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Description

Process for the preparation of ethylene (co)polymers

5 The invention relates to a process for the (co)polymerization of ethylene to give coarse polymer particles having a narrow particle size distribution, high bulk density and broad molecular weight distribution by using a catalyst whose support component is obtained by
10 reacting a titanium(III) compound with dissolved magnesium alkoxide.

The process for the preparation of the titanium(III) compounds to be used according to the invention is known (cf. US Patent 3,773,735). The catalyst described
15 therein, which comprises said titanium(III) compound and a trialkylaluminum compound, gives, in the polymerization, a polyolefin having relatively small particles. The catalyst activity is unsatisfactory.

A catalyst has been proposed for the polymerization of olefins which comprises a trialkylaluminum compound and the entire product from the reaction of a magnesium alkoxide dissolved in an inert solvent with a tetra-
20 valent titanium compound and an organoaluminum compound. The use of this type of catalyst gives polyolefins having a narrow molecular weight distribution which are particularly suitable for further processing by injection
25 molding. Polymers having a broad molecular weight distribution, as are required, for example, for the production of films, tubes or large blow moldings, cannot
30 be obtained using this type of catalyst.

The object was thus to find a process for the preparation of catalysts of this type which is as simple as possible, gives catalysts of high activity and enables preparation of a polymer having a uniform, coarse particle shape, low

fine-particle content, high bulk density and variable molecular weight distribution.

5 This object is achieved by using a catalyst prepared by reacting a chlorine-containing titanium(III) compound with a dissolved magnesium alkoxide, a tetravalent transition metal compound and an organoaluminum compound.

10 The present invention thus relates to a process for the preparation of an ethylene polymer having a uniform, coarse particle shape and high bulk density by polymerizing ethylene or ethylene with up to 10% by weight, based on the total amount of the monomers, of a 1-olefin of the formula $R^8-CH=CH_2$ in which R^8 is a straight-chain or branched alkyl radical having 1 to 12 carbon atoms, in suspension, solution or in the gas phase, at a temperature of from 20 to 120°C and a pressure of from 2 to 15 60 bar and in the presence of a catalyst comprising a component a containing a transition metal and an organoaluminum component b, which comprises carrying out the polymerization in the presence of a catalyst which 20 comprises

- a) the entire product from the reaction of
 - a1) a chlorine-containing titanium(III) compound with
 - a2) a magnesium alkoxide of the formula I



25 in which R^1 and R^2 are either identical and are a $-CH_2CHR^6R^7$ or $-(CH_2)_nOR^6$ radical where R^6 is a hydrogen atom or a C_1-C_6 -alkyl radical, R^7 is a C_2-C_6 -alkyl radical, R^8 is a C_1-C_4 -alkyl radical and n is an integer from 2 to 6, or R^1 and R^2 are different and 30 R^1 has the abovementioned meaning and R^2 is a C_1-C_{20} -alkyl radical, dissolved in an inert solvent, and with

- a3) a tetravalent transition metal compound of the formula II





in which M is titanium, zirconium or hafnium, R^3 is a C_1 - C_6 -alkyl radical, X is a halogen atom and m is an integer from zero to 4, and with

- 5 a4) an organoaluminum compound of the formula III



10 in which R^4 and R^5 are identical or different and are a C_1 - C_6 -alkyl radical, X is a halogen atom, q is a number from zero to 3, and p is a number from zero to 1,

15 in an Mg:Ti:M:Al ratio of from 1 : 0.05 to 2 : 0.05 to 2 : 0.3 to 4, the reaction of component a1 with components a2 to a4 either being carried out simultaneously or a1 first being reacted simultaneously with a2 and a3 and the reaction with a4 being carried out subsequently, or component a1 being reacted successively with components a2 to a4, and

- 20 b) a trialkylaluminum compound having 1 to 6 carbon atoms in the alkyl radicals or the product of the reaction of a trialkylaluminum compound or dialkylaluminum hydride with isoprene.

25 The chlorine-containing titanium(III) compound used to prepare the catalyst component a is titanium trichloride or an alkoxytitanium chloride, preferably titanium trichloride. The preparation is carried out, for example, by reducing a chloroalkoxytitanate of the formula $Ti(OR)_rCl_{3-r}$ where $r = 1$ to 4 and $R = C_2$ - C_8 -alkyl using an alkylaluminum sesquichloride and/or isoprenyl-aluminum in
30 an inert dispersant at a temperature of from -60 to $+70^\circ C$, preferably from -30 to $0^\circ C$, and if desired subsequently heating the reaction product at from 60 to $150^\circ C$ and washing with an inert dispersant.

35 This titanium(III) compound is preferably employed as a suspension in an inert solvent.





The magnesium alkoxide used is a compound of the formula I



In this formula R^1 and R^2 are identical or different. If R^1 and R^2 are identical, they are a $\text{CH}_2\text{CHR}^6\text{R}^7$ radical or a $-(\text{CH}_2)_n\text{OR}^8$ radical, where R^6 is a hydrogen atom or a $\text{C}_1\text{-C}_6\text{-}$, preferably $\text{C}_1\text{-C}_3\text{-alkyl}$ radical, R^7 is a $\text{C}_2\text{-C}_6\text{-}$, preferably $\text{C}_3\text{-C}_5\text{-alkyl}$ radical, R^8 is a $\text{C}_1\text{-C}_4\text{-}$, preferably $\text{C}_1\text{-C}_2\text{-alkyl}$ radical, and n is an integer from 2 to 6. If R^1 and R^2 are different, R^1 is as defined above and R^2 is a $\text{C}_1\text{-C}_{20}\text{-}$, preferably $\text{C}_3\text{-C}_{10}\text{-alkyl}$ radical.

Examples of magnesium alkoxides of this type are
magnesium bis(2-methyl-1-pentoxide),
magnesium bis(2-methyl-1-hexoxide),
magnesium bis(2-methyl-1-heptoxide),
magnesium bis(2-ethyl-1-pentoxide),
magnesium bis(2-ethyl-1-hexoxide),
magnesium bis(2-ethyl-1-heptoxide),
magnesium bis(2-propyl-1-heptoxide),
magnesium bis(2-methoxy-1-ethoxide),
magnesium bis(3-methoxy-1-propoxide),
magnesium bis(4-methoxy-1-butoxide),
magnesium bis(6-methoxy-1-hexoxide),
magnesium bis(2-ethoxy-1-ethoxide),
magnesium bis(3-ethoxy-1-propoxide),
magnesium bis(4-ethoxy-1-butoxide),
magnesium bis(6-ethoxy-1-hexoxide).
magnesium bis-pentoxide and
magnesium bis-hexoxide.

Other suitable magnesium alkoxides are the products of the reaction of magnesium metal, alkylmagnesium compounds or magnesium alkoxides with alcohols R^1OH (R^1 as above). Of these products, the product of the reaction of a magnesium alkoxide with an alcohol R^1OH in the presence of from 0.02 to 0.2 mol-% of triethylaluminum (as viscosity reducer) at from 100 to 140°C is preferred.

The tetravalent transition metal compound is one of the formula II

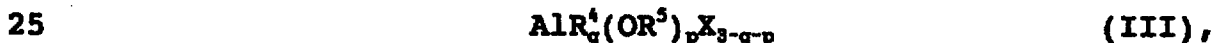


5 in which M is titanium, zirconium or hafnium, preferably titanium or zirconium, R^3 is an alkyl radical having 1 to 9, preferably 1 to 4, carbon atoms, X is a halogen atom, preferably chlorine, and m is zero to 4, preferably 2 to 4. The tetravalent transition metal compound of the
10 formula II or an adduct thereof with an electron donor which can be used according to the invention is soluble in hydrocarbons.

Examples of compounds of the formula II are:

15 $TiCl_4$, $TiCl_3(OC_2H_5)$, $TiCl_2(OC_2H_5)_2$, $TiCl(OC_2H_5)_3$, $Ti(OC_2H_5)_4$,
 $TiCl_3(OC_3H_7)$, $TiCl_2(OC_3H_7)_2$, $TiCl(OC_3H_7)_3$, $Ti(OC_3H_7)_4$,
 $TiCl_3(OC_4H_9)$, $TiCl_2(OC_4H_9)_2$, $TiCl(OC_4H_9)_3$, $Ti(OC_4H_9)_4$,
 $TiCl_3(OC_6H_{13})$, $TiCl_2(OC_6H_{13})_2$, $TiCl(OC_6H_{13})_3$, $Ti(OC_6H_{13})_4$,
 $Ti(OC_8H_{18})_4$, $TiBr_4$, $TiBr_3(OR^3)$, $TiBr_2(OR^3)_2$, $TiBr(OR^3)_3$, TiI_4 ,
 $TiI_3(OR^3)$, $TiI_2(OR^3)_2$, $TiI(OR^3)_3$, $ZrCl_4$, $ZrBr_4$, ZrI_4 ,
20 $Zr(OC_2H_5)_4$, $Zr(OC_3H_7)_4$, $Zr(OC_4H_9)_4$, $ZrCl_2(OC_3H_7)_2$, preferably
 $TiCl_4$, $Ti(OC_2H_5)_4$, $Ti(OC_3H_7)_4$, $Zr(OC_3H_7)_4$, $Ti(OC_4H_9)_4$ and
 $Zr(OC_4H_9)_4$.

The fourth reactant in the preparation of the catalyst component a is an organoaluminum compound of the formula III



in which R^4 and R^5 are identical or different and are an alkyl radical having 1 to 6, preferably 1 to 4, carbon atoms, X is a halogen atom, preferably chlorine, q is a
30 number from zero to 3, preferably 1 to 2, and p is a number from zero to 1, preferably less than 0.5.

Suitable organoaluminum compounds are:





$\text{Al}(\text{C}_2\text{H}_5)_3$, $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$, $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$, AlCl_3 ,
 $\text{Al}(\text{C}_3\text{H}_7)_3$, $\text{Al}(\text{C}_3\text{H}_7)_2\text{Cl}$, $\text{Al}_2(\text{C}_3\text{H}_7)_3\text{Cl}_3$, $\text{Al}(\text{C}_3\text{H}_7)\text{Cl}_2$, $\text{Al}(\text{C}_4\text{H}_9)_3$,
 $\text{Al}(\text{C}_4\text{H}_9)_2\text{Cl}$, $\text{Al}_2(\text{C}_4\text{H}_9)_3\text{Cl}_3$, $\text{Al}(\text{C}_4\text{H}_9)\text{Cl}_2$,

and monohalides and dihalides of various compositions.

5 From this group, preference is given to $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$,
 $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$ and $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$.

10 A possible fifth reactant, but one which is not
absolutely necessary, for the preparation of the catalyst
component a is an electron donor. This electron donor is
an aliphatic or alicyclic ester, an aliphatic ether, an
aliphatic aldehyde or an aliphatic carboxylic acid.
Examples of electron donors (ED) of this type are:
dimethyl ether, diethyl ether, di-n-propyl ether,
di-n-butyl ether, di-i-amyl ether, tetrahydrofuran,
15 dioxane, ethyl acetate, butyl acetate, and acetic acid.
Preference is given to diethyl ether, dibutyl ether and
ethyl acetate.

20 If an electron donor is used, it can be added to at least
one of the four other reactants before or during the
reaction. The molar electron donor : magnesium alkoxide
ratio is from 0 : 1 to 2 : 1, preferably from 0 : 1 to
1 : 1.

There are several methods of preparing component a:

25 The chlorine-containing titanium(III) compound is either
1) reacted simultaneously with the dissolved magnesium
alkoxide, the tetravalent transition metal compounds
and the organoaluminum compound (= reaction sequence
($a^1+a^2+a^3+a^4$)), or
2) reacted successively with the dissolved magnesium
30 alkoxide, the tetravalent transition metal compound
and the organoaluminum compound (= reaction sequence
(a^1)+(a²)+(a³)+(a⁴)), or
3) reacted first with the dissolved magnesium alkoxide
and the tetravalent transition metal compound, and
35 the reaction product formed is then reacted with the



organoaluminum compound (= reaction sequence
($a^1+a^2+a^3$)+(a⁴)).

5 The simultaneous reaction of components a1 to a4 to give the catalyst component a gives polymers having a narrow molecular weight distribution when component a is used for the polymerization. Conversely, successive reaction of component a1 with components a2 to a4 gives a catalyst component a which, in the polymerization, gives a polymer having a broad molecular weight distribution.

10 The simultaneous reaction of the chlorine-containing titanium(III) compound with reactants a2) to a4) is carried out at a temperature of from -50 to 150°C, preferably at from -20 to 120°C, within from 0.1 to 10 hours, preferably from 0.25 to 4 hours. If a1) is
15 first reacted simultaneously with a2) and a3), this reaction is carried out at a temperature of from -50 to 150°C, preferably at from -20 to 120°C, within from 0.1 to 10 hours, preferably from 0.25 to 4 hours. The subsequent reaction of the reaction product formed is
20 carried out at from -50 to 150°C, preferably at from -20 to 120°C, within from 0.1 to 10 hours, preferably from 0.25 to 4 hours. If the titanium(III) compound is reacted successively with the other reactants, each reaction step is carried out at from -50 to 150°C, preferably at from
25 -20 to 120°C, within from 0.1 to 10 hours, preferably from 0.25 to 4 hours.

The entire reaction sequence, including the preparation of the Ti(III) compound, can be carried out without changing the solvent. Suitable inert solvents for the
30 abovementioned reactions are aliphatic and cycloaliphatic hydrocarbons, such as butane, pentane, hexane, heptane, cyclohexane and isooctane, and aromatic hydrocarbons, such as benzene and xylene. It is also possible to employ petroleum ether and hydrogenated diesel oil fractions
35 which have been carefully freed from oxygen, sulfur compounds and moisture. Corresponding solvent mixtures



are also suitable. Preference is given to a petroleum ether fraction having a boiling range of from 140 to 170°C or hexane.

5 The titanium(III) compound, the magnesium alkoxide, the tetravalent transition metal compound (II) and the organoaluminum compound of the formula III are reacted in the (molar) Mg:Ti:M:Al ratio of from 1 : 0.05 to 2 : 0.05 to 2 : 0.3 to 4, preferably from 1 : 0.05 to 1 : 0.05 to 1 : 0.3 to 2.

10 After the reaction, the suspension of catalyst component a is stirred for from zero to 48 hours, preferably for from zero to 16 hours, at from 0 to 160°C, preferably at from 80 to 150°C.

15 The catalyst component a suspension prepared in this way can be used directly for the polymerization without removing the dispersant and by-products.

20 The catalyst component b (or activator) used is a tri-alkylaluminum compound having from 1 to 6 carbon atoms in the alkyl radicals, such as, for example, triethylaluminum, triisobutylaluminum, triisohexylaluminum or the product of the reaction of a trialkylaluminum or dialkylaluminum hydride with isoprene, known as isoprenylaluminum. Preference is given to triethylaluminum and isoprenylaluminum.

25 The polymerization is carried out in one or two steps, preferably as a suspension polymerization, in an inert dispersant. Suitable dispersants are the same organic solvents as described for the preparation of catalyst component a. However, polymerization in the gas phase is
30 also possible.

The polymerization temperature is from 20 to 120°C, preferably from 70 to 90°C; the pressure is in the range from 2 to 60 bar, preferably from 4 to 20 bar.

If the reaction is carried out in two steps, the mixing ratio between the polyolefins formed in each of steps 1 and 2 is in the range from 30:70 to 70:30, the polymer formed in step 1 being transferred continuously into step 2. The final polymer mixture is withdrawn continuously from step 2.

The catalyst system to be used according to the invention is used to polymerize ethylene or ethylene with up to 10% by weight, based on the total amount of monomer, of a 1-olefin of formula $R^9-CH=CH_2$ in which R^9 is a straight-chain or branched alkyl radical having 1 to 12, preferably 1 to 10, carbon atoms. Examples are propylene, 1-butene, 1-pentene, 1-hexene, 1-octene and 4-methyl-1-pentene. Preference is given to propylene, 1-butene and 1-hexene. The comonomer is preferably introduced in the first step, in which a polymer of relatively high molecular weight is formed.

All the polymer from the second step is separated off from the dispersant and dried in an known manner.

An advantage of the process according to the invention is the very simple preparation of the transition metal component of the catalyst. This is obtained by simply combining the individual components under the appropriate reaction conditions.

Washing with an inert hydrocarbon is not necessary.

No washing liquors are thus formed which only decompose again in only further process steps and must be worked up with production of effluent.

Furthermore, no polymer deposits on the reactor walls and in the connecting lines form in the case of long-term continuous operation, and the content in the product of particles having a size of less than $100\ \mu m$ is significantly lower.



However, the major advantage of the process according to the invention is that the catalyst according to the invention has higher activity and produces an ethylene polymer having a very large mean particle diameter of from 250 to 700 μm , high bulk density and variable molecular weight distribution. The polymer has a low residual moisture content, which reduces the drying costs.

The particle size distribution is extremely uniform.

In addition, the fine-particle content ($\% < 100 \mu\text{m}$) in the polymer prepared according to the invention is very low.

Furthermore, regulation of the molecular weight of the polyolefins using hydrogen is significantly more efficient than in conventional processes.

The examples below are intended to illustrate the invention.

The following abbreviations are used:

CA	: catalyst activity [kg of product/mmol of Ti]
MFI 190/5	: melt flow index in accordance with DIN 53 735, measured at 190°C at a load of 5 kg
MFI 190/15	: measured at 190°C at a load of 15 or
MFI 190/21.6	: 21.6 kg respectively
MFR 15/5	: MFI 190/15/MFI 190/5
d_{50}	: median particle size, obtained by sieve fractionation
BD	: bulk density, measured in accordance with DIN 53 468
VN	: viscosity number, measured in accordance with DIN 53 728





Example 1: Preparation of the Ti(III) compound

400 cm³ of petroleum ether fraction (b.p. 140-170°C), 0.25 mol of ethylaluminum sesquichloride and 0.5 mol of isoprenylaluminum were introduced into a 1 dm³ reactor. 220 cm³ of TiCl₄ (2 mol) were metered in at -40°C over the course of 5 hours. The batch was subsequently stirred for 1 hour at 0°C, for 1 hour at 40°C and for 1 hour at 80°C. The suspension was then made up to 1000 cm³ using the petroleum ether fraction.

10 Preparation of the catalyst component a

15 mmol of Ti from the abovementioned TiCl₄ suspension in 200 cm³ of a petroleum ether fraction (b.p. 140-170°C) were introduced into a 1 dm³ stirred reactor with exclusion of air and moisture. A solution of 0.1 mol of magnesium bis(2-methyl-1-pentoxide) in 200 cm³ of the petroleum ether fraction, 100 cm³ of a 0.3 molar solution of TiCl₄ in the petroleum ether fraction and 100 cm³ of a 0.8 molar solution of ethylaluminum sesquichloride in the petroleum ether fraction were added simultaneously over the course of 120 minutes at a temperature of 20°C with stirring and under a blanket of argon. The reddish brown suspension was subsequently stirred for 120 minutes at 105°C.

Table 1 Preparation of the catalyst component a

25	Example	Ti(III) compound (suspension) as per	Ti(III) suspension a1) employed	
			[mmol of Ti]	[cm ³]
	2	Comp. Example A	60	200
	3	Comp. Example B	15	200
30	4	Example 1	7.5	50
	5	Example 1	7.5	40

The solutions (reactants a2 - a4) were added as described in Example 1. The postreaction was carried out at 110°C

for 60 minutes.

Before use in the polymerization experiments, the suspensions were generally diluted with the petroleum ether fraction to a Ti concentration of 0.02 mol/dm^3 .

5 Example 6

A TiCl_3 suspension containing 15 mmol of Ti (as described in Example 1) in 200 cm^3 of a petroleum ether fraction (b.p. $140\text{--}170^\circ\text{C}$) were introduced into a 1 dm^3 stirred reactor in the absence of air and moisture.

10 A solution of 0.1 mol of magnesium bis(2-methyl-1-pentoxide) in 200 cm^3 of the petroleum ether fraction and 100 cm^3 of a 0.3 molar solution of TiCl_4 in the petroleum ether fraction were added simultaneously over the course of 120 minutes at a temperature of 25°C with stirring and
15 under a blanket of argon. The suspension was subsequently reacted for 60 minutes at 80°C with 100 cm^3 of a 0.8 molar solution of ethylaluminum sesquichloride in the petroleum ether fraction.

Example 7: Ethylene polymerization

20 5 cm^3 of a 1 molar isoprenylaluminum solution and 1 cm^3 of the suspension prepared as in Example 1 (20 mmol/dm^3 , based on Ti) were introduced at 85°C under a blanket of N_2 into a 1.5 dm^3 reactor charged with 750 cm^3 of the petroleum ether fraction. 2 bar of hydrogen and 5 bar of
25 ethylene were then injected. The total pressure of 7 bar was maintained for 2 hours by replenishing the consumed ethylene. The polymerization was terminated by releasing the gases, the polymer was separated off from the dispersant by filtration and drying.



IPRA : Isoprenylaluminum, TEA : Triethylaluminum

Comparative Example A

200 cm³ of a petroleum ether fraction (b.p. 140-170°C),
0.1 mol of ethylaluminum sesquichloride and 0.4 mol of
isoprenylaluminum were introduced into a 1 dm³ reactor.
5 55 cm³ of TiCl₄ (0.5 mol) were metered in at -20°C over
the course of 3 hours, and 55 cm³ of TiCl₄ (0.5 mol) were
metered in at 10°C over the course of 3 hours. The batch
was subsequently stirred at 80°C for 2 hours.

10 The ethylene polymerization was carried out as in Example
7 using 5 mmol of isoprenylaluminum.

58 g of polyethylene having a bulk density of 300 g/dm³,
a mean particle size of 210 μm and a fine-particle
content of 3.8% smaller than 100 μm were obtained.

15 The product had an MFI 190/5 of 1.2 g/10 min. The MFR
15/5 and MFR 21.6/5 were 5.7 and 11.5 respectively. The
catalyst activity corresponded to 2.9 kg of PE/mmol of
Ti.

Comparative Example B (in accordance with US 3,773,735)

20 400 cm³ of a petroleum ether fraction (b.p. 140-170°C),
0.5 mol of ethylaluminum dichloride and 0.5 mol of
isoprenylaluminum were introduced into a 1 dm³ reactor.
220 cm³ of TiCl₄ (2 mol) were metered in at -25°C over the
course of 3.5 hours. The mixture was subsequently stirred
for 1 hour at 0°C and for 1 hour at 20°C. The catalyst
25 was washed 4 times with 600 cm of the petroleum ether
fraction. The polymerization (amounts of material) was
carried out as in Example 7 using 5 mmol of IPRA. 51 g of
polyethylene having a bulk density of 310 g/dm³, a mean
particle size of 240 μm and a fine-particle content of
30 2.6% smaller than 100 μm were obtained. The product had
an MFI 190/5 of 0.5 g/10 min. The MFR 15/5 and MFR 21.6/5
were 5.6 and 11.6 respectively. The catalyst activity
corresponded to 1.5 kg of PE/mmol of Ti.



Example 8

1 cm³ of a 1 molar triethylaluminum solution and 12 cm³ of component a prepared as described in Example 4 (undiluted, 1 mmol of Ti) were introduced at 70°C under a blanket of N₂ into a 1.5 dm³ reactor charged with 500 cm³ of the petroleum ether fraction. 1 bar of ethylene was then injected and the pressure was maintained for 1 hour by replenishing the consumed ethylene. The polymerization was terminated by releasing the gases, and the polymer suspension was transferred into a Schlenk flask under a blanket of nitrogen, and the volume of the suspension was made up to 1000 cm³ by adding the petroleum ether fraction. The prepolymerization yield was 94 g/mmol of Ti. The viscosity number (VN) of the prepolymer was greater than 4000 cm³/g.

Example 9

The polymerization was carried out as in Example 7 using 5 mmol of isoprenylaluminum and 20 cm³ of the suspension prepared in Example 8. The hydrogen content was 45% by volume and the total pressure was 7 bar. The polymerization result was as follows:

CA	: 7.4 kg/mmol of Ti,	Bulk density	: 440 g/dm ³
d ₅₀	: 260 μm	Fine-particle content	: 0.9% < 100 μm
MFI 190/5	: 15.1 g/10 min,	MFR 15/5	: 5.4
9.6% < 200 μm,	90.8% < 315 μm,	98.8% < 400 μm,	
99.9% < 500 μm			

Example 10

The prepolymer was prepared as in Example 8, but using 120 cm³ (10 mmol of Ti) of component a, Example 4, and 3 mmol of triethylaluminum. The yield was 10.4 g/mmol of Ti at a VN of 2600 cm³/g. The volume of the suspension obtained was made up to 1000 cm³ using the petroleum ether fraction.



Example 11

The polymerization was carried out as in Example 9, but using 3 mmol of triethylaluminum and 2 cm³ of the suspension prepared as in Example 10.

5	CA	: 10.2 kg/mmol of Ti,	Bulk density	: 420 g/dm ³
	d ₅₀	: 280 μm	Fine-particle content	: 0.6% < 100 μm
	MFI 190/5	: 29.6 g/10 min,	MFR 15/5	: 5.0
	5.4% < 200 μm, 83.2% < 315 μm, 94.8% < 400 μm,			
	99.7% < 500 μm			

10 Example 12

The polymerization was carried out as in Example 7 using 3 mmol of triethylaluminum and 0.5 cm³ of component a as prepared in Example 4 (0.01 mmol of Ti) at 80°C, without hydrogen and at an ethylene pressure of 6 bar.

15	CA	: 18.6 kg/mmol of Ti,	Bulk density	: 410 g/dm ³
	d ₅₀	: 330 μm	Fine-particle content	: 0.2% < 100 μm
	VN	: 1300 cm ³ /g.		

Example 13

20 The prepolymer was prepared as in Example 8 using 89 cm³ of component a prepared as in Example 5 (10 mmol of Ti).

Example 14

25 100 dm³ of the petroleum ether fraction, 50 mmol of isoprenylaluminum and 200 cm³ of suspension 10 (2 mmol of Ti) were introduced into a 150 dm³ reactor. 5 kg/h of ethylene and sufficient H₂ so that the H₂ content in the gas space was 45% by volume were subsequently introduced at a polymerization temperature of 85°C. After 6 hours, the polymerization was terminated at a pressure of 5.2 bar by decompression. The suspension was filtered, and the polyethylene powder was dried by passing hot nitrogen over it.

30





24.8 kg of polyethylene were obtained. This corresponds to a catalyst activity of 12.4 kg of PE/mmol of Ti. The polyethylene powder had an MFI 190/5 of 5.9 g/10 min and an MFR 15/5 and MFR 21.6/5 of 4.9 and 10.2 respectively. The density was 0.960 and the bulk density was 430 g/dm³. The median particle size d₅₀ was 380 μm at a fine-particle content of 1% < 100 μm.

Example 15

33 cm³ (65 mmol of Ti) of the TiCl₃ suspension, prepared as described in Example 1, in 50 cm³ of a petroleum ether fraction (b.p. 140-170°C) were introduced into a 1 dm³ stirred reactor in the absence of air and moisture, and were reacted with a solution of 0.1 mol of magnesium bis(2-methyl-1-pentoxide) in 200 cm³ of the petroleum ether fraction for 20 minutes at a temperature of 25°C with stirring and under a blanket of argon. 100 cm³ of a 0.3 molar solution of TiCl₃ in the petroleum ether fraction were subsequently metered in at 25°C over the course of 60 minutes. A solution of 60 mmol of Al₂Et₃Cl₃ in 70 cm³ of the petroleum ether fraction was subsequently metered in at 80°C over the course of 20 minutes.

Table 3 Preparation of catalyst component a

	Example	Ti(III) compound (suspension) as per	Ti(III) suspension a) employed	
			[mmol of Ti]	[cm ³]
25	16	Comp. Example A	30	200
	17	Comp. Example B	22	200
	18	Example 15	15	50
	19	Example 15	11	200
30	20	Example 15	7	200

The magnesium compound was added as described in Example 15, but over the course of 60 minutes. The titanium(IV) compound was added as described in Example 15. In Examples 16 to 20, 80 mmol of Al₂Et₃Cl₃ dissolved in

100 cm³ of the petroleum ether fraction were added over the course of 60 minutes.

5 Before use in the polymerization experiments, suspensions a from Examples 15 to 20 were diluted to a Ti concentration of 0.02 mol/dm³.

Example 21: Ethylene polymerization

10 2.5 cm³ of a 1 molar isoprenylaluminum solution and 1 cm³ of the suspension prepared as described in Example 15 (20 mmol/dm³, based on Ti) were introduced at 85°C under a blanket of N₂ into a 1.5 dm³ reactor charged with 750 cm³ of the petroleum ether fraction. 2 bar of hydrogen and 5 bar of ethylene were then injected. The total pressure of 7 bar was maintained for 2 hours by replenishing the consumed ethylene. The polymerization was terminated 15 by releasing the gases, and the polymer was separated off from the dispersant by filtration and drying.



Table 4: Polymerization results (conditions as described in Example 21)

Catalyst comp. a from Example	15	16	16	17	17	18	19	19	20
Activator (b) [mmol]	IPRA 2.5	IPRA 2.5	IPRA 5	TEA 2.5	IPRA 5	IPRA 5	TEA 2.5	IPRA 5	IPRA 5
CA [kg/mmoll]	3.4	6.1	7.3	4.7	5.8	8.7	10.1	8.5	10.9
Bulk density [g of PE/dm ³]	330	290	300	350	330	350	340	360	350
d ₅₀ [μm]	600	600	680	460	480	450	340	300	410
Fine-particle content [% < 100 μm]	2.0	1.7	0.9	0.8	0.4	0.8	0.5	1.0	0.1
MFI 190/5 [g/10 min]	0.9	1.5	2.1	2.4	2.0	1.6	4.0	2.2	2.6
MFR 15/5	7.1	7.6	6.4	6.3	5.8	8.1	5.6	6.2	5.2
MFR 21.6/5	13.2	13.3	12.3	12.8	11.9	15.2	12.0	12.1	10.1

IPRA: Isoprenylaluminum, TEA: Triethylaluminum



Example 22

100 dm³ of a petroleum ether fraction, 100 mmol of isoprenylaluminum and 37.4 cm³ of the undiluted suspension from Example 18 (4 mmol of Ti) were introduced into a
5 150 dm³ reactor. 7.5 kg/h of ethylene and sufficient H₂ so that the H₂ content in the gas space was 30% by volume were subsequently introduced at a polymerization temperature of 85°C. After 4.5 hours, the polymerization was terminated at a pressure of 3.1 bar by decompression.
10 The suspension was filtered, and the polyethylene powder was dried by passing hot nitrogen over it.

32.6 kg of polyethylene were obtained. This corresponds to a catalyst activity of 8.2 kg of PE/mmol of Ti. The polyethylene powder had an MFI 190/5 of 3.2 g/10 min and
15 an MFR 15/5 and MFR 21.6/5 of 5.9 and 14.1 respectively. The density was 0.958 and the bulk density was 380 g/dm³. The median particle size d₅₀ was 410 μm at a fine-particle content of 1% < 100 μm.





Patent claims:

1. A process for the preparation of an ethylene polymer having a uniform, coarse particle shape and high bulk density by polymerizing ethylene or ethylene with up to 10% by weight, based on the total amount of the monomers, of a 1-olefin of the formula $R^9-CH=CH_2$ in which R^9 is a straight-chain or branched alkyl radical having 1 to 12 carbon atoms, in suspension, solution or in the gas phase, at a temperature of from 20 to 120°C and a pressure of from 2 to 60 bar and in the presence of a catalyst comprising a component containing a transition metal and an organoaluminum component b, which comprises carrying out the polymerization in the presence of a catalyst which comprises

- a) the entire product from the reaction of
a1) a chlorine-containing titanium(III) compound with
a2) a magnesium alkoxide of the formula I



in which R^1 and R^2 are either identical and are a $-CH_2CHR^6R^7$ or $-(CH_2)_nOR^8$ radical where R^6 is a hydrogen atom or a C_1-C_6 -alkyl radical, R^7 is a C_2-C_6 -alkyl radical, R^8 is a C_1-C_4 -alkyl radical and n is an integer from 2 to 6, or R^1 and R^2 are different and R^1 has the abovementioned meaning and R^2 is a C_1-C_{20} -alkyl radical, dissolved in an inert solvent, and with

- a3) a tetravalent transition metal compound of the formula II



in which M is titanium, zirconium or hafnium, R^3 is a C_1-C_9 -alkyl radical, X is a halogen atom and m is an integer from zero to 4, and with

- a4) an organoaluminum compound of the formula III





in which R^4 and R^5 are identical or different and are a C_1 - C_6 -alkyl radical, X is a halogen atom, q is a number from zero to 3, and p is a number from zero to 1,

5 in an Mg:Ti:M:Al ratio of from 1 : 0.05 to 2 : 0.05 to 2 : 0.3 to 4, the reaction of component a1 with components a2 to a4 either being carried out simultaneously or a1 first being reacted simultaneously with a2 and a3 and the reaction with a4 being
10 carried out subsequently, or component a1 being reacted successively with components a2 to a4, and

b) a trialkylaluminum compound having 1 to 6 carbon atoms in the alkyl radicals or the product of the reaction of a trialkylaluminum compound or dialkylaluminum hydride with isoprene.
15

2. The process as claimed in claim 1, wherein component a1) is reacted simultaneously with components a2) to a4).

3. The process as claimed in claim 1, wherein the
20 Mg:Ti:M:Al ratio in the preparation of catalyst component a is from 1 : 0.05 to 1 : 0.05 to 1 : 0.3 to 2.

4. The process as claimed in claim 1, wherein the chlorine-containing titanium(III) compound a1 is titanium trichloride.



Abstract of the Disclosure

Process for the preparation of ethylene (co)polymers.

The homopolymerization of ethylene or the copolymerization of ethylene with other 1-olefins is carried out using a catalyst which comprises a trialkylaluminum compound and the entire product from the reaction of chlorine-containing Ti(III) compound with a magnesium alkoxide dissolved in an inert solvent, a tetravalent transition metal compound and an organoaluminum compound and, if desired, an electron donor. A polymer having large particles, a high bulk density and a variable molecular weight distribution is obtained.

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Description**Process for the preparation of ethylene (co)polymers**

The invention relates to a process for the (co)polymerization of ethylene to give coarse polymer particles having a narrow particle size distribution, high bulk density and broad molecular weight distribution by using a catalyst whose support component is obtained by reacting a titanium(III) compound with dissolved magnesium alkoxide.

The process for the preparation of the titanium(III) compounds to be used according to the invention is known (cf. US Patent 3,773,735). The catalyst described therein, which comprises said titanium(III) compound and a trialkylaluminum compound, gives, in the polymerization, a polyolefin having relatively small particles. The catalyst activity is unsatisfactory.

A catalyst has been proposed for the polymerization of olefins which comprises a trialkylaluminum compound and the entire product from the reaction of a magnesium alkoxide dissolved in an inert solvent with a tetra-valent titanium compound and an organoaluminum compound. The use of this type of catalyst gives polyolefins having a narrow molecular weight distribution which are particularly suitable for further processing by injection molding. Polymers having a broad molecular weight distribution, as are required, for example, for the production of films, tubes or large blow moldings, cannot be obtained using this type of catalyst.

The object was thus to find a process for the preparation of catalysts of this type which is as simple as possible, gives catalysts of high activity and enables preparation of a polymer having a uniform, coarse particle shape, low

fine-particle content, high bulk density and variable molecular weight distribution.

This object is achieved by using a catalyst prepared by reacting a chlorine-containing titanium(III) compound with a dissolved magnesium alkoxide, a tetravalent transition metal compound and an organoaluminum compound.

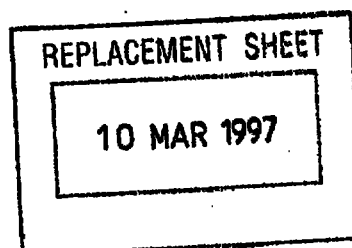
The present invention thus relates to a process for the preparation of an ethylene polymer having a uniform, coarse particle shape and high bulk density by polymerizing ethylene or ethylene with up to 10% by weight, based on the total amount of the monomers, of a 1-olefin of the formula $R^0-CH=CH_2$ in which R^0 is a straight-chain or branched alkyl radical having 1 to 12 carbon atoms, in suspension, solution or in the gas phase, at a temperature of from 20 to 120°C and a pressure of from 2 to 60 bar and in the presence of a catalyst comprising a component a containing a transition metal and an organoaluminum component b, which comprises carrying out the polymerization in the presence of a catalyst which comprises

- a) the entire product from the reaction of
 - a1) a chlorine-containing titanium(III) compound with
 - a2) a magnesium alkoxide of the formula I



in which R^1 and R^2 are either identical and are a $-CH_2CHR^6R^7$ or $-(CH_2)_nOR^8$ radical where R^6 is a hydrogen atom or a C_1-C_6 -alkyl radical, R^7 is a C_2-C_6 -alkyl radical, R^8 is a C_1-C_4 -alkyl radical and n is an integer from 2 to 6, or R^1 and R^2 are different and R^1 has the abovementioned meaning and R^2 is a C_1-C_{20} -alkyl radical, dissolved in an inert solvent, and with

- a3) a tetravalent transition metal compound of the formula II





in which M is titanium, zirconium or hafnium, R^3 is a C_1 - C_9 -alkyl radical, X is a halogen atom and m is an integer from zero to 4, and with

a4) an organoaluminum compound of the formula III



in which R^4 and R^5 are identical or different and are a C_1 - C_9 -alkyl radical, X is a halogen atom, q is a number from zero to 3, and p is a number from zero to 1,

in an Mg:Ti:M:Al ratio of from 1 : 0.05 to 2 : 0.05 to 2 : 0.3 to 4, the reaction of component a1 with components a2 to a4 either being carried out simultaneously or a1 first being reacted simultaneously with a2 and a3 and the reaction with a4 being carried out subsequently, or component a1 being reacted successively with components a2 to a4, and

b) a trialkylaluminum compound having 1 to 6 carbon atoms in the alkyl radicals or the product of the reaction of a trialkylaluminum compound or dialkylaluminum hydride with isoprene.

The chlorine-containing titanium(III) compound used to prepare the catalyst component a is titanium trichloride or an alkoxytitanium chloride, preferably titanium trichloride. The preparation is carried out, for example, by reducing a chloroalkoxytitanate of the formula $Ti(OR)_4-xCl_x$ where $x = 1$ to 4 and $R = C_2$ - C_9 -alkyl using an alkylaluminum sesquichloride and/or isoprenyl-aluminum in an inert dispersant at a temperature of from -60 to $+70^\circ C$, preferably from -30 to $0^\circ C$, and if desired subsequently heating the reaction product at from 60 to $150^\circ C$ and washing with an inert dispersant.

This titanium(III) compound is preferably employed as a suspension in an inert solvent.

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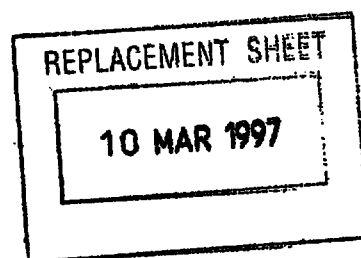
The magnesium alkoxide used is a compound of the formula I



In this formula R^1 and R^2 are identical or different. If R^1 and R^2 are identical, they are a $\text{CH}_2\text{CHR}^6\text{R}^7$ radical or a $-(\text{CH}_2)_n\text{OR}^8$ radical, where R^6 is a hydrogen atom or a $\text{C}_1\text{-C}_6-$, preferably $\text{C}_1\text{-C}_3$ -alkyl radical, R^7 is a $\text{C}_2\text{-C}_6-$, preferably $\text{C}_3\text{-C}_5$ -alkyl radical, R^8 is a $\text{C}_1\text{-C}_4-$, preferably $\text{C}_1\text{-C}_2$ -alkyl radical, and n is an integer from 2 to 6. If R^1 and R^2 are different, R^1 is as defined above and R^2 is a $\text{C}_1\text{-C}_{20}-$, preferably $\text{C}_3\text{-C}_{10}$ -alkyl radical.

Examples of magnesium alkoxides of this type are

magnesium bis(2-methyl-1-pentoxide),
magnesium bis(2-methyl-1-hexoxide),
magnesium bis(2-methyl-1-heptoxide),
magnesium bis(2-ethyl-1-pentoxide),
magnesium bis(2-ethyl-1-hexoxide),
magnesium bis(2-ethyl-1-heptoxide),
magnesium bis(2-propyl-1-heptoxide),
magnesium bis(2-methoxy-1-ethoxide),
magnesium bis(3-methoxy-1-propoxide),
magnesium bis(4-methoxy-1-butoxide),
magnesium bis(6-methoxy-1-hexoxide),
magnesium bis(2-ethoxy-1-ethoxide),
magnesium bis(3-ethoxy-1-propoxide),
magnesium bis(4-ethoxy-1-butoxide),
magnesium bis(6-ethoxy-1-hexoxide).
magnesium bis-pentoxide and
magnesium bis-hexoxide.



Other suitable magnesium alkoxides are the products of the reaction of magnesium metal, alkylmagnesium compounds or magnesium alkoxides with alcohols R^1OH (R^1 as above). Of these products, the product of the reaction of a magnesium alkoxide with an alcohol R^1OH in the presence of from 0.02 to 0.2 mol-% of triethylaluminum (as viscosity reducer) at from 100 to 140°C is preferred.

The tetravalent transition metal compound is one of the formula II



in which M is titanium, zirconium or hafnium, preferably titanium or zirconium, R^3 is an alkyl radical having 1 to 9, preferably 1 to 4, carbon atoms, X is a halogen atom, preferably chlorine, and m is zero to 4, preferably 2 to 4. The tetravalent transition metal compound of the formula II or an adduct thereof with an electron donor which can be used according to the invention is soluble in hydrocarbons.

Examples of compounds of the formula II are:

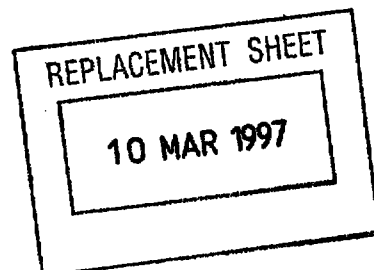
$TiCl_4$, $TiCl_3(OC_2H_5)$, $TiCl_2(OC_2H_5)_2$, $TiCl(OC_2H_5)_3$, $Ti(OC_2H_5)_4$, $TiCl_3(OC_3H_7)$, $TiCl_2(OC_3H_7)_2$, $TiCl(OC_3H_7)_3$, $Ti(OC_3H_7)_4$, $TiCl_3(OC_4H_9)$, $TiCl_2(OC_4H_9)_2$, $TiCl(OC_4H_9)_3$, $Ti(OC_4H_9)_4$, $TiCl_3(OC_6H_{13})$, $TiCl_2(OC_6H_{13})_2$, $TiCl(OC_6H_{13})_3$, $Ti(OC_6H_{13})_4$, $Ti(OC_8H_{17})_4$, $TiBr_4$, $TiBr_3(OR^3)$, $TiBr_2(OR^3)_2$, $TiBr(OR^3)_3$, TiI_4 , $TiI_3(OR^3)$, $TiI_2(OR^3)_2$, $TiI(OR^3)_3$, $ZrCl_4$, $ZrBr_4$, ZrI_4 , $Zr(OC_2H_5)_4$, $Zr(OC_3H_7)_4$, $Zr(OC_4H_9)_4$, $ZrCl_2(OC_3H_7)_2$, preferably $TiCl_4$, $Ti(OC_2H_5)_4$, $Ti(OC_3H_7)_4$, $Zr(OC_3H_7)_4$, $Ti(OC_4H_9)_4$ and $Zr(OC_4H_9)_4$.

The fourth reactant in the preparation of the catalyst component a is an organoaluminum compound of the formula III



in which R^4 and R^5 are identical or different and are an alkyl radical having 1 to 6, preferably 1 to 4, carbon atoms, X is a halogen atom, preferably chlorine, q is a number from zero to 3, preferably 1 to 2, and p is a number from zero to 1, preferably less than 0.5.

Suitable organoaluminum compounds are:



$\text{Al}(\text{C}_2\text{H}_5)_3$, $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$, $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$, AlCl_3 ,
 $\text{Al}(\text{C}_3\text{H}_7)_3$, $\text{Al}(\text{C}_3\text{H}_7)_2\text{Cl}$, $\text{Al}_2(\text{C}_3\text{H}_7)_3\text{Cl}_3$, $\text{Al}(\text{C}_3\text{H}_7)\text{Cl}_2$, $\text{Al}(\text{C}_4\text{H}_9)_3$,
 $\text{Al}(\text{C}_4\text{H}_9)_2\text{Cl}$, $\text{Al}_2(\text{C}_4\text{H}_9)_3\text{Cl}_3$, $\text{Al}(\text{C}_4\text{H}_9)\text{Cl}_2$,
and monohalides and dihalides of various compositions.
From this group, preference is given to $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$,
 $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$ and $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$.

A possible fifth reactant, but one which is not absolutely necessary, for the preparation of the catalyst component a is an electron donor. This electron donor is an aliphatic or alicyclic ester, an aliphatic ether, an aliphatic aldehyde or an aliphatic carboxylic acid. Examples of electron donors (ED) of this type are: dimethyl ether, diethyl ether, di-n-propyl ether, di-n-butyl ether, di-i-amyl ether, tetrahydrofuran, dioxane, ethyl acetate, butyl acetate, and acetic acid. Preference is given to diethyl ether, dibutyl ether and ethyl acetate.

If an electron donor is used, it can be added to at least one of the four other reactants before or during the reaction. The molar electron donor : magnesium alkoxide ratio is from 0 : 1 to 2 : 1, preferably from 0 : 1 to 1 : 1.

There are several methods of preparing component a:

The chlorine-containing titanium(III) compound is either

- 1) reacted simultaneously with the dissolved magnesium alkoxide, the tetravalent transition metal compounds and the organoaluminum compound (= reaction sequence $(a^1+a^2+a^3+a^4)$), or
- 2) reacted successively with the dissolved magnesium alkoxide, the tetravalent transition metal compound and the organoaluminum compound (= reaction sequence $(a^1)+(a^2)+(a^3)+(a^4)$), or
- 3) reacted first with the dissolved magnesium alkoxide and the tetravalent transition metal compound, and the reaction product formed is then reacted with the

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organoaluminum compound (= reaction sequence $(a^1+a^2+a^3)+(a^4)$).

The simultaneous reaction of components a1 to a4 to give the catalyst component a gives polymers having a narrow molecular weight distribution when component a is used for the polymerization. Conversely, successive reaction of component a1 with components a2 to a4 gives a catalyst component a which, in the polymerization, gives a polymer having a broad molecular weight distribution.

The simultaneous reaction of the chlorine-containing titanium(III) compound with reactants a2) to a4) is carried out at a temperature of from -50 to 150°C, preferably at from -20 to 120°C, within from 0.1 to 10 hours, preferably from 0.25 to 4 hours. If a1) is first reacted simultaneously with a2) and a3), this reaction is carried out at a temperature of from -50 to 150°C, preferably at from -20 to 120°C, within from 0.1 to 10 hours, preferably from 0.25 to 4 hours. The subsequent reaction of the reaction product formed is carried out at from -50 to 150°C, preferably at from -20 to 120°C, within from 0.1 to 10 hours, preferably from 0.25 to 4 hours. If the titanium(III) compound is reacted successively with the other reactants, each reaction step is carried out at from -50 to 150°C, preferably at from -20 to 120°C, within from 0.1 to 10 hours, preferably from 0.25 to 4 hours.

The entire reaction sequence, including the preparation of the Ti(III) compound, can be carried out without changing the solvent. Suitable inert solvents for the abovementioned reactions are aliphatic and cycloaliphatic hydrocarbons, such as butane, pentane, hexane, heptane, cyclohexane and isooctane, and aromatic hydrocarbons, such as benzene and xylene. It is also possible to employ petroleum ether and hydrogenated diesel oil fractions which have been carefully freed from oxygen, sulfur compounds and moisture. Corresponding solvent mixtures

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are also suitable. Preference is given to a petroleum ether fraction having a boiling range of from 140 to 170°C or hexane.

The titanium(III) compound, the magnesium alkoxide, the tetravalent transition metal compound (II) and the organoaluminum compound of the formula III are reacted in the (molar) Mg:Ti:M:Al ratio of from 1 : 0.05 to 2 : 0.05 to 2 : 0.3 to 4, preferably from 1 : 0.05 to 1 : 0.05 to 1 : 0.3 to 2.

After the reaction, the suspension of catalyst component a is stirred for from zero to 48 hours, preferably for from zero to 16 hours, at from 0 to 160°C, preferably at from 80 to 150°C.

The catalyst component a suspension prepared in this way can be used directly for the polymerization without removing the dispersant and by-products.

The catalyst component b (or activator) used is a tri-alkylaluminum compound having from 1 to 6 carbon atoms in the alkyl radicals, such as, for example, triethylaluminum, triisobutylaluminum, triisohexylaluminum or the product of the reaction of a trialkylaluminum or dialkylaluminum hydride with isoprene, known as isoprenylaluminum. Preference is given to triethylaluminum and isoprenylaluminum.

The polymerization is carried out in one or two steps, preferably as a suspension polymerization, in an inert dispersant. Suitable dispersants are the same organic solvents as described for the preparation of catalyst component a. However, polymerization in the gas phase is also possible.

The polymerization temperature is from 20 to 120°C, preferably from 70 to 90°C; the pressure is in the range from 2 to 60 bar, preferably from 4 to 20 bar.

However, the major advantage of the process according to the invention is that the catalyst according to the invention has higher activity and produces an ethylene polymer having a very large mean particle diameter of from 250 to 700 μm , high bulk density and variable molecular weight distribution. The polymer has a low residual moisture content, which reduces the drying costs.

The particle size distribution is extremely uniform.

In addition, the fine-particle content ($\% < 100 \mu\text{m}$) in the polymer prepared according to the invention is very low.

Furthermore, regulation of the molecular weight of the polyolefins using hydrogen is significantly more efficient than in conventional processes.

The examples below are intended to illustrate the invention.

The following abbreviations are used:

CA	: catalyst activity [kg of product/mmol of Ti]
MFI 190/5	: melt flow index in accordance with DIN 53 735, measured at 190°C at a load of 5 kg
MFI 190/15	: measured at 190°C at a load of 15 or
MFI 190/21.6	: 21.6 kg respectively
MFR 15/5	: MFI 190/15/MFI 190/5
d_{50}	: median particle size, obtained by sieve fractionation
BD	: bulk density, measured in accordance with DIN 53 468
VN	: viscosity number, measured in accordance with DIN 53 728

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Example 1: Preparation of the Ti(III) compound

400 cm³ of petroleum ether fraction (b.p. 140-170°C), 0.25 mol of ethylaluminum sesquichloride and 0.5 mol of isoprenylaluminum were introduced into a 1 dm³ reactor. 220 cm³ of TiCl₄ (2 mol) were metered in at -40°C over the course of 5 hours. The batch was subsequently stirred for 1 hour at 0°C, for 1 hour at 40°C and for 1 hour at 80°C. The suspension was then made up to 1000 cm³ using the petroleum ether fraction.

Preparation of the catalyst component a

15 mmol of Ti from the abovementioned TiCl₄ suspension in 200 cm³ of a petroleum ether fraction (b.p. 140-170°C) were introduced into a 1 dm³ stirred reactor with exclusion of air and moisture. A solution of 0.1 mol of magnesium bis(2-methyl-1-pentoxide) in 200 cm³ of the petroleum ether fraction, 100 cm³ of a 0.3 molar solution of TiCl₄ in the petroleum ether fraction and 100 cm³ of a 0.8 molar solution of ethylaluminum sesquichloride in the petroleum ether fraction were added simultaneously over the course of 120 minutes at a temperature of 20°C with stirring and under a blanket of argon. The reddish brown suspension was subsequently stirred for 120 minutes at 105°C.

Table 1 Preparation of the catalyst component a

Example	Ti(III) compound (suspension) as per	Ti(III) suspension a1) employed	
		[mmol of Ti]	[cm ³]
2	Comp. Example A	60	200
3	Comp. Example B	15	200
4	Example 1	7.5	50
5	Example 1	7.5	40

The solutions (reactants a2 - a4) were added as described in Example 1. The postreaction was carried out at 110°C

for 60 minutes.

Before use in the polymerization experiments, the suspensions were generally diluted with the petroleum ether fraction to a Ti concentration of 0.02 mol/dm^3 .

Example 6

A TiCl_3 suspension containing 15 mmol of Ti (as described in Example 1) in 200 cm^3 of a petroleum ether fraction (b.p. $140\text{--}170^\circ\text{C}$) were introduced into a 1 dm^3 stirred reactor in the absence of air and moisture.

A solution of 0.1 mol of magnesium bis(2-methyl-1-pentoxide) in 200 cm^3 of the petroleum ether fraction and 100 cm^3 of a 0.3 molar solution of TiCl_3 in the petroleum ether fraction were added simultaneously over the course of 120 minutes at a temperature of 25°C with stirring and under a blanket of argon. The suspension was subsequently reacted for 60 minutes at 80°C with 100 cm^3 of a 0.8 molar solution of ethylaluminum sesquichloride in the petroleum ether fraction.

Example 7: Ethylene polymerization

5 cm^3 of a 1 molar isoprenylaluminum solution and 1 cm^3 of the suspension prepared as in Example 1 (20 mmol/dm^3 , based on Ti) were introduced at 85°C under a blanket of N_2 into a 1.5 dm^3 reactor charged with 750 cm^3 of the petroleum ether fraction. 2 bar of hydrogen and 5 bar of ethylene were then injected. The total pressure of 7 bar was maintained for 2 hours by replenishing the consumed ethylene. The polymerization was terminated by releasing the gases, the polymer was separated off from the dispersant by filtration and drying.

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Table 2: Polymerization results (conditions corresponding to Example 7)

* No postreaction, # polymerization at 45% by volume of H ₂	1	1*	2	2	3	4#	4#	5	5	6
Catalyst component	1	IPRA	IPRA	TEA	IPRA	IPRA	TEA	IPRA	TEA	TEA
a) according to Example		5	5	3	5	5	3	5	3	3
Activator (b)										
[mmol]										
CA [kg/mmol]	17.5	23.1	9.3	10.7	9.2	7.6	9.4	11.3	14.9	7.4
Bulk density										
[g of PE/dm ³]	360	300	390	330	380	350	330	360	330	340
MFI 190/5	1.1	1.1	1.6	1.8	1.3	16.7	33.1	2.8	7.7	5.6
[g/10 min]										
MFR 15/5	4.8	5.2	5.0	5.4	5.0	5.0	5.1	4.9	5.0	5.0
MFR 21.6/5	9.5	9.8	9.1	10.0	8.6			9.8	9.0	10.2
d ₅₀ [μm]	420	460	430	460	330	270	290	400	510	650
Fine-particle content										
[% < 100 μm]	0.3	0.3	0.2	0.2	0.8	0.9	0.4	1.2	0.6	0.3
[% < 200 μm]	2.5		1.1				5.7			0.9
[% < 250 μm]										1.2
[% < 315 μm]										2.2
[% < 400 μm]	41.2		14.1				87.6			4.6
[% < 500 μm]							97.5			20.5
[% < 600 μm]	84.2		98.8				99.8			58.6
[% < 800 μm]	98.9		99.6							88.4
[% < 1000 μm]	99.7									99.5

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IPRA : Isoprenylaluminum, TEA : Triethylaluminum

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Comparative Example A

200 cm³ of a petroleum ether fraction (b.p. 140-170°C), 0.1 mol of ethylaluminum sesquichloride and 0.4 mol of isoprenylaluminum were introduced into a 1 dm³ reactor. 55 cm³ of TiCl₄ (0.5 mol) were metered in at -20°C over the course of 3 hours, and 55 cm³ of TiCl₄ (0.5 mol) were metered in at 10°C over the course of 3 hours. The batch was subsequently stirred at 80°C for 2 hours.

The ethylene polymerization was carried out as in Example 7 using 5 mmol of isoprenylaluminum.

58 g of polyethylene having a bulk density of 300 g/dm³, a mean particle size of 210 μm and a fine-particle content of 3.8% smaller than 100 μm were obtained.

The product had an MFI 190/5 of 1.2 g/10 min. The MFR 15/5 and MFR 21.6/5 were 5.7 and 11.5 respectively. The catalyst activity corresponded to 2.9 kg of PE/mmol of Ti.

Comparative Example B (in accordance with US 3,773,735)

400 cm³ of a petroleum ether fraction (b.p. 140-170°C), 0.5 mol of ethylaluminum dichloride and 0.5 mol of isoprenylaluminum were introduced into a 1 dm³ reactor. 220 cm³ of TiCl₄ (2 mol) were metered in at -25°C over the course of 3.5 hours. The mixture was subsequently stirred for 1 hour at 0°C and for 1 hour at 20°C. The catalyst was washed 4 times with 600 cm of the petroleum ether fraction. The polymerization (amounts of material) was carried out as in Example 7 using 5 mmol of IPRA. 51 g of polyethylene having a bulk density of 310 g/dm³, a mean particle size of 240 μm and a fine-particle content of 2.6% smaller than 100 μm were obtained. The product had an MFI 190/5 of 0.5 g/10 min. The MFR 15/5 and MFR 21.6/5 were 5.6 and 11.6 respectively. The catalyst activity corresponded to 1.5 kg of PE/mmol of Ti.

Example 8

1 cm³ of a 1 molar triethylaluminum solution and 12 cm³ of component a prepared as described in Example 4 (undiluted, 1 mmol of Ti) were introduced at 70°C under a blanket of N₂ into a 1.5 dm³ reactor charged with 500 cm³ of the petroleum ether fraction. 1 bar of ethylene was then injected and the pressure was maintained for 1 hour by replenishing the consumed ethylene. The polymerization was terminated by releasing the gases, and the polymer suspension was transferred into a Schlenk flask under a blanket of nitrogen, and the volume of the suspension was made up to 1000 cm³ by adding the petroleum ether fraction. The prepolymerization yield was 94 g/mmol of Ti. The viscosity number (VN) of the prepolymer was greater than 4000 cm³/g.

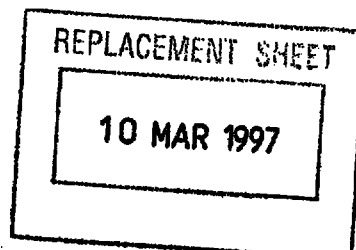
Example 9

The polymerization was carried out as in Example 7 using 5 mmol of isoprenylaluminum and 20 cm³ of the suspension prepared in Example 8. The hydrogen content was 45% by volume and the total pressure was 7 bar. The polymerization result was as follows:

CA	: 7.4 kg/mmol of Ti,	Bulk density	: 440 g/dm ³
d ₅₀	: 260 μm	Fine-particle content	: 0.9% < 100 μm
MFI 190/5	: 15.1 g/10 min,	MFR 15/5	: 5.4
9.6% < 200 μm, 90.8% < 315 μm, 98.8% < 400 μm,			
99.9% < 500 μm			

Example 10

The prepolymer was prepared as in Example 8, but using 120 cm³ (10 mmol of Ti) of component a, Example 4, and 3 mmol of triethylaluminum. The yield was 10.4 g/mmol of Ti at a VN of 2600 cm³/g. The volume of the suspension obtained was made up to 1000 cm³ using the petroleum ether fraction.



Example 11

The polymerization was carried out as in Example 9, but using 3 mmol of triethylaluminum and 2 cm³ of the suspension prepared as in Example 10.

CA	: 10.2 kg/mmol of Ti,	Bulk density	: 420 g/dm ³
d ₅₀	: 280 μm	Fine-particle content	: 0.6% < 100 μm
MFI 190/5	: 29.6 g/10 min,	MFR 15/5	: 5.0
5.4% < 200 μm, 83.2% < 315 μm, 94.8% < 400 μm,			
99.7% < 500 μm			

Example 12

The polymerization was carried out as in Example 7 using 3 mmol of triethylaluminum and 0.5 cm³ of component a as prepared in Example 4 (0.01 mmol of Ti) at 80°C, without hydrogen and at an ethylene pressure of 6 bar.

CA	: 18.6 kg/mmol of Ti,	Bulk density	: 410 g/dm ³
d ₅₀	: 330 μm	Fine-particle content	: 0.2% < 100 μm
VN	: 1300 cm ³ /g.		

Example 13

The prepolymer was prepared as in Example 8 using 89 cm³ of component a prepared as in Example 5 (10 mmol of Ti).

Example 14

100 dm³ of the petroleum ether fraction, 50 mmol of isoprenylaluminum and 200 cm³ of suspension 10 (2 mmol of Ti) were introduced into a 150 dm³ reactor. 5 kg/h of ethylene and sufficient H₂ so that the H₂ content in the gas space was 45% by volume were subsequently introduced at a polymerization temperature of 85°C. After 6 hours, the polymerization was terminated at a pressure of 5.2 bar by decompression. The suspension was filtered, and the polyethylene powder was dried by passing hot nitrogen over it.

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24.8 kg of polyethylene were obtained. This corresponds to a catalyst activity of 12.4 kg of PE/mmol of Ti. The polyethylene powder had an MFI 190/5 of 5.9 g/10 min and an MFR 15/5 and MFR 21.6/5 of 4.9 and 10.2 respectively. The density was 0.960 and the bulk density was 430 g/dm³. The median particle size d_{50} was 380 μm at a fine-particle content of 1% < 100 μm .

Example 15

33 cm³ (65 mmol of Ti) of the TiCl₃ suspension, prepared as described in Example 1, in 50 cm³ of a petroleum ether fraction (b.p. 140-170°C) were introduced into a 1 dm³ stirred reactor in the absence of air and moisture, and were reacted with a solution of 0.1 mol of magnesium bis(2-methyl-1-pentoxide) in 200 cm³ of the petroleum ether fraction for 20 minutes at a temperature of 25°C with stirring and under a blanket of argon. 100 cm³ of a 0.3 molar solution of TiCl₄ in the petroleum ether fraction were subsequently metered in at 25°C over the course of 60 minutes. A solution of 60 mmol of Al₂Et₃Cl₃ in 70 cm³ of the petroleum ether fraction was subsequently metered in at 80°C over the course of 20 minutes.

Table 3 Preparation of catalyst component a

Example	Ti(III) compound (suspension) as per	Ti(III) suspension a) employed	
		[mmol of Ti]	[cm ³]
16	Comp. Example A	30	200
17	Comp. Example B	22	200
18	Example 15	15	50
19	Example 15	11	200
20	Example 15	7	200

The magnesium compound was added as described in Example 15, but over the course of 60 minutes. The titanium(IV) compound was added as described in Example 15. In Examples 16 to 20, 80 mmol of Al₂Et₃Cl₃ dissolved in

100 cm³ of the petroleum ether fraction were added over the course of 60 minutes.

Before use in the polymerization experiments, suspensions a from Examples 15 to 20 were diluted to a Ti concentration of 0.02 mol/dm³.

Example 21: Ethylene polymerization

2.5 cm³ of a 1 molar isoprenylaluminum solution and 1 cm³ of the suspension prepared as described in Example 15 (20 mmol/dm³, based on Ti) were introduced at 85°C under a blanket of N₂ into a 1.5 dm³ reactor charged with 750 cm³ of the petroleum ether fraction. 2 bar of hydrogen and 5 bar of ethylene were then injected. The total pressure of 7 bar was maintained for 2 hours by replenishing the consumed ethylene. The polymerization was terminated by releasing the gases, and the polymer was separated off from the dispersant by filtration and drying.

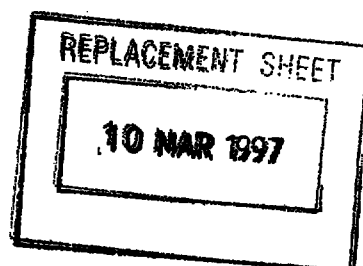
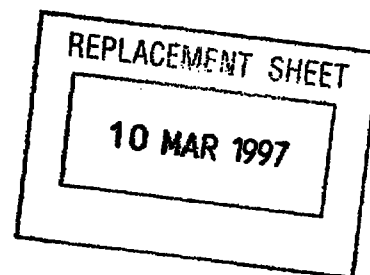


Table 4: Polymerization results (conditions as described in Example 21)

Catalyst comp. a from Example	15	16	16	17	17	18	19	19	20
Activator (b) [mmol]	IPRA 2.5	IPRA 2.5	IPRA 5	TEA 2.5	IPRA 5	IPRA 5	TEA 2.5	IPRA 5	IPRA 5
CA [kg/mmole]	3.4	6.1	7.3	4.7	5.8	8.7	10.1	8.5	10.9
Bulk density [g of PE/dm ³]	330	290	300	350	330	350	340	360	350
d ₅₀ [μm]	600	600	680	460	480	450	340	300	410
Fine-particle content [% < 100 μm]	2.0	1.7	0.9	0.8	0.4	0.8	0.5	1.0	0.1
MFI 190/5 [g/10 min]	0.9	1.5	2.1	2.4	2.0	1.6	4.0	2.2	2.6
MFR 15/5	7.1	7.6	6.4	6.3	5.8	8.1	5.6	6.2	5.2
MFR 21.6/5	13.2	13.3	12.3	12.8	11.9	15.2	12.0	12.1	10.1

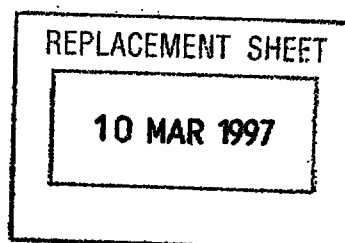
IPRA: Isoprenylaluminum, TEA: Triethylaluminum



Example 22

100 dm³ of a petroleum ether fraction, 100 mmol of isoprenylaluminum and 37.4 cm³ of the undiluted suspension from Example 18 (4 mmol of Ti) were introduced into a 150 dm³ reactor. 7.5 kg/h of ethylene and sufficient H₂ so that the H₂ content in the gas space was 30% by volume were subsequently introduced at a polymerization temperature of 85°C. After 4.5 hours, the polymerization was terminated at a pressure of 3.1 bar by decompression. The suspension was filtered, and the polyethylene powder was dried by passing hot nitrogen over it.

32.6 kg of polyethylene were obtained. This corresponds to a catalyst activity of 8.2 kg of PE/mmol of Ti. The polyethylene powder had an MFI 190/5 of 3.2 g/10 min and an MFR 15/5 and MFR 21.6/5 of 5.9 and 14.1 respectively. The density was 0.958 and the bulk density was 380 g/dm³. The median particle size d₅₀ was 410 μm at a fine-particle content of 1% < 100 μm.





Patent claims:

1. A process for the preparation of an ethylene polymer having a uniform, coarse particle shape and high bulk density by polymerizing ethylene or ethylene with up to 10% by weight, based on the total amount of the monomers, of a 1-olefin of the formula $R^9-CH=CH_2$ in which R^9 is a straight-chain or branched alkyl radical having 1 to 12 carbon atoms, in suspension, solution or in the gas phase, at a temperature of from 20 to 120°C and a pressure of from 2 to 60 bar and in the presence of a catalyst comprising a component containing a transition metal and an organoaluminum component b, which comprises carrying out the polymerization in the presence of a catalyst which comprises

a) the entire product from the reaction of

a1) a chlorine-containing titanium(III) compound with

a2) a magnesium alkoxide of the formula I



in which R^1 and R^2 are either identical and are a $-CH_2CHR^6R^7$ or $-(CH_2)_nOR^8$ radical where R^6 is a hydrogen atom or a C_1-C_6 -alkyl radical, R^7 is a C_2-C_6 -alkyl radical, R^8 is a C_1-C_4 -alkyl radical and n is an integer from 2 to 6, or R^1 and R^2 are different and R^1 has the abovementioned meaning and R^2 is a C_1-C_{20} -alkyl radical, dissolved in an inert solvent, and with

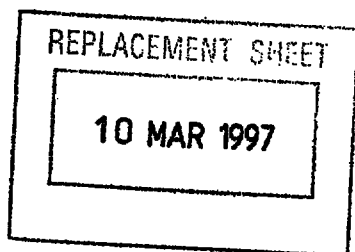
a3) a tetravalent transition metal compound of the formula II



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in which M is titanium, zirconium or hafnium, R^3 is a C_1-C_9 -alkyl radical, X is a halogen atom and m is an integer from zero to 4, and with

a4) an organoaluminum compound of the formula III



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in which R^4 and R^5 are identical or different and are a C_1 - C_6 -alkyl radical, X is a halogen atom, q is a number from zero to 3, and p is a number from zero to 1,

in an Mg:Ti:M:Al ratio of from 1 : 0.05 to 2 : 0.05 to 2 : 0.3 to 4, the reaction of component a1 with components a2 to a4 either being carried out simultaneously or a1 first being reacted simultaneously with a2 and a3 and the reaction with a4 being carried out subsequently, or component a1 being reacted successively with components a2 to a4, and

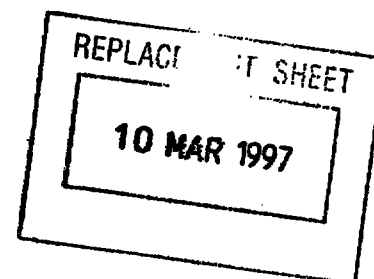
- b) a trialkylaluminum compound having 1 to 6 carbon atoms in the alkyl radicals or the product of the reaction of a trialkylaluminum compound or dialkylaluminum hydride with isoprene.

2. The process as claimed in claim 1, wherein component a1) is reacted simultaneously with components a2) to a4).

3. The process as claimed in claim 1, wherein the Mg:Ti:M:Al ratio in the preparation of catalyst component a is from 1 : 0.05 to 1 : 0.05 to 1 : 0.3 to 2.

4. The process as claimed in claim 1, wherein the chlorine-containing titanium(III) compound a1 is titanium trichloride.

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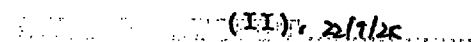
Abstract of the Disclosure

Process for the preparation of ethylene (co)polymers.

The homopolymerization of ethylene or the copolymerization of ethylene with other 1-olefins is carried out using a catalyst which comprises a trialkylaluminum compound and the entire product from the reaction of chlorine-containing Ti(III) compound with a magnesium alkoxide dissolved in an inert solvent, a tetravalent transition metal compound and an organoaluminum compound and, if desired, an electron donor. A polymer having large particles, a high bulk density and a variable molecular weight distribution is obtained.

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a4) an organoaluminum compound of the formula III

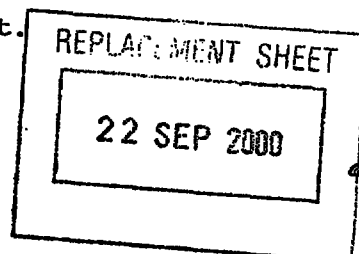


in an Mg:Ti:M:Al ratio of from 1 : 0.05 to 2 : 0.05 to 2 : 0.3 to 4, the reaction of component a1 with components a2 to a4 either being carried out simultaneously or a1 first being reacted simultaneously with a2 and a3 and the reaction with a4 being carried out subsequently, or component a1 being reacted successively with components a2 to a4, and

- b) a trialkylaluminum compound having 1 to 6 carbon atoms in the alkyl radicals or the product of the reaction of a trialkylaluminum compound or dialkylaluminum hydride with isoprene.

The chlorine-containing titanium(III) compound used to prepare the catalyst component a may be titanium trichloride or an alkoxytitanium chloride, preferably titanium trichloride. The preparation is carried out, for example, by reducing a chloroalkoxytitanate of the formula $Ti(OR)_{4-r}Cl_r$, where $r = 1$ to 4 and $R = C_2-C_8$ -alkyl using an alkylaluminum sesquichloride and/or isoprenyl-aluminum in an inert dispersant at a temperature of from -60 to $+70^\circ C$, preferably from -30 to $0^\circ C$, and if desired subsequently heating the reaction product at from 60 to $150^\circ C$ and washing with an inert dispersant.

This titanium(III) compound is preferably employed as a suspension in an inert solvent.



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Patent claims:

1. A process for the preparation of an ethylene polymer having a uniform, coarse particle shape and high bulk density by polymerizing ethylene or ethylene with up to 10% by weight, based on the total amount of the monomers, of a 1-olefin of the formula $R^0-CH=CH_2$ in which R^0 is a straight-chain or branched alkyl radical having 1 to 12 carbon atoms, in suspension, solution or in the gas phase, at a temperature of from 20 to 120°C and a pressure of from 2 to 60 bar and in the presence of a catalyst comprising a component containing a transition metal and an organoaluminum component b, which comprises carrying out the polymerization in the presence of a catalyst which comprises

a) the entire product from the reaction of

a1) a chloride-containing titanium(III) compound, such as titanium trichloride or an alkoxytitanium chloride with

a2) a magnesium alkoxide of the formula I



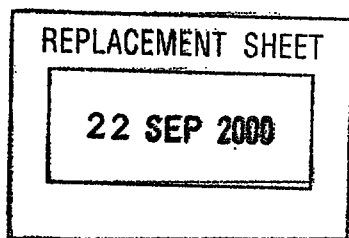
in which R^1 and R^2 are either identical and are a $-CH_2CHR^6R^7$ or $-(CH_2)_nOR^6$ radical where R^6 is a hydrogen atom or a C_1-C_6 -alkyl radical, R^7 is a C_2-C_6 -alkyl radical, R^6 is a C_1-C_4 -alkyl radical and n is an integer from 2 to 6, or R^1 and R^2 are different and R^1 has the abovementioned meaning and R^2 is a C_1-C_{20} -alkyl radical, dissolved in an inert solvent, and with

a3) a tetravalent transition metal compound of the formula II



in which M is titanium, zirconium or hafnium, R^3 is a C_1-C_6 -alkyl radical, X is a halogen atom and m is an integer from zero to 4, and with

a4) an organoaluminum compound of the formula III





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in which R^4 and R^5 are identical or different and are a C_1 - C_6 -alkyl radical, X is a halogen atom, q is a number from zero to 3, and p is a number from zero to 1,

in an Mg:Ti:M:Al ratio of from 1 : 0.05 to 2 : 0.05 to 2 : 0.3 to 4, the reaction of component a1 with components a2 to a4 either being carried out simultaneously or a1 first being reacted simultaneously with a2 and a3 and the reaction with a4 being carried out subsequently, or component a1 being reacted successively with components a2 to a4, and

- b) a trialkylaluminum compound having 1 to 6 carbon atoms in the alkyl radicals; or the product of the reaction of a trialkylaluminum compound or dialkylaluminum hydride with isoprene.
2. The process as claimed in claim 1, wherein component a1) is reacted simultaneously with components a2) to a4).
3. The process as claimed in claim 1, wherein the Mg:Ti:M:Al ratio in the preparation of catalyst component a is from 1 : 0.05 to 1 : 0.05 to 1 : 0.3 to 2.
4. The process as claimed in claim 1, wherein the chlorine-containing titanium(III) compound a1 is titanium trichloride.

