension with the component b, but it can also firstly be isolated as a solid, stored 20 and resuspended for further use later.

Preference is given to using organoaluminum compounds as component b. Suitable organoaluminum compounds include chlorine-containing organoaluminum compounds such as dialkylaluminum monochlorides of the formula R<sup>3</sup><sub>2</sub>AlCl or alkylaluminum 25 sesquichlorides of the formula R<sup>3</sup><sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>, where R<sup>3</sup> is an alkyl radical having from 1 to 16 carbon atoms. Examples which may be mentioned are (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AlCl, (iC<sub>4</sub>H<sub>9</sub>)<sub>2</sub>AlCl, (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>. It is also possible to use mixtures of these compounds.

Further suitable organoaluminum compounds are chlorine-free organoaluminum 30 compounds such as aluminum trialkyls AlR<sup>3</sup><sub>3</sub> or dialkylaluminum hydrides of the formula AlR<sup>3</sup><sub>2</sub>H, where R<sup>3</sup> is an alkyl radical having from 1 to 16 carbon atoms. Examples are

Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>H, Al(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>, Al(C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>H, Al(iC<sub>4</sub>H<sub>9</sub>)<sub>3</sub>, Al(iC<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H, Al(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>, Al(C<sub>12</sub>H<sub>25</sub>)<sub>3</sub>, Al(C<sub>2</sub>H<sub>5</sub>)(C<sub>12</sub>H<sub>25</sub>)<sub>2</sub>, Al(iC<sub>4</sub>H<sub>9</sub>)(C<sub>12</sub>H<sub>25</sub>)<sub>2</sub>.

It is also possible to use mixtures of organometallic compounds of metals of group 1, 2 or 13 of the Periodic Table, in particular mixtures of various organoaluminum compounds.

The following mixtures may be mentioned by way of example:

Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and Al(iC<sub>4</sub>H<sub>9</sub>)<sub>3</sub>, Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl and Al(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>, Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and Al(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>,  
10 Al(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H and Al(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>, Al(iC<sub>4</sub>H<sub>9</sub>)<sub>3</sub> and Al(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>, Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and Al(C<sub>12</sub>H<sub>25</sub>)<sub>3</sub>,  
Al(iC<sub>4</sub>H<sub>9</sub>)<sub>3</sub> and Al(C<sub>12</sub>H<sub>25</sub>)<sub>3</sub>, Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and Al(C<sub>16</sub>H<sub>33</sub>)<sub>3</sub>, Al(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub> and Al(C<sub>18</sub>H<sub>37</sub>)<sub>2</sub>(iC<sub>4</sub>H<sub>9</sub>),  
Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and isoprenylaluminum (= reaction product of isoprene with Al(iC<sub>4</sub>H<sub>9</sub>)<sub>3</sub> or  
Al(iC<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H).

15 Mixing of the component a and the component b can be carried out prior to the polymerization in a stirred vessel at a temperature in the range from -30 to +150°C, preferably from -10 to +120°C. It is also possible to combine the two components directly in the polymerization vessel at a temperature in the range from 20 to 200°C. However, the addition of the component b can also be carried out in two steps, by the  
20 component a being preactivated with a first part of the compound b at a temperature in the range from -30 to +150°C prior to the polymerization reaction and the further addition of a further part of the same component b or another component b being effected in the polymerization reactor at a temperature in the range from 20 to 200°C.

25 The polymerization catalyst to be used according to the invention is employed for the polymerization of 1-olefins of the formula R<sup>4</sup>-CH=CH<sub>2</sub>, where R<sup>4</sup> is a hydrogen atom or an alkyl radical having from 1 to 10 carbon atoms, for example ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene or 1-octene.

30 Preference is given to polymerizing ethylene either alone or as a mixture of at least 50% by weight of ethylene and not more than 50% by weight of another 1-olefin of the

above formula. In particular, ethylene is polymerized either alone or as a mixture of at least 90% by weight of ethylene and not more than 10% by weight of another 1-olefin of the above formula.

5 The polymerization is carried out in a known manner in solution, in suspension or in the gas phase, continuously or batchwise, in one or more stages, preferably in two or three stages, at a temperature of from 20 to 200°C, preferably from 50 to 150°C. The pressure is from 0.5 to 50 bar. Preference is given to carrying out the polymerization in the industrially particularly interesting pressure range from 1.5 to 30 bar.

10

Here, the component a or the reaction product of the component a with the component b is used in a concentration, based on transition metal, of from 0.0001 to 1 mmol, preferably from 0.001 to 0.5 mmol, of transition metal per dm<sup>3</sup> of dispersion medium. However, higher concentrations are also possible in principle.

15

The suspension polymerization is carried out in an inert suspension medium customary for the Ziegler low-pressure process, for example in an aliphatic or cycloaliphatic hydrocarbon; examples of such a hydrocarbon are butane, pentane, hexane, heptane, isooctane, cyclohexane, methylcyclohexane. It is also possible to employ petroleum spirit fractions or hydrogenated diesel oil fractions which have carefully been freed of oxygen, sulfur compounds and moisture.

20 Suspension polymerizations or gas-phase polymerizations can be carried out directly or after prepolymerization of the catalyst, with the prepolymerization advantageously being carried out by the suspension process.

25 The molar mass of the polymer is regulated in a known manner; preference is given to using an appropriate amount of hydrogen for this purpose.

Owing to the high activity of the catalyst used, the process of the invention gives polymers having a very low transition metal and halogen content and therefore extremely good results in the color stability test and corrosion test.

5 The process of the invention surprisingly makes it possible to prepare the catalysts in such a way that their particle size distribution and, to a certain extent, also the particle shape of the polymer powder formed and particularly surprisingly also the polymerization activity and the response to hydrogen of the catalyst can be set optimally without prior dispersion of the  $Mg(OEt)_2$  being necessary.

10 An improved particle morphology, especially a surprisingly narrow particle size distribution expressed as the S value in accordance with DIN 66 144, no coarse and fine fractions and high catalyst productivities are obtained according to the invention. The bulk densities are comparable to those of the prior art.

15 Thus, when the magnesium alkoxide suspensions prepared according to the invention by dry milling and subsequent simple suspension of the milled magnesium alkoxide in an inert hydrocarbon in which the magnesium alkoxide particles are not soluble are used, the morphological properties of the polymer powder can be influenced, which 20 brings with it valuable advantages for an industrial process in that the transport of the polymer powder in the plant is simpler and the powder flow is better. The high catalyst productivity gives lower residual catalyst contents in the product and thus improved quality.

25 Furthermore, the preparation of the component a requires a lower amount of energy and a significantly shorter time.

The examples described below are intended to give a person skilled in the art a clearer understanding of the invention.

10

The reported results on the element composition of the catalysts described were obtained by the following analytical methods:

Ti: photometrically via the peroxide complex

5 Mg, Cl : titrimetrically by conventional methods

The product properties reported for the polymer powders in table 1 have been determined by the following methods:

10 MFR<sub>5/190</sub>: in accordance with ISO1133

VN (viscosity number): in accordance with DIN EN ISO 1628-3

Bulk density: in accordance with DIN EN ISO 60

d<sub>50</sub> (mean particle diameter): in accordance with DIN 53477 and DIN 66144

s value: s = ln(d<sub>50</sub>/d<sub>16</sub>) in accordance with DIN 66144

15

### **Example 1 (according to the invention)**

Preparation of the catalyst component a using Mg(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> which has been milled in an opposed jet mill of the type 200 AFG from Hosokawa Alpine AG, Augsburg/Germany, at 20 a throughput of about 25 kg/h starting from commercial Mg(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> to a mean particle diameter of 5.3 µm.

22.9 g of the above-described Mg(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> were placed in a 1 dm<sup>3</sup> stirred vessel 25 provided with reflux condenser, 2-blade blade stirrer and inert gas blanketing (Ar) and suspended in 500 cm<sup>3</sup> of diesel oil having a boiling range of 140 - 170°C (hydrogenated petroleum spirit fraction). This Mg(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> suspension was immediately brought to 70°C at a stirrer speed of 250 rpm and 0.06 mol of TiCl<sub>4</sub> in 50 cm<sup>3</sup> of diesel oil (hydrogenated petroleum spirit fraction having a boiling range of 140 - 170°C) was metered in over a period of 4 hours. After an after-reaction time of 30 minutes at T = 30 70°C, the mixture was heated to 110°C and 0.14 mol of Al<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Cl<sub>3</sub> in 100 cm<sup>3</sup> of diesel oil (hydrogenated petroleum spirit fraction having a boiling range of 140 - 170°C)

was metered in over a period of 2 hours at a stirrer speed of 250 rpm. The temperature was subsequently maintained at 110°C for a further 2 hours.

This concluded the preparation of the catalyst component a.

5

The suspension of the solid was cooled to room temperature. The molar ratio was:  
 $Mg:Ti:Cl = 1:0.3:2.5$ .

### Example 2 (according to the invention)

10

In a 1 dm<sup>3</sup> stirred vessel provided with reflux condenser, 2-blade blade stirrer and inert gas blanketing (Ar), 500 cm<sup>3</sup> of diesel oil having a boiling range of 140 - 170°C (hydrogenated petroleum spirit fraction) were heated to 70°C. 22.9 g of the milled Mg(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> prepared as described in example 1 and having a mean particle diameter of 5.0 µm were subsequently suspended therein. Immediately afterward, 0.06 mol of TiCl<sub>4</sub> in 50 cm<sup>3</sup> of diesel oil (hydrogenated petroleum spirit fraction having a boiling range of 140 - 170°C) was metered in at a stirrer speed of 250 rpm over a period of 4 hours. After an after-reaction time of 30 minutes at T = 70°C, the mixture was heated to 110°C and 0.14 mol of Al<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Cl<sub>3</sub> in 100 cm<sup>3</sup> of diesel oil (hydrogenated petroleum spirit fraction having a boiling range of 140 - 170°C) was metered in at a stirrer speed of 250 rpm over a period of 2 hours. The temperature was subsequently maintained at 110°C for a further 2 hours.

This concluded the preparation of the catalyst component a.

25

The suspension of the solid was cooled to room temperature. The molar ratio was:  
 $Mg:Ti:Cl = 1:0.3:2.4$ .

**Example 3 (according to the invention)**

3.3 kg of the milled  $Mg(OC_2H_5)_2$  prepared as described in example 1 and having a mean particle diameter of 5.3  $\mu m$  were placed in a 130 l reactor equipped with impeller stirrer and baffles and suspended in 49  $dm^3$  of diesel oil having a boiling range of 140 - 170°C (hydrogenated petroleum spirit fraction). This  $Mg(OC_2H_5)_2$  suspension was immediately brought to 70°C at a stirrer speed of 100 rpm and 8.7 mol of  $TiCl_4$  in 4  $dm^3$  of diesel oil (hydrogenated petroleum spirit fraction having a boiling range of 140 - 170°C) were metered in over a period of 4 hours. After an after-reaction time of 30 minutes at  $T = 70^\circ C$ , the mixture was heated to 110°C and 41.8  $dm^3$  of a 15% strength by weight solution of  $Al_2(C_2H_5)_3Cl_3$  in diesel oil having a boiling range of 100 to 120°C (hydrogenated petroleum spirit fraction) (corresponding to 20.2 mol) were metered in over a period of 2 hours at a stirrer speed of 250 rpm. The temperature was subsequently maintained at 110°C for a further 2 hours. The mixture was then cooled to room temperature and 52  $dm^3$  of the suspension of the catalyst component a was discharged. After addition of 55  $dm^3$  of diesel oil having a boiling range of 140 - 170°C (hydrogenated petroleum spirit fraction), the mixture was heated to  $T = 65^\circ C$  and 1.8  $dm^3$  of a 10% strength by weight solution of triethylaluminum in hexane (corresponding to 1 mol) were added. At a stirrer speed of 120 rpm, the reactor was flushed three times with hydrogen and pressurized with 2 bar of hydrogen. A total of 3.7 kg of ethylene were subsequently metered in at a rate of 1 kg/h.

This concluded the preparation of the prepolymerized catalyst component.

The suspension of the solid was cooled to room temperature. The molar ratio was:  
25  $Mg:Ti:Cl = 1:0.3:2.3$ .

**Comparative example 1**

Preparation of the catalyst component a as described under example 1 with the  
30 difference that milled  $Mg(OC_2H_5)_2$  having a mean particle diameter of 50  $\mu m$  was used.

The molar ratio of the catalyst component was: Mg:Ti:Cl = 1:0.3:2.6.

### Comparative example 2

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Preparation of the catalyst component a using a gel-like  $Mg(OC_2H_5)_2$  dispersion which had been obtained by stirring a suspension of milled  $Mg(OC_2H_5)_2$  in an inert hydrocarbon.

10 A suspension of 22.9 g of the milled  $Mg(OC_2H_5)_2$  prepared as described in example 1 and having a mean particle diameter of 5.6  $\mu m$  in 0.5  $dm^3$  of diesel oil having a boiling range of 140 - 170°C (hydrogenated petroleum spirit fraction) was stirred up in a 1  $dm^3$  stirred vessel provided with reflux condenser, 2-blade blade stirrer and inert gas blanketing (Ar) at  $T = 60^\circ C$  for a period of 20 hours at a stirrer speed of 60 rpm

15 (revolutions per minute). The settling time of the resulting gel-like  $Mg(OC_2H_5)_2$  dispersion after switching off the stirrer was more than 30 minutes.

This  $Mg(OC_2H_5)_2$  dispersion was brought to 70°C at a stirrer speed of 250 rpm and 0.06 mol of  $TiCl_4$  in 50  $cm^3$  of diesel oil (hydrogenated petroleum spirit fraction having a boiling range of 140 - 170°C) was metered in over a period of 4 hours. The mixture was then heated to 110°C and 0.14 mol of  $Al_2(C_2H_5)_3Cl_3$  in 100  $cm^3$  of diesel oil (hydrogenated petroleum spirit fraction having a boiling range of 140 - 170°C) was metered in over a period of 2 hours at a stirrer speed of 250 rpm. The temperature was subsequently maintained at 110°C for a further 2 hours.

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This concluded the preparation of the catalyst component a.

The suspension of the solid was cooled to room temperature. The molar ratio was:

$Mg:Ti:Cl = 1:0.3:2.5$ .

**Comparative example 3**

Preparation of the catalyst component a as described under comparative example 2 with the difference that unmilled commercial  $Mg(OC_2H_5)_2$  having a mean particle 5 diameter of from 600 to 700  $\mu m$  was used.

The molar ratio of the catalyst component a was:  $Mg:Ti:Cl = 1:0.3:2.7$ .

**Example 4**

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Polymerization experiments using the catalysts from examples 1 to 3 and also the comparative examples.

The polymerization experiments were carried out batchwise in a 200  $dm^3$  reactor. This 15 reactor was equipped with an impeller stirrer and baffles. The temperature in the reactor was measured and automatically kept constant. The polymerization temperature was  $85 \pm 1^\circ C$ .

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The polymerization reaction was carried out in the following manner:  
100  $dm^3$  of diesel oil (hydrogenated petroleum spirit fraction having a boiling range of 140 - 170°C) were placed in the  $N_2$ -blanketed reactor and heated to 85°C. Under a blanket of inert gas ( $N_2$ ), the cocatalyst ( $Al(C_2H_5)_3$ ) was added in such an amount that a cocatalyst concentration of 0.50 mmol/ $dm^3$  was present in the reactor. The catalyst 25 component a was then introduced into the reactor in an amount corresponding to 2.0 mmol of titanium as a suspension diluted with diesel oil.

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The reactor was pressurized a number of times to 8 bar with  $H_2$  (hydrogen) and depressurized again in order to remove the nitrogen completely from the reactor (the procedure was monitored by measuring the  $H_2$  concentration in the gas space of the reactor, which was finally 95% by volume). The polymerization was started by opening

the ethylene inlet. Ethylene was introduced in an amount of 8.0 kg/h over the entire polymerization time, with the pressure in the reactor slowly increasing. The hydrogen concentration was continually measured in the gas space of the reactor and the proportion by volume was kept constant by metering in appropriate amounts of 5 hydrogen (% by volume of  $H_2$  = 40).

The polymerization was stopped after 225 minutes (30 kg of ethylene introduced) and the total pressure was read off. The contents of the reactor were drained onto a filter. The polymer which was moist with diesel oil was dried for a number of hours in a 10 stream of nitrogen. The results of the polymerizations are shown in table 1.

It can clearly be seen from the values in the table that a catalyst having an excellent property spectrum can be prepared in an advantageous manner by the process of the invention without a time-consuming dispersion step. The catalyst activity, expressed in 15 final pressure in bar, is high. A low final pressure indicates that a low ethylene partial pressure is established in order to obtain the same amount of polymer using the same amount of catalyst under the same experimental conditions (cf.: L. L. Böhm, Chem. Ing. Techn. 56 (1984) 674, eq. (2)). The high values for  $MFR_{5/190}$  indicate a very good response to hydrogen. In particular, a very narrow particle size distribution of the 20 polymer, expressed by the s value in accordance with DIN 66 144, is obtained. This means a reduction in the proportion of fines in the polymer powder, which in industry has the advantages that discharge of troublesome fine dust no longer takes place, that the drying time is shortened and that better transport behavior of the powder leads to a higher intake into the extruder for pelletization. Furthermore, the polymers prepared 25 using the catalyst prepared by the process of the invention have a very low proportion of coarse material ( $> 800 \mu m$ ). This is advantageous for speck-free homogenization in the extruder.

Comparison with comparative example 1 shows that a particle diameter higher than that 30 used according to the process of the invention produces a catalyst having a significantly lower activity and that the polymer has an unsatisfactory particle size distribution.

Comparison with comparative example 2 and comparative example 3 shows that a costly dispersion step of 20 hours does not give an improved catalyst.

**Table 1:** Polymerization experiments in 200 dm<sup>3</sup> reactor,  
 50 mmol of triethylaluminum, 2.0 mmol of Ti (catalyst component a),  
 100 dm<sup>3</sup> of diesel oil, 8.0 kg/h of ethylene, polymerization temperature of 85°C,  
 polymerization time of 225 min, 40% by volume of hydrogen in the gas space  
 5.

Catalyst component from	Ex. 1	Ex. 2	Ex. 3	Comp. ex. 1	Comp. ex. 2	Comp. ex. 3
d <sub>50</sub> of Mg(OEt) <sub>2</sub> / μm	5.3	5.0	5.3	50	5.6	600 - 700
Dispersion time of Mg(OEt) <sub>2</sub> / [h]	0	0	0	0	20	20
Final pressure / bar	4.7	4.0	4.9	8.7	4.7	5.2
Yield of PE / kg	29.9	30.0	30.1	30.0	30.3	29.9
MFR <sub>5/190</sub> / g/10min	5.5	4.3	5.2	4.8	3.3	4.8
VN / cm <sup>3</sup> /g	178	200	196	219	208	195
Bulk density / g/L	378	370	306	332	339	346
d <sub>50</sub> / μm	257	221	251	513	262	355
>800 μm/ %	0.10	0.11	0.05	22.4	0.03	1.4
s value	0.209	0.249	0.229	0.468	0.256	0.292

\* \* \* \* \*

## Claims:

1. A process for preparing a poly-1-olefin by polymerization of a 1-olefin of the formula  $R^4CH=CH_2$ , where  $R^4$  is hydrogen or an alkyl radical having from 1 to 10 carbon atoms, in suspension, in solution or in the gas phase, at a temperature of from 20 to 200°C and a pressure of from 0.5 to 50 bar, in the presence of a catalyst which comprises the reaction product of a magnesium alkoxide with a transition metal compound (= component a) and an organometallic compound (= component b) and whose component a has been prepared in a manner having the feature that a magnesium alkoxide powder having a mean particle size, expressed as the  $d_{50}$ , in the range from 100 to 1000  $\mu m$ , preferably from 200 to 800  $\mu m$ , is firstly processed by dry milling in a mill under inert conditions to produce magnesium alkoxide powder having a mean particle size, expressed as the  $d_{50}$ , of less than 15  $\mu m$ , then suspended in an inert hydrocarbon in which the magnesium alkoxide is insoluble, and is reacted immediately without further pretreatment with a transition metal compound of titanium, zirconium, vanadium or chromium.
2. The process according to claim 1, wherein the inert hydrocarbon used is an aliphatic or cycloaliphatic hydrocarbon such as butane, pentane, hexane, heptane, isooctane, cyclohexane, methylcyclohexane, or an aromatic hydrocarbon such as toluene, xylene or a hydrogenated diesel oil fraction or petroleum spirit fraction which has carefully been freed of oxygen, sulfur compounds and moisture.
3. The process according to claim 1 or 2, wherein the milled and suspended magnesium alkoxide is reacted in one stage or in a plurality of stages with a Ti compound such as  $TiCl_4$  or  $Ti(OR)_4$ , a Zr compound such as  $ZrCl_4$  or  $Zr(OR)_4$ , a V compound such as  $VCl_4$  or  $VOCl_3$  or a chromium compound such as  $CrO_2Cl_2$ .

4. The process according to any of claims 1 to 3, wherein the milled and suspended magnesium alkoxide is reacted with the transition metal compound at a temperature in the range from 20 to 100°C, preferably from 60 to 90°C, in the presence of an inert hydrocarbon while stirring, using from 0.05 to 5 mol of transition metal compound per 1 mol of magnesium alkoxide, preferably from 0.1 to 3.5 mol per mole of magnesium alkoxide.
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5. The process according to any of claims 1 to 4, wherein the reaction time is from 0.5 to 8 hours, preferably from 2 to 6 hours.
6. The process according to any of claims 1 to 5, wherein organoaluminum compounds, chlorine-containing organoaluminum compounds such as dialkylaluminum monochlorides of the formula  $R^3_2AlCl$  or alkylaluminum sesquichlorides of the formula  $R^3_3Al_2Cl_3$ , where  $R^3$  is an alkyl radical having from 1 to 16 carbon atoms, e.g.  $(C_2H_5)_2AlCl$ ,  $(iC_4H_9)_2AlCl$ ,  $(C_2H_5)_3Al_2Cl_3$ , or mixtures of these compounds are used as component b.
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7. The process according to any of claims 1 to 6, wherein mixing of the component a and the component b is carried out prior to the polymerization in a stirred vessel at a temperature in the range from -30 to 150°C, preferably from -10 to 120°C, or the two components are combined directly in the polymerization vessel at a temperature in the range from 20 to 200°C or the addition of the component b is carried out in two steps, with the component a being preactivated with a first part of a component b at a temperature in the range from -30 to 20
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- +150°C prior to the polymerization reaction and the further addition of a further part of the same component b or another component b being effected in the polymerization reactor at a temperature of from 20 to 200°C.
8. The process according to any of claims 1 to 7, wherein the catalyst is added in the prepolymerized state to the polymerization reaction.
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9. The process according to any of claims 1 to 8 used for the polymerization of 1-olefins of the formula  $R^4\text{-CH=CH}_2$ , where  $R^4$  is a hydrogen atom or an alkyl radical having from 1 to 10 carbon atoms, preferably for the polymerization of ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene or 1-octene, with particular preference being given to polymerizing ethylene either alone or as a mixture of at least 50% by weight of ethylene and not more than 50% by weight of another 1-olefin of the above formula, wherein the regulation of the molar mass of the polymer is preferably effected by means of hydrogen.

10. 10. The process according to any of claims 1 to 9, wherein the polymerization is carried out in solution, in suspension or in the gas phase, continuously or batchwise, in one or more stages at a temperature in the range from 20 to 200°C, preferably from 50 to 150°C, and the pressure is from 0.5 to 50 bar, preferably from 1.5 to 30 bar.

11. 11. The process according to any of claims 1 to 10, wherein the component a or the reaction product of the component a with the component b is used in a concentration, based on transition metal, of from 0.0001 to 1 mmol, preferably from 0.001 to 0.5 mmol, of transition metal per dm<sup>3</sup> of dispersion medium and the polymerization is carried out in an inert dispersion medium selected from the group consisting of aliphatic or cycloaliphatic hydrocarbons such as butane, pentane, hexane, heptane, isoctane, cyclohexane, methylcyclohexane, and petroleum spirit fractions or hydrogenated diesel oil fractions which have carefully been freed of oxygen, sulfur compounds and moisture.

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP2005/008127

A. CLASSIFICATION OF SUBJECT MATTER		
C08F10/00 C08F4/654 C08F4/655		
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 practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 223 011 A (RUHRCHEMIE AKTIENGESELLSCHAFT) 27 May 1987 (1987-05-27) page 2, line 48 – line 49 page 3, line 1 – line 4 page 3, line 10 – line 12 examples -----	1-11
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X	US 4 613 581 A (MARUYAMA ET AL) 23 September 1986 (1986-09-23) comparative example 1 -----	1-11
<input type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.
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Information on patent family members

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