

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
21 January 2010 (21.01.2010)

PCT

(10) International Publication Number  
**WO 2010/006756 A1**

(51) International Patent Classification:  
C08F 10/02 (2006.01) C08F 4/654 (2006.01)

(21) International Application Number:  
PCT/EP2009/005102

(22) International Filing Date:  
10 July 2009 (10.07.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
08012990.1 18 July 2008 (18.07.2008) EP

(71) Applicant (for all designated States except US): SAUDI  
BASIC INDUSTRIES CORPORATION [SA/SA]; P.O.  
Box 5101, 11422 Riyadh (SA).

(72) Inventor; and

(75) Inventor/Applicant (for US only): FRIEDERICHS,  
Nicolaas, Hendrika [NL/NL]; P.O. Box 3008, NL-6160  
GA Geleen (NL).

(74) Agent: BOOTSMA, J., P., C.; Sabic Corporate Patent  
Group, P.O. Box 3008, NL-6160 GA Geleen (NL).

(81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,  
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,  
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO,  
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,  
HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP,  
KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD,  
ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI,  
NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD,  
SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT,  
TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,  
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ,  
TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,  
MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM,  
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,  
ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))



WO 2010/006756 A1

(54) Title: PROCESS FOR THE PRODUCTION OF POLYETHYLENE

(57) Abstract: The invention relates to a catalyst for the production of polyethylene comprising a solid reaction product obtained by reaction of: (a) a hydrocarbon solution comprising (1) an organic oxygen containing magnesium compound and (2) an organic oxygen containing titanium compound and (b) a compound comprising a transition metal from Group IV or V of Mendeleev's Periodic System of Chemical Elements and containing at least two halogen atoms. Preferably the catalyst is applied during the polymerisation of ethylene to obtain ultra high molecular weight polyethylene and to obtain bimodal polyethylene.

## PROCESS FOR THE PRODUCTION OF POLYETHYLENE

The present invention relates to a catalyst and to a process for the production of polyethylene in the presence of this catalyst system.

5           The production of polyethylene in the presence of a catalyst system is very well known. Dall'Occo et al. disclose in "Transition Metals and Organometallics as Catalysts for Olefin Polymerisation" (Kaminsky, W.; Sinn, H., Eds.) Springer, 1988, page 209 that the main requirements of industrial  
10 kinetic, no reactor fouling, control of morphology, average particle size and bulk density of the polymer particles.

The bulk density of the polyethylene powder refers to the mass of the powder per unit of volume. This is an important parameter because the obtained powder has to be stored and to be transported. A  
15 higher bulk density may decrease clogging at its transportation and it is possible to increase the storable amount per unit volume. By increasing the bulk density, the weight of the polyethylene per unit volume present in a polymerisation vessel will be increased and the concentration of the polyethylene powder in the polymerisation vessel can be enhanced.

20           The bulk density can be highly affected by the shape of the polymer particles. It is also well known that the shape of the polymer powder particles is translated from the shape of the catalyst particles, also known as the replica phenomenon. In general, when this replication takes place, the average particle size of the polymer is proportional to the cube root of the  
25 catalyst yield, i.e. the grams of polymer produced per gram of catalyst. See for example Dall'Occo et al, in "Transition Metals and Organometallics as Catalysts for Olefin Polymerization" (Kaminsky, W.; Sinn, H., Eds.) Springer, 1988, page 209-222. In order to have control over the bulk density of the polymer powder it is important to have control over the shape of the catalyst  
30 particles.

It is the object of the present invention to provide a catalyst which results in polyethylene displaying a high powder bulk density and a high catalyst activity.

The catalyst system according to the invention comprises a

solid reaction product obtained by reaction of

(a) a liquid hydrocarbon solution comprising

(1) an organic oxygen containing magnesium compound and

(2) an organic oxygen containing titanium compound and

- 5 (b) a compound comprising a transition metal from Group IV or V of Mendeleev's Periodic System of Chemical Elements and containing at least two halogen atoms.

According to a preferred embodiment of the invention the solid reaction product from (a) and (b) is treated with

- 10 (c) an aluminium compound having the formula  $AlR_nX_{3-n}$  wherein X is an halogenide and R is a hydrocarbon radical containing 1 – 10 carbon atoms and  $0 < n \leq 3$ .

Preferably the aluminium compound has the formula  $AlR_nCl_{3-n}$  wherein R is a hydrocarbon radical containing 1 – 10 carbon atoms and  $0 < n \leq 3$ .

The catalyst according to the present invention is the solid reaction product obtained from the reaction of two liquid compounds. In order to have control over the shape of the catalyst particles, it is essential that the hydrocarbon solution comprising

- 20 (1) an organic oxygen containing magnesium compound and  
(2) an organic oxygen containing titanium compound  
is a liquid because the presence of any solid particles in the starting compounds might undesirably influence the size and shape of the subsequent catalyst particles

25 Suitable organic oxygen containing magnesium compounds include for example magnesium alkoxides such as magnesium methylete, magnesium ethylete and magnesium isopropylete and magnesium alkylalkoxides such as magnesium ethylethylete.

According to a preferred embodiment of the invention the  
30 organic oxygen containing magnesium compound is a magnesium alkoxide.

Preferably, the magnesium alkoxide is a magnesium ( $C_1-C_3$ ) alkoxide.

More preferably the magnesium alkoxide is magnesium ethoxide  $Mg(OC_2H_5)_2$

According to a preferred embodiment of the invention, the organic oxygen containing titanium compound may be represented by the general formula  $[TiO_x (OR)_{4-2x}]_n$  in which R represents an organic radical, x ranges between 0 and 1 and n ranges between 1 and 6.

5 Suitable examples of organic oxygen containing titanium compounds include alkoxides, phenoxides, oxyalkoxides, condensed alkoxides, carboxylates and enolates.

According to a preferred embodiment of the invention the organic oxygen containing titanium compound is a titanium alkoxide.

10 Suitable titanium alkoxides include for example  $Ti(OC_2H_5)_4$ ,  $Ti(OC_3H_7)_4$ ,  $Ti(OC_4H_9)_4$  and  $Ti(OC_8H_{17})_4$ .

According to a preferred embodiment of the invention the titanium alkoxide is  $Ti(OC_4H_9)_4$ .

15 Preferred compounds comprising a transition metal from Group IV or V of Mendeleev's Periodic System of Chemical Elements and containing at least two halogen atoms are Ti (IV) halogenide, V (III) halogenide, V (IV) halogenide and V (V) oxyhalogenide.

Preferably Ti (IV) halogenide is  $TiCl_4$ .

Preferably V (III) halogenide is  $VCl_3$ .

20 Preferably V (V)oxyhalogenide is  $VOCl_3$ .

The most preferred transition metal compound is  $TiCl_4$ .

25 Suitable examples of the aluminium compound having the formula  $AlR_nCl_{3-n}$  include ethyl aluminium dichloride, propyl aluminium dichloride, n- butyl aluminium dichloride, iso butyl aluminium dichloride, diethyl aluminium chloride and diisobutyl aluminium chloride, triethyl aluminium, triisobutyl aluminium and trihexyl aluminium.

According to a preferred embodiment of the invention the organo aluminium compound is ethyl aluminium dichloride.

30 The hydrocarbon solution comprising an organic oxygen containing magnesium compound and an organic oxygen containing titanium compound can be prepared according to procedures as disclosed for example in US 4178300 and EP 876318. The solutions are in general clear liquids. In case there are any solid particles, for example due to unreacted starting materials, these can be removed via filtration prior to the use of the

solution in the catalyst synthesis.

The molar ratio the organic oxygen containing magnesium compound from (a) (1) to the organic oxygen containing titanium compound from (a) (2) may range between 0.1:1 and 3:1.

5 Preferably this ratio is between 0.5:1 and 3:1.

More preferably this ratio is between 1.5:1 and 2.5:1.

The molar ratio of the halogen from (b) to magnesium from (a) (1) is at least 0.25:1.

More preferably this ratio is at least 0.5:1.

10 Preferably the halogen is chlorine.

The molar ratio of the aluminium compound from (c): the transition metal compounds from (a) (2) and (b) ranges between 0.1: 1 and 20:1.

More preferable this ratio ranges between 0.3:1 and 10:1.

15 The catalyst may be obtained for example by a first reaction between a magnesium alkoxide and a titanium alkoxide, followed by dilution with a hydrocarbon solvent such as for example pentane, hexane or heptane, resulting in a soluble complex consisting of a magnesium alkoxide and a titanium alkoxide and thereafter a reaction between a hydrocarbon solution of  
20 said complex and the transition metal compound.

The transition metal compound, for example  $TiCl_4$ , is preferably used as a solution in a hydrocarbon such as for example pentane, hexane or heptane.

25 The temperature for the reaction between (a) and (b) may be any temperature below the boiling point of the applied hydrocarbon.

Preferably the temperature is below 60°C and more preferably below 50°C. Generally the addition takes place during more than 10 minutes.

30 During the reaction of the hydrocarbon solution comprising the organic oxygen containing magnesium compound and the organic oxygen containing titanium compound with the transition metal compound a solid precipitates and after the precipitation reaction the resulting mixture is heated and refluxed to finish the reaction. After the reaction the precipitate is filtered and washed with a hydrocarbon. Other means of separation of the solids from the diluent and subsequent washings can also be applied, like for

example multiple decantation steps. All steps should be performed in an inert atmosphere of nitrogen or another suitable inert gas. The post treatment step with the aluminium compound may be performed either before the filtration and washing steps or after this procedure.

5                    Generally the average particle size of the catalyst ranges between 3  $\mu\text{m}$  and 30  $\mu\text{m}$ .

                    Preferably the average particle size of the catalyst ranges between 3  $\mu\text{m}$  and 10  $\mu\text{m}$ .

10                   Generally the span of the particle size distribution is lower than 3.

                    The catalyst system according to the invention results in polyethylene having the desired values for powder bulk density, span and an average particle size below for example 400  $\mu\text{m}$ .

15                   The catalyst shows high catalyst activity and productivity and the catalyst residues in the polymer are very low.

                    An additional advantage is the relatively simple and cheap synthesis to produce the catalyst because the synthesis is based on compounds which are readily available and relatively easy to handle.

20                   The process to obtain the polyethylene takes place in the presence of a catalyst and a co catalyst wherein the catalyst comprises the solid reaction product obtained by reaction of:

(a) a hydrocarbon solution comprising

(1) an organic oxygen containing magnesium compound

(2) an organic oxygen containing titanium compound and

25                   (b) a compound comprising a transition metal from Group IV or V of

Mendeleev's Periodic System of Chemical Elements and containing at least two halogen atoms and wherein

the co catalyst is an organo aluminium compound having the formula  $\text{AlR}_3$  in which R is a hydrocarbon radical containing 1 – 10 carbon atoms.

30                   Suitable examples of the organo aluminum compound of the formula  $\text{AlR}_3$  include for example triethylaluminium, triisobutyl aluminium tri-n-hexyl aluminium and tri octyl aluminium.

                    According to a preferred embodiment of the invention the solid reaction product from (a) and (b) is post treated with (c) an aluminium

compound having the formula  $AlR_nX_{3-n}$  wherein R is a hydrocarbon radical containing 1 – 10 carbon atoms, X is a halogenide and  $0 < n \leq 3$ .

Preferably the halogenide is a chloride.

The obtained particle morphology of the catalyst is excellent,  
5 which is beneficial to all particle forming polymerisation processes.

Generally the bulk density of the polyethylene powder of the invention ranges between  $200 \text{ kg/m}^3$  and  $500 \text{ kg/m}^3$  and preferably this bulk density ranges between  $250 \text{ kg/m}^3$  and  $400 \text{ kg/m}^3$ .

The ethylene homo polymer and/or co polymer obtained with  
10 the process according to the invention is a powder having the following characteristics:

- an average molecular weight higher than  $10,000 \text{ g/mol}$  and lower than  $10,000,000 \text{ g/mol}$
- an average particle size ( $d_{50}$ ) between  $50$  and  $400 \mu\text{m}$  and
- 15 • a bulk density in a range between  $200$  and  $500 \text{ kg/m}^3$

The polymerisation reaction of ethylene may be performed in the gas phase or in bulk in the absence of an organic solvent or carried out in liquid slurry in the presence of an organic diluent. The polymerisation can be carried out batchwise or in a continuous mode. The polymerisation can also  
20 be carried out in multiple interconnected reactors, for example in 2 reactors in series using different conditions in each reactor in order to broaden the molecular weight and compositional distribution of the polyethylene and to obtain bimodal polyethylene. These reactions are performed in the absence of oxygen, water, or any other compounds that may act as a catalyst poison.

Suitable solvents include for example alkanes and cycloalkanes such as pentane, hexane, heptane, n-octane, iso-octane, cyclohexane, and methylcyclohexane; alkylaromatics such as toluene, xylene, ethylbenzene, isopropylbenzene, ethyltoluene, n-propylbenzene and diethylbenzene. The polymerisation temperature may range between  $20^\circ\text{C}$  and  $200^\circ\text{C}$  and  
30 preferably ranges between  $20^\circ\text{C}$  and  $120^\circ\text{C}$ . The partial pressure of a monomer during polymerisation may be the atmospheric pressure and more preferably a partial pressure between 2 and 40 bars.

The polymerisation can be carried out in the presence of a

so-called anti-static agent or anti fouling agent, in an amount ranging from 1 to 500 ppm related to the total reactor contents.

Also so-called external donors may be applied during the polymerisation in order to further modify the catalyst performance if this is desired. Suitable external donors are organic compounds containing hetero atoms which have at least one lone pair of electrons available for coordination to the catalyst components or aluminum alkyls. Suitable examples of external donors include alcohols, ethers, esters, silanes and amines.

The catalyst according to the invention may be applied in ethylene polymerisation processes to produce for example high density polyethylene, linear low density polyethylene and ultra high molecular weight polyethylene. Polyethylenes and production processes are disclosed in "Handbook of polyethylene" by Peacock ; pages 1-66 (ISBN 0-8247-9546-6).

According to a preferred embodiment of the invention the catalyst is applied in the production of ultra high molecular weight polyethylene (UHMWPE).

Ultra high molecular weight polyethylene is a special class of polyethylene. A polymer synthesis to obtain UHMWPE is disclosed in Journal of Macromolecular Science Part C Polymer Reviews, Vol. C42, no 3, pp 355-371, 2002. Generally UHMWPE is a linear polyethylene with a very high average molecular weight ranging from about 1,000,000 to well above 6,000,000 grams/mole.

The molecular mass of the polymer can be controlled by any means as known in the art, like for example by adjustment of the polymerisation temperature or by the addition of molecular weight control agents, like hydrogen. In the case of UHMWPE, it is difficult to analyze its molar mass by for instance Gel Permeation Chromatography (GPC) due to the very high molecular weight of UHMWPE. Hence it is common to measure the viscosity of a dilute solution of UHMWPE, for instance in decalin at 135°C. This viscosity can subsequently be translated to the molecular weight.

According to a further preferred embodiment of the invention the catalyst is applied in the production of bimodal polyethylene. The production of polyethylene in a so-called bimodal process and the use of the

bimodal products are disclosed at pages 15-20 of "PE 100 pipe systems" (second edition, editor Bromstrup, ISBN 3-8027-2728-2).

WO 01/00692 discloses a method of halogenating a solid precursor to form a solid polymerization procatalyst. A solid  
5 magnesium/transition metal-containing alkoxide complex precursor is separately prepared and subsequently contacted with a halogenating agent selected from alkylaluminum halide,  $TiX_4$ ,  $SiX_4$ ,  $BX_3$ , and  $Br_2$ , where halide and X are each respectively a halogen, and when an alkylaluminum halide,  $TiX_4$ ,  $SiX_4$ , and  $Br_2$  are used as the halogenating agent, they are used  
10 together or in combination in a multi-step halogenation. The procatalyst then can be converted to an olefin polymerization catalyst by contacting it with a cocatalyst and optionally a selectivity control agent. In contrast to the present invention the precursor of WO 01/00692 is solid. Therefore, the halogenation step according to WO 01/00692 must be carefully carried out in order to  
15 preserve the morphology as dictated by the solid magnesium/transition metal-containing alkoxide complex precursor. WO 01/00692 is not directed to UHMWPE or to bimodal polyethylene.

EP1661917 is directed to a process for the preparation of a catalyst component for the polymerization of an olefin wherein a solid  
20 compound with formula  $Mg(OAlk)_x Cl_y$  is contacted with a titanium tetraalkoxide in the presence of an inert dispersant to give an intermediate reaction product and wherein the intermediate reaction product is contacted with titanium tetrachloride in the presence of an internal electron donor. The catalyst component of the invention is very suitable for the preparation of poly  
25 propylene. According to this disclosure, the solid particles are obtained by treating a solution of a magnesium Grignard compound with an alkoxy silane using a mixing device in order to improve the morphology of the catalyst particles. The resulting solid particles are subsequently treated with a titanium tetraalkoxide to obtain a solid intermediate reaction product which  
30 than is contacted with titanium tetrachloride in the presence of an internal electron donor. This product may be applied during the preparation of a polypropylene catalyst. However, the synthesis involves multiple steps and would be too elaborate to result in a cost effective catalyst for polyethylene.

EP 398167 discloses the polymerisation of ethylene using a

catalyst which comprises a trialkyl aluminium compound and the entire product from the reaction of a very special magnesium alkoxide compound dissolved in an inert solvent with a tetravalent transition-metal compound and an organoaluminium compound and optionally an electron donor. Contrary to the catalyst according to the present invention, the catalyst according to EP 398167 is prepared via solid particles obtained from the reaction of the special magnesium compound, like for example magnesiumbis(2-methyl-1pentyl-oxide), with a titanium compound and an aluminum compound. According to the present invention relatively cheap magnesium alkoxides like Mg(OC<sub>2</sub>H<sub>5</sub>) are applied. These alkoxides are excluded in the invention according to EP398167.

US6114271 discloses a process for the preparation of a catalyst component for the polymerization and copolymerization of ethylene to give ultrahigh-molecular-weight ethylene polymers. Reaction of a Grignard compound with a halogenating agent, a titanium compound, a perhalogen compound and an electron-donor compound and subsequent comminution of the resultant solid to a mean particle size of from 0.5 to 5 micrometers gives a catalyst component which, together with an organoaluminum compound, results in ultrahigh-molecular-weight ethylene polymers having a mean particle diameter of from 50 to 200 micrometers and a viscosity index of greater than 2,000 cm<sup>3</sup>/g. The preparation of the catalyst component consists essentially of (A) reacting a dialkyl magnesium compound with a halogenating agent of the formula R<sub>3</sub>Cl to give a solid product and (B) reacting the solid product with a hydrocarbon-soluble titanium compound together with a perhalogen compound. US6114271 does not disclose the use of an organic oxygen containing magnesium compound. Additionally US6114271 teaches the use of toxic compounds like tetrachloromethane or chloroform. These undesired compounds are not required for the preparation of the catalyst according to the present invention.

EP574153 discloses a process for preparing an ultra-high molecular weight polyethylene, using a solid catalyst obtained by contacting a reaction product resulting from the reaction of a magnesium halide and a titanium containing compound and a reaction product resulting from the reaction of an aluminum halide like AlCl<sub>3</sub> and a compound of the formula

$R^2OR^3$ . Essential differences between EP574153 and the present invention are the use of the magnesium halide instead of the organic oxygen containing magnesium compound and the use of  $AlCl_3$  instead of an aluminium compound having the formula  $AlR_nX_{3-n}$  wherein X is a halogenide and R is a hydrocarbon radical containing 1 – 10 carbon atoms and  $0 < n \leq 3$ . EP574153 teaches that the use of a halogenated transition metal compound like  $TiCl_4$  leads to relatively low catalyst activities and reduced bulk density.

EP 317200 discloses a process for preparing an ultra-high molecular weight polyethylene by the polymerization of ethylene using a catalyst comprising a solid catalyst component and an organometallic compound wherein the solid catalyst component is a product obtained by contacting the reaction product of a magnesium dihalide and a titanium compound represented by the general formula  $Ti(OR)_4$  and the reaction product of an aluminum trihalide and a silicon compound represented by the general formula  $Si(OR)_4$ . Essential differences are the use of the magnesium halide instead of the organic oxygen containing magnesium compound and the use of  $AlCl_3$  instead of an aluminium compound having the formula  $AlR_nX_{3-n}$  wherein X is a halogenide and R is a hydrocarbon radical containing 1 – 10 carbon atoms and  $0 < n \leq 3$ .

The invention will be elucidated by means of the following non-restrictive examples.

### Examples

All examples were carried out under a blanket of nitrogen. The poured bulk density of the polyethylene polymer powder is determined by measuring the bulk density of the polymer powder according to ASTM D1895/A.

The Flow Value is determined according to DIN53493.

The average particle size ( $D_{50}$ ) of the catalyst was determined by the so called laser light scattering method in hexanes diluent using a Malvern Mastersizer equipment.

The average particle size and particle size distribution (“span”) of the polymer powders were determined by sieve analyses according to DIN53477

The solids content in the catalyst suspension was determined in triplo by drying 10 ml of a catalyst suspension under a stream of nitrogen, followed by evacuating for 1 hour and subsequently weighing the obtained amount of dry catalyst.

5

### Example I

#### Preparation of a hydrocarbon solution comprising the organic oxygen containing magnesium compound and the organic oxygen containing titanium compound

10 100 grams of granular Mg (OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> and 150 millilitres of Ti (OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> were brought in a 2 Litre round bottomed flask equipped with a reflux condensor and stirrer. While gently stirring, the mixture was heated to 180°C and subsequently stirred for 1, 5 hours. During this, a clear liquid was obtained. The mixture was cooled down to 120°C and subsequently diluted with 1480  
15 ml of hexane. Upon addition of the hexane, the mixture cooled further down to 67°C. The mixture was kept at this temperature for 2 hours and subsequently cooled down to room temperature. The resulting clear solution was stored under nitrogen atmosphere and was used as obtained. Analyses on the solution showed a titanium concentration of 0, 25 mol/l.

20

### Example II

#### Preparation of the catalyst

400 ml hexane was added to a three neck glass vessel, equipped with baffles, a stirrer, a dropping funnel and a condenser. To this, 2 ml (18, 2  
25 mmol) TiCl<sub>4</sub> was added. The stirrer was set at 650 RPM. Via the dropping funnel, 80 ml of the hydrocarbon solution comprising the organic oxygen containing magnesium and titanium compound prepared according to Example I was dosed in 30 minutes time. During this dosing a white precipitate was formed. The mixture was heated to 50°C and stirred at this  
30 temperature for 1 hour. Subsequently the mixture was cooled down to ambient temperature. Then 75 ml of a 50wt% solution of ethyl aluminium dichloride was dosed in 20 minutes time, after which the mixture was heated to 70°C and kept at this temperature for 3 hours.

The red-brown suspension was filtered and the solids were washed 3 times

with hexanes. The solids were resuspended in hexanes.

### Example III

#### Preparation of the catalyst

5 400 ml hexane was added to a three neck glass vessel, equipped with baffles', a stirrer and a dropping funnel and condenser To this, 4 ml (36,4 mmol)  $\text{TiCl}_4$  was added. The stirrer was set at 900 RPM. Via the dropping funnel, 75 ml of the hydrocarbon solution comprising the organic oxygen containing magnesium and titanium compound prepared according to

10 Example I was dosed in 90 minutes time. During this dosing a white precipitate was formed. The mixture was heated to  $70^\circ\text{C}$  and stirred at this temperature for 1 hour. Subsequently the mixture was cooled down to ambient temperature. Then 50 ml of a 50wt% solution of ethyl aluminium dichloride was dosed in 60 minutes time, after which the mixture was heated

15 to  $70^\circ\text{C}$  and kept at this temperature for 2 hours.

The red-brown suspension was filtered and the solids were washed 3 times with hexanes. The solids were resuspended in hexanes.

### Example IV

#### Preparation of the catalyst

20 400 ml hexane was added to a three neck glass vessel, equipped with baffles, a stirrer and a dropping funnel and condenser. To this, 1 ml (9.1 mmol)  $\text{TiCl}_4$  was added. The stirrer was set at 930 RPM. Via the dropping funnel, a mixture of 50 ml hexanes and 75 ml of the hydrocarbon solution

25 comprising the organic oxygen containing magnesium and titanium compound prepared according to Example I was dosed in 20 minutes time. During this dosing a white precipitate was formed. The mixture was heated to  $50^\circ\text{C}$  and stirred at this temperature for 1 hour. Subsequently the mixture was cooled down to ambient temperature. Then 50 ml of a 50wt% solution of

30 ethylaluminiumdichloride was dosed in 15 minutes time, after which the mixture was heated to  $70^\circ\text{C}$  and kept at this temperature for 2 hours.

The red-brown suspension was filtered and the solids were washed 3 times with hexanes. The solids were resuspended in hexanes.

Example VPolymerisation in the presence of the catalyst according to Example II

To a 10L autoclave, containing 5 L purified hexanes as a diluent, 8 mmols of  
5 tri-iso butylaluminium were added. The mixture was heated to 75°C and  
pressurized with 1.5 bars of ethylene. Subsequently a slurry containing 20  
milligrams of the catalyst prepared according to Example II was dosed. The  
temperature was maintained at 75°C and the pressure was kept constant by  
10 feeding ethylene. The reaction was stopped when approximately 1000 grams  
of ethylene had been supplied to the reactor. Stopping was performed by de-  
pressurizing and cooling down the reactor. The reactor contents were passed  
through a filter; the wet polymer powder was collected and subsequently  
dried.

1083 grams of free flowing polyethylene were produced in 104 minutes.

15 The polymer powder was characterized by

- an average particle size of 136  $\mu\text{m}$
- a span of 1.0 and
- a bulk density of 340  $\text{kg/m}^3$

20 Example VI

Polymerisation in the presence of the catalyst according to Example III

The polymerisation was carried out in a similar manner as described under  
Example V, using 20 milligrams of catalyst, with the exception that the  
ethylene pressure was 1 bar and that the reaction was stopped when  
25 approximately 1300 grams of ethylene had been dosed to the reactor.

1334 grams of free flowing polyethylene were produced in 102 minutes.

The polymer was characterized by

- an average particle size of 194  $\mu\text{m}$
- a span of 0.95 and
- 30 • a bulk density of 295  $\text{kg/m}^3$

### Example VII

#### Polymerisation in the presence of the catalyst according to Example IV

The polymerisation was carried out in a similar manner as described under  
5 Example V, this time using 40 milligrams of catalyst and an ethylene  
pressure of 1 bar and the reaction was stopped when approximately 1100  
grams of ethylene had been supplied to the reactor.

1150 grams of free flowing polyethylene were produced in 120 minutes

The polymer was characterized by

- 10
- an average particle size of 121  $\mu\text{m}$
  - a span of 0.69 and
  - a bulk density of 300  $\text{kg/m}^3$

The Examples V-VII demonstrate that the polyethylene  
15 obtained with the catalyst obtained according to Examples II - IV have a  
combination of desired values of activity , particle size , particle size  
distribution and bulk density. The values for the span indicate the uniform  
particle size distribution.

#### 20 Comparative Example A

Example I was repeated with the exception of the addition of hexane.

The obtained product was a hard solid being unsuitable for further catalyst  
synthesis.

**CLAIMS**

1. A catalyst for the production of polyethylene comprising a solid reaction product obtained by reaction of:
  - 5 (a) a hydrocarbon solution comprising
    - (1) an organic oxygen containing magnesium compound and
    - (2) an organic oxygen containing titanium compound and
  - (b) a compound comprising a transition metal from Group IV or V of Mendeleev's Periodic System of Chemical Elements and
- 10 containing at least two halogen atoms.
2. A catalyst according to Claim 1 characterized in that the solid reaction product is treated with an aluminium compound having the formula  $AlR_nX_{3-n}$  wherein X is a halogenide and R is a hydrocarbon radical containing 1 – 10 carbon atoms and  $0 < n \leq 3$ .
- 15 3. A catalyst according to any one of Claims 1-2 characterized in that the organic oxygen magnesium compound is a magnesium alkoxide.
4. A catalyst according to Claim 3 characterized in that the magnesium alkoxide is magnesium ethoxide.
5. A catalyst according to any one of Claims 1-4 characterized in that the
- 20 organic oxygen containing titanium compound is a titanium alkoxide.
6. A catalyst according to Claim 5 characterized in that the titanium alkoxide is  $Ti(OC_4H_9)_4$
7. A catalyst according to any one of Claims 1-6 characterized in that compound (b) comprising a transition metal compound is Ti (IV)
- 25 halogenide, V (III) halogenide, V (IV) halogenide or V (V) oxyhalogenide.
8. A catalyst according to Claim 7 characterized in that compound (b) is titanium halogenide.
9. A catalyst according to Claim 8 characterized in that the titanium
- 30 halogenide is  $TiCl_4$ .
10. A process for the production of polyethylene characterized in that the polymerisation takes place in the presence of a catalyst according to any one of the Claims 1-9.
11. A process for the production of polyethylene according to Claim 10

wherein the polymerisation takes place in the presence of a cocatalyst wherein the cocatalyst is an organo aluminium compound having the formula  $AlR_3$  in which R is a hydrocarbon radical containing 1 – 10 carbon atoms .

- 5 12. A process according to any one of Claims 10-11 characterized in that the polyethylene has the following characteristics:
- an average molecular weight higher than 10,000 g/mol and lower than 10,000,000 g/mol
  - an average particle size between 50 and 400  $\mu\text{m}$  and
  - 10 • a bulk density between 200 and 500  $\text{kg/m}^3$
13. A process according to any one of Claims 10-12 characterized in that the polyethylene is ultra high molecular weight polyethylene
14. A process according to any one of Claims 10-12 characterized in that the polyethylene is bimodal polyethylene

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/005102

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. C08F10/02 C08F4/654				
According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b> 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				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	WO 01/00692 A (UNION CARBIDE CHEM PLASTIC [US]) 4 January 2001 (2001-01-04) claims; examples	1-14		
X	EP 1 661 917 A (SAUDI BASIC IND CORP SABIC [SA]) 31 May 2006 (2006-05-31) paragraph [0045]; claims; examples	1,3-9		
X	EP 0 398 167 A (HOECHST AG [DE]) 22 November 1990 (1990-11-22) claims; examples	1-14		
X	US 6 114 271 A (BILDA DIETER [DE] ET AL) 5 September 2000 (2000-09-05) column 1, line 55 - line 60 column 3, line 53 - line 60 claims; examples	1-14		
	----- -/--			
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.				
* Special categories of cited documents : <table border="0"> <tr> <td style="vertical-align: top;">           *A* document defining the general state of the art which is not considered to be of particular relevance            *E* earlier document but published on or after the international filing date            *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)            *O* document referring to an oral disclosure, use, exhibition or other means            *P* document published prior to the international filing date but later than the priority date claimed         </td> <td style="vertical-align: top;">           *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention            *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone            *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.            *&amp;* document member of the same patent family         </td> </tr> </table>			*A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family
*A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family			
Date of the actual completion of the international search	Date of mailing of the international search report			
21 September 2009	30/09/2009			
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Kaumann, Edgar			

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2009/005102

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 574 153 A (NIPPON OIL CO LTD [JP]) 15 December 1993 (1993-12-15) claims; examples -----	1-14
X	EP 0 317 200 A (NIPPON OIL CO LTD [JP]) 24 May 1989 (1989-05-24) claims; examples -----	1-19

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/005102

Patent document cited in search report	Publication date	Patent family member(s)	Publication date			
WO 0100692	A	04-01-2001	AT 294823 T 15-05-2005			
			AU 763949 B2 07-08-2003			
			AU 6060200 A 31-01-2001			
			CA 2369208 A1 04-01-2001			
			CN 1358202 A 10-07-2002			
			CZ 20014646 A3 11-09-2002			
			DE 60019930 D1 09-06-2005			
			DE 60019930 T2 16-02-2006			
			EP 1196461 A1 17-04-2002			
			ES 2238297 T3 01-09-2005			
			JP 2003503562 T 28-01-2003			
			NO 20016426 A 26-02-2002			
			PL 352905 A1 22-09-2003			
			TR 200103809 T2 21-05-2002			
			US 2001051586 A1 13-12-2001			
			EP 1661917	A	31-05-2006	BR PI0517871 A 21-10-2008
						CN 101065404 A 31-10-2007
WO 2006056338 A1 01-06-2006						
JP 2008521944 T 26-06-2008						
KR 20070092237 A 12-09-2007						
US 2008312389 A1 18-12-2008						
EP 0398167	A	22-11-1990	AU 622026 B2 26-03-1992			
			AU 5507190 A 22-11-1990			
			BR 9002291 A 13-08-1991			
			CA 2016930 A1 17-11-1990			
			JP 3009903 A 17-01-1991			
US 6114271	A	05-09-2000	NONE			
EP 0574153	A	15-12-1993	CA 2096782 A1 22-11-1993			
			DE 69312586 D1 04-09-1997			
			JP 5320244 A 03-12-1993			
EP 0317200	A	24-05-1989	CA 1295780 C 11-02-1992			
			DE 3865181 D1 31-10-1991			
			JP 1129006 A 22-05-1989			
			JP 1996548 C 08-12-1995			
			JP 7017709 B 01-03-1995			
			US 4962167 A 09-10-1990			