

REPLACED SHEETS		SG
☒	Description : paged 1 to paged 18	
☒	Claim(s) : paged 19 to paged 30	
☐	Drawing(s) : paged 41-253 to paged	
☒	Abstract : paged 1 to paged	
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HOE 92/F 410

Dr.DA/-

Description

Process for the homo- and copolymerization of 1-olefins ✓

The invention relates to a process for polymerizing
5 1-olefins by means of a supported Ziegler catalyst containing a number of different transition metals.

Supported Ziegler-Natta catalysts which contain a number of transition metals together are known (cf. EP 137 258, EP 286 148, DE 32 42 150, DE 33 24 136, US 4 518 751,
10 US 4 472 523, WO 91/13914, DE 41 02 300). However, these catalysts are frequently synthesized in complicated processes in which, for example, the solid produced is dried, sometimes also calcined and isolated. Some catalysts require for their synthesis and catalytic
15 activity additional electron-donors in the form of nonmetal chlorides (such as SiCl_4 , BCl_3). Furthermore, frequently the support material has to be specially produced and prepared from SiO_2 , $\text{SiO}_2/\text{Al}_2\text{O}_3$ or combinations such as $\text{SiO}_2/\text{MgCl}_2$.

20 A further known process for producing a poly-1-olefin is one in which a supported catalyst based on a gel-type magnesium alkoxide is used (cf. WO 91/18934). The catalyst used has excellent activity, very good response to hydrogen, good copolymerization behavior and produces an
25 excellent polymer powder morphology (large average particle sizes, narrow particle size distribution and a high bulk density). However, with this catalyst it is impossible to produce in a single-stage process products which have a broad molecular weight distribution, since
30 this catalyst basically gives only polyolefins having a narrow molecular weight distribution ($M_w/M_n \leq 6$; $\text{MFR} \leq 10$).

Finally, a catalyst has been proposed which gives a

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22



- 2 -

polyolefin having a molecular weight distribution of medium breadth ($M_w/M_n \leq 8$; MFR ≤ 13) (cf. DE 41 26 093). However, this catalyst is complicated and expensive to synthesize.

- 5 It an object of the present invention to create a supported catalyst which gives a polyolefin having a broad molecular weight distribution. Furthermore the synthesis of the catalyst should be as simple as possible. In addition, the catalyst should have high activity, good
10 response to hydrogen and good copolymerization behavior and give an excellent morphology of the polymer powder produced.

This object is achieved by providing a support which consists essentially of $MgCl_2$, with different active centers with different transition metals which give different chain lengths during polymerization.
15

The invention accordingly provides a process for producing a polyolefin having an MFR value equal to or greater than 10 by polymerization of a 1-olefin of the
20 formula $R^1CH=CH_2$, in which R^1 is hydrogen or an alkyl radical having from 1 to 10 carbon atoms, in suspension, in solution or in the gas phase, at a temperature of from 20 to 200°C and a pressure of from 0.5 to 50 bar, in the presence of a catalyst composed of the reaction product
25 of a magnesium alkoxide dispersion having a particle size of from 100 to 3000 nm with a transition metal compound (component a) and an organometallic compound of a metal of group I, II or III of the Periodic Table (component b), which comprises carrying out the polymerization in
30 the presence of a catalyst whose component a was prepared by reacting the magnesium alkoxide dispersion simultaneously with different compounds of a number of transition metals selected from the group consisting of titanium, zirconium, vanadium and chromium and then
35 reacting the mixture with a chlorine-containing organoaluminum compound.



- 3 -

The invention further provides the catalyst used in this process.

Component a is synthesized using a commercially available magnesium alkoxide.

- 5 This magnesium alkoxide is a compound of the formula $Mg(OR^1)(OR^2)$, in which R^1 and R^2 are identical or different and each is an alkyl radical having from 1 to 6 carbon atoms. Examples are $Mg(CH_3)_2$, $Mg(OC_2H_5)_2$, $Mg(OiC_3H_7)_2$, $Mg(OnC_4H_9)_2$, $Mg(OCH_3)(OC_2H_5)$, $Mg(OC_2H_5)(OnC_3H_7)$. Preference is
10 given to using $Mg(OC_2H_5)_2$, $Mg(OnC_3H_7)_2$ and $Mg(OiC_3H_7)_2$. The magnesium alkoxide is used in pure form.

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

- | | |
|----------------------------|--------------------------|
| Mg content | from 21 to 22% by weight |
| 15 Total $Mg(OH)_2/MgCO_3$ | $\leq 1\%$ by weight |
| C_2H_5OH content | $< 0.3\%$ by weight |

The average particle diameter is 500 μm . 90% of the particles have a particle diameter in the range from 200 to 1200 μm .

- 20 The magnesium alkoxide is suspended in an inert saturated hydrocarbon. This suspension is subjected in a reactor under a protective gas (Ar , N_2) to the action of a high-speed mixer (e.g. $\text{\textcircled{U}}$ Ultra-Turrax or $\text{\textcircled{D}}$ Dispax from IKA-Maschinenbau Janke & Kunkel GmbH) to convert it into a
25 magnesium alkoxide dispersion.

- The magnesium alkoxide suspension contains the magnesium alkoxide as solid insoluble particles suspended in the saturated hydrocarbon or hydrocarbon mixture. This suspension is turbid and not transparent. It displays
30 Newtonian behavior and at 25°C has a viscosity of from 0.0003 to 0.0008 Pa.s. If this magnesium alkoxide suspension is treated with the high-speed mixer at 25°C, there is observed over a period of about 1/2 hour a rapid

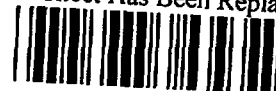


- 4 -

size reduction of the suspended particles, a strong increase in turbidity and an increase in the viscosity to from 0.0015 to 0.0025 Pa.s. Over a longer period (from about 2 to 8 hours) the turbidity disappears and the
5 viscosity increases further to from 0.006 to 0.010 Pa.s. The magnesium alkoxide particles are no longer visible. A magnesium alkoxide dispersion (lyogel) has been formed. These magnesium alkoxide dispersions (1.2 mol of magnesium ethoxide/dm³ of diesel oil) no longer display
10 Newtonian behavior. The shear viscosity as a function of the shear rate is measured at 25°C by means of a rotation viscometer. These magnesium alkoxide dispersions have a pseudoplastic flow behavior. Pseudoplastic flow behavior is characterized by shear flow only starting above a
15 certain shear stress (in the present case: 1.2 mol of magnesium ethoxide/dm³ of diesel oil (C₁₀/C₁₁ gasoline cut) at about 2 Pa) and the shear viscosity then having a constant value (here 0.006 Pa.s).

If this magnesium alkoxide dispersion is greatly diluted
20 with saturated hydrocarbons or hydrocarbon mixtures (1:100), the average diameter of the magnesium alkoxide particles can be determined by dynamic light scattering with a measuring instrument (Malvern System 4700). It is in the range of from 100 to 3000 nm (from 0.1 to 3 μm).
25 This means that the average diameter of the suspended particle (about 500 μm) has decreased by a factor of more than 100.

The magnesium alkoxide dispersion is distinguished from the suspension by two essential features. It is, as shown
30 above, substantially more viscous than the suspension and the dispersed magnesium alkoxide settles much more slowly than the suspended magnesium alkoxide and to a much lesser degree (after some hours, volume of the supernatant hydrocarbon for suspended magnesium alkoxide
35 about 80% by volume, for dispersed magnesium alkoxide about 10% by volume for the same content (131 g/dm³)).



The dispersed magnesium alkoxide can also be prepared by mechanical comminution with glass beads (diameter 1 cm) in a round-bottom flask, the flask contents being agitated with a twin-blade stirrer. However, this process
5 is very time-consuming.

Suitable inert saturated hydrocarbons are aliphatic or cycloaliphatic hydrocarbons such as butane, pentane, hexane, heptane, isooctane, cyclohexane, methylcyclohexane, and aromatic hydrocarbons such as
10 toluene, xylene; even hydrogenated diesel oil or gasoline fractions which have been carefully freed of oxygen, sulfur compounds and moisture can be used.

The magnesium alkoxide dispersion is then in one step simultaneously reacted with a Ti compound (TiCl_4 , $\text{Ti}(\text{OR})_4$,
15 inter alia), Zr compound ($\text{Zr}(\text{OR})_4$, inter alia), V compound (VCl_4 , VOCl_3 , inter alia) or Cr compound (CrO_2Cl_2 , inter alia).

It is advantageous to use vanadium compounds together with CHCl_3 .

20 Suitable combinations are

- a) TiCl_4 and VOCl_3 or VCl_4 and CHCl_3 ,
- b) TiCl_4 and ZrCl_4 ,
- c) TiCl_4 and CrCl_3 or CrO_2Cl_2 ,
- d) VOCl_3 or VCl_4 and ZrCl_4 and CHCl_3 ,
- 25 e) VOCl_3 or VCl_4 and CrCl_3 or CrO_2Cl_2 and CHCl_3 ,
- f) CrO_2Cl_2 or CrCl_3 and ZrCl_4 ,
- g) TiCl_4 and ZrCl_4 and VOCl_3 or VCl_4 and CHCl_3 ,
- h) TiCl_4 and ZrCl_4 and CrCl_3 or CrO_2Cl_2 ,
- i) TiCl_4 and VOCl_3 or VCl_4 and CrCl_3 or CrO_2Cl_2 and CHCl_3 ,
- 30 or
- k) VOCl_3 or VCl_4 and ZrCl_4 and CrO_2Cl_2 or CrCl_3 and CHCl_3 .

Preference is given to combination (a).

The result is a finely divided precipitate which



comprises mainly $MgCl_2$ and the transition metals used, and in which the transition metals used are present in approximately the ratio in which they were added. This suspension is then reacted with $Et_3Al_2Cl_3$, the transition
5 metals being partially reduced and the color of the solid changing from white to dark brown. Subsequently the suspension is washed repeatedly with diesel oil.

The magnesium alkoxide is reacted with the transition metal compounds at a temperature of from 50 to 100°C,
10 preferably from 60 to 90°C, in the presence of an inert hydrocarbon while stirring. Per 1 mol of magnesium alkoxide up to 0.7 mol of transition metal compound is used, preferably from 0.2 to 0.4 mol of transition metal compound per 1 mol of magnesium alkoxide.

15 The reaction time is from 0.5 to 8 hours, preferably from 2 to 6 hours.

A hydrocarbon-insoluble solid which contains magnesium and transition metals is obtained, which is designated as component a.

20 The production of the polymerization catalyst to be used according to the invention is carried out by combining the component a and an organometallic compound of a metal of group I, II or III of the Periodic Table (component b).

25 Component a can be reacted as a suspension directly with component b; it can however also first be isolated as a solid, stored and again suspended for later further use.

Preferably, the component b used is an organoaluminum compound. Suitable organoaluminum compounds are chlorine-
30 containing organoaluminum compounds, the dialkylaluminum monochlorides of the formula R^3_2AlCl or alkylaluminum sesquichlorides of the formula $R^3_3Al_2Cl_3$, in which R^3 is an alkyl radical having from 1 to 16 carbon atoms. Examples



- 7 -

are $(C_2H_5)_2AlCl$, $(iC_4H_9)_2AlCl$, $(C_2H_5)_2Al_2Cl_3$. Mixtures of these compounds can also be used.

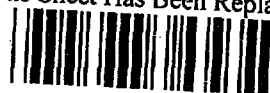
Particularly preferred organoaluminum compounds are chlorine-free compounds. Suitable compounds here are on the one hand the reaction products of aluminum trialkyls or dialkylaluminum hydrides having hydrocarbon radicals having from 1 to 6 carbon atoms, preferably $Al(iC_4H_9)_3$ or $Al(iC_4H_9)_2H$, with diolefins containing from 4 to 20 carbon atoms, preferably isoprene. An example is isoprenylaluminum.

On the other hand, such chlorine-free organoaluminum compounds may be aluminum trialkyls of the formula AlR^3 , or dialkylaluminum hydrides of the formula AlR^3_2H in which R^3 is an alkyl radical having from 1 to 12 carbon atoms. Examples are $Al(C_2H_5)_3$, $Al(C_2H_5)_2H$, $Al(C_3H_7)_3$, $Al(C_3H_7)_2H$, $Al(iC_4H_9)_3$, $Al(iC_4H_9)_2H$, $Al(C_8H_{17})_3$, $Al(C_{12}H_{25})_3$, $Al(C_{12}H_{25})_2H$, $Al(C_2H_5)(C_{12}H_{25})_2$, $Al(iC_4H_9)(C_{12}H_{25})_2$.

Mixtures of various organoaluminum compounds can also be used.

Examples of such mixtures are: $Al(C_2H_5)_3$ and $Al(C_4H_9)_3$, $Al(C_2H_5)_2Cl$ and $Al(C_8H_{17})_3$, $Al(C_2H_5)_3$ and $Al(C_8H_{17})_3$, $Al(C_4H_9)_3$ and $Al(C_8H_{17})_3$, $Al(iC_4H_9)_3$ and $Al(C_8H_{17})_3$, $Al(C_2H_5)_3$ and $Al(C_{12}H_{25})_3$, $Al(iC_4H_9)_3$ and $Al(C_{12}H_{25})_3$, $Al(C_2H_5)_3$ and $Al(C_{16}H_{33})_3$, $Al(C_3H_7)_3$ and $Al(C_{18}H_{37})_3$, $Al(iC_4H_9)_3$ and isoprenylaluminum (reaction product of isoprene with $Al(iC_4H_9)_3$ or $Al(iC_4H_9)_2H$).

Mixing of component a and component b can be carried out prior to the polymerization in a stirred reactor at a temperature of from -30 to $150^\circ C$, preferably from -10 to $120^\circ C$. It is also possible to combine the two components directly in the polymerization reactor at a temperature of from 20 to $200^\circ C$. However, addition of component b can also be carried out in two steps, in that prior to the polymerization reaction component a is pre-activated with



a part of component b at a temperature of from -30 to 150°C and the further addition of component b is carried out in the polymerization reactor at a temperature of from 20 to 200°C.

- 5 The polymerization catalyst to be used according to the invention is used for the polymerization of 1-olefins of the formula $R^4-CH=CH_2$, in which R^4 is a hydrogen atom or an alkyl radical having from 1 to 10 carbon atoms, for example ethylene, propylene, but-1-ene, hex-1-ene,
10 4-methylpent-1-ene, oct-1-ene.

Preferably, ethylene is polymerized alone or as a mixture of at least 50% by weight of ethylene and at most 50% by weight of another 1-olefin of the above formula.

- In particular, ethylene is polymerized alone or as a
15 mixture of at least 90% by weight of ethylene and at most 10% by weight of another 1-olefin of the above formula.

- The polymerization is carried out in a known manner in solution, in suspension or in the gas phase, continuously or batchwise, in one or more stages at a temperature of
20 from 20 to 200°C, preferably from 50 to 150°C. The pressure is from 0.5 to 50 bar. Preferably, the polymerization is carried out within the pressure range from 5 to 30 bar which is of particular interest in industry.

- 25 In this process, component a is used in a concentration, based on the transition metal, of from 0.0001 to 1, preferably from 0.001 to 0.5 mmol of transition metal per dm³ of dispersion medium. The organometallic compound is used in a concentration of from 0.1 to 5 mmol, preferably
30 from 0.5 to 4 mmol per dm³ of dispersion medium. In principle, however, higher concentrations are also possible.

The suspension polymerization is carried out in an inert



- 9 -

dispersion medium customarily used for the Ziegler low pressure process, for example in an aliphatic or cycloaliphatic hydrocarbon; examples thereof are propane, butane, pentane, hexane, heptane, isooctane, cyclohexane, 5 methylcyclohexane. In addition, gasoline or hydrogenated diesel oil fractions which have been carefully freed of oxygen, sulfur compounds and moisture can be used.

The gas phase polymerization can be carried out directly or after pre-polymerization of the catalyst in a 10 suspension process.

The molecular weight of the polymer is controlled in a known manner, preferably using hydrogen.

The process of the invention, as a result of the high activity of the catalyst used, gives polymers having very 15 low transition metal and halogen contents in the range of from 2 to 20 ppm.

Furthermore, the process of the invention makes it possible to produce the catalysts in such a way that using them the particle size distribution and to a 20 certain extent also the particle shape of the polymer powder produced can be adjusted.

An improved particle morphology, high average particle diameters (d_{50} values), narrow particle size distribution, no coarse or fine fractions, and high catalyst produc- 25 tivities are obtained. The bulk densities are comparable with the prior art.

Thus the use of these dispersions of magnesium alkoxides allows the morphological properties of the polymer powder to be influenced, which is advantageous in an industrial 30 process (filtration of the polymer powder is simpler, the residual dispersion medium contents are lower, so energy consumption for drying is lower), the transport of the polymer powder in the plant is simpler, the flowability



is better, the fine fraction in the cyclones of the dryers is lower). The high catalyst productivity gives lower residual catalyst contents in the product.

Polymerization experiments with the catalysts produced according to the invention have shown that different transition metal centers are present and that the melt flow ratio values (MFR values; $MFR = MFI\ 190/21.6/MFI\ 190/5$, where the MFI (melt flow index) is measured in accordance with DIN 53737) are significantly higher in comparison with the prior art and can be adjusted by variation of the H_2/C_2H_4 ratio. M_w/M_n is above 15 and MFR is equal to or greater than 10, preferably greater than 25.

The examples which follow illustrate the invention.

15 In the examples a hydrogenated diesel oil fraction having a boiling range of from 130 to 170°C was used for catalyst synthesis and for polymerization.

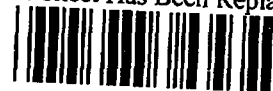
The ratios $Mg:Ti(Zr, V, Cr):Cl$ for characterizing the catalysts were determined by the usual analytical methods.

The titanium content per unit mass of catalyst required for calculating the catalyst productivity CP (cf. Tables) was determined in the following way:

25 A particular volume was pipetted from the catalyst suspension. The catalyst was hydrolyzed with sulfuric acid and the titanium content determined by known methods. Result: titanium content (mmol) per unit volume (cm^3).

30 A second sample was taken from the suspension, the suspension medium was drawn off in vacuo and the solid was weighed.

Result: solid (g) per unit volume (cm^3).



Forming the quotient gives mmol of Ti/g of catalyst.

Example 1

1.2 mol (= 137 g) of commercially available $\text{Mg}(\text{OC}_2\text{H}_5)_2$ (Mg content from 21 to 22% by weight, $\text{C}_2\text{H}_5\text{OH}$ content < 0.3% by weight, average particle diameter 500 μm , 90% of the particles have a particle diameter in the range of from 200 to 1200 μm) were suspended in 1.0 dm^3 of diesel oil. The magnesium ethoxide particles are insoluble in the hydrocarbon mixture and therefore formed a suspension.

- 10 This suspension in a cylindrical glass vessel under protective gas (Ar , N_2) and exclusion of air (O_2) and moisture (H_2O) was converted with a commercially available mixer (*ULTRA-TURRAX T 50, Janke & Kunkel GmbH & Co. KG, D-7813 Staufen) into a magnesium ethoxide/diesel
15 oil dispersion. This procedure took at least 3 hours when starting at room temperature. The vessel had to be strongly cooled, so as to prevent the temperature in the vessel from rising greatly (to at most 50°C).

- The magnesium ethoxide/diesel oil suspension contained
20 the magnesium ethoxide particles in suspended form. Without stirring, these particles settled in about 10 minutes into the lower part of the vessel. The shear viscosity of this suspension was 0.00065 Pa.s at 25°C. The magnesium ethoxide/diesel oil suspension was there-
25 fore not viscous and contained coarse particles of magnesium ethoxide (from 200 to 1200 μm). After switching on the mixer the following could be observed: during the course of half an hour the suspended magnesium ethoxide particles were rapidly reduced in size. This was con-
30 nected with a strong increase in turbidity and an increase in viscosity. The viscosity (measurement with a rotation viscometer from Haake) rose to 0.0020 Pa.s. Over a longer period the viscosity rose further to from 0.006 to 0.010 Pa.s and the suspended particles disappeared. A
35 magnesium ethoxide/diesel oil dispersion (lyogel) had



- 12 -

been formed. The average particle size measured with a Malvern System 4700 (for this measurement it was necessary to dilute with diesel oil by a factor of 1:100) was from 100 to 3000 nm (from 0.1 to 3 μm).

- 5 The magnesium ethoxide/diesel oil dispersion displayed the following characteristic differences from the magnesium ethoxide/diesel oil suspension. The average particle size sank from about 500 μm to from 100 to 300 nm. The magnesium ethoxide/diesel oil suspension
10 displayed Newtonian flow behavior with a viscosity of 0.00065 Pa.s/25°C. The magnesium ethoxide/diesel oil dispersion on the other hand displayed pseudoplastic behavior with a substantially higher viscosity of 0.006 Pa.s/25°C. Flow commenced at a shear stress of
15 2.0 Pa.

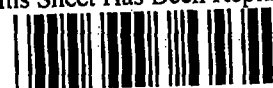
- After sedimentation, the sedimentation volume of this magnesium alkoxide/diesel oil dispersion could be determined. At a magnesium alkoxide content of 137 g in 1 dm³ of diesel oil it was from 30 to 40% by volume. The
20 sedimented fraction had a gray color and was a thixotropic lyogel having a high viscosity. When the vessel was rotated the lyogel remained on the bottom of the vessel and separated from the diesel oil. On vigorous shaking, the lyogel and the supernatant diesel oil formed a low
25 viscosity dispersion.

Example 2

- A 2 dm³ four-necked flask with precision glass stirrer was charged with 500 mmol of dispersed $\text{Mg}(\text{OEt})_2$ in 1000 cm³ of diesel oil. The gel-type dispersion was
30 heated while stirring (300 rpm) to 85°C and reacted with the transition metal compounds.

Variant A (Ti:V = 9:1)

135 mmol of TiCl_4 and 15 mmol of VCl_3 were added dropwise over a period of 4 hours, each from separate metering



equipment.

Variant B (Ti:V = 8:2)

120 mmol of TiCl_4 and 30 mmol of VOCl_3 were added dropwise over a period of 4 hours, each from separate metering
5 equipment.

Variant C (Ti:V = 7:3)

105 mmol of TiCl_4 and 45 mmol of VOCl_3 , dissolved in 160 cm^3 of diethyl ether, were added dropwise over a period of 4 hours, each from separate metering equipment.

10 Variant D (Ti:V = 1:1)

75 mmol of TiCl_4 and 75 mmol of VOCl_3 with 3.75 mol of CHCl_3 , diluted with 89 cm^3 of diesel oil, were added dropwise over a period of 4 hours, each from separate metering equipment.

15 Variant E (Ti:Zr = 1:1)

150 mmol of TiCl_4 and 150 mmol of ZrCl_4 , suspended in 150 cm^3 of diesel oil, were added dropwise over a period of 4 hours, each from separate metering equipment.

Variant F (Ti:Cr = 1:1)

20 150 mmol of TiCl_4 and 150 mmol of CrO_2Cl_2 , suspended in 200 cm^3 of diesel oil, were added dropwise over a period of 4 hours, each from separate metering equipment.

Subsequently the mixture was heated to 110°C and reacted at this temperature with 350 mmol of $\text{Et}_2\text{Al}_2\text{Cl}_3$, dissolved
25 in 500 cm^3 of diesel oil, at a stirrer rotation rate of 300 rpm over a period of 2 hours.

The suspension was analyzed after cooling (Table 1). The catalysts C and D were washed with 4 portions of 650 cm^3 of hot ($T = 75^\circ\text{C}$) diesel oil until the Cl content of the
30 dispersion medium had dropped below 10 mmol/ dm^3 . The analyses of these washed solids are shown in Table 2.



- 14 -

Table 1: Analyses of the unwashed catalysts based on Mg.

Catalyst	Mg	Ti	V, Zr or Cr	Cl
Variant A	1	0.259	0.021	2.875
5 Variant B	1	0.219	0.051	2.546
Variant C	1	0.190	0.072	2.837
Variant D	1	0.106	0.150	4.067
Variant E	1	0.137	0.117	3.895
Variant F	1	0.130	0.104	3.805

10 Table 2: Analyses of the washed catalysts based on Mg.

Catalyst	Mg	Ti	V	Cl
Variant C	1	0.208	0.078	2.168
Variant D	1	0.047	0.141	2.24

15 Example 3

The catalysts described in Example 2 were used for the polymerization of ethylene under the following conditions:

20 To a 1.5 dm³ steel autoclave, which was charged with 750 dm³ of diesel oil, were added the indicated amount of the diluted catalyst suspension and the likewise indicated amount of a cocatalyst solution at 85°C under N₂ blanketing. The autoclave was then closed and flushed twice with H₂. Subsequently it was pressurized with 1.5
25 or 2 bar of H₂ and 5.5 or 5 bar of ethylene. The total pressure of 7 bar was kept constant over 2 hours by continuously metering in further ethylene to replace that consumed in the polymerization. After 2 hours the reaction was terminated by decompression and stopping the
30 ethylene feed, and the polymer was separated from the diesel oil by filtration and drying. The exact conditions and also the values of CP, melt indices, bulk density, M_w/M_n, VN are summarized in Tables 3 to 9 below.

Table 3: Catalyst type A (1 bar H_2 , 5 bar C_2H_4)

No.	Cata- lyst amount mmol Ti	Activator and amount mmol	CP(Ti+V) kg/ mmol	MFI, g/ 10 min	MFR 21.6/ 5	M_w/M_n	VN cm ³ / g	BD g/ cm ³
5								
1	0.01	TEA, 3.0	11.000	0.99	9.82	-	290	0.26
2	0.01	TEA, 3.0						
10		CHCl ₃ , 0.76	4.000	0.72	11.16	-	275	0.23
3	0.01	TiBA, 5.0	10.400	0.82	10.8	6.3	310	0.26
4	0.01	TiBA, 3.5						
		CHCl ₃ , 0.09	2.500	1.59	11.85	6.2	260	0.20

CP = catalyst productivity

15 Table 4: Catalyst type B (1 bar H_2 , 5 bar C_2H_4)

No.	Cata- lyst amount mmol Ti	Activator and amount mmol	CP(Ti+V) kg/ mmol	MFI, g/ 10 min	MFR 21.6/ 5	M_w/M_n	VN cm ³ / g	BD g/ cm ³
20								
5	0.01	TEA, 3.0						
		CHCl ₃ , 1.8	0.900	0.76	10.33	-	270	-
8	0.01	TiBA, 5.0						
25		CHCl ₃ , 0.25	5.800	1.08	12.24	6.1	250	0.27

Table 5: Catalyst type C (1 bar H_2 , 5 bar C_2H_4)

No.	Cata- lyst amount	Activator and amount	CP(Ti+V)	MFI, g/ mmol	MFR 21.6/ 10 min 5	M_w/M_n	VN cm ³ / g	BD g/ cm ³
5	mmol Ti	mmol	kg/ mmol					
unwashed catalyst								
9	0.01	TEA, 3.0						
10		CHCl ₃ , 1.6	1.600	1.27	11.80	-	240	0.21
washed catalyst								
10	0.01	TiBA, 5.0	4.800	0.53	12.40	6.0	330	0.25
11	0.01	TiBA, 5.0						
		CHCl ₃ , 1.6	2.300	0.58	12.91	-	300	0.27

15 Table 6: Catalyst type D, unwashed (1.0 bar H_2 , 5.0 bar C_2H_4)

No.	Cata- lyst amount	Activator and amount	CP(Ti+V)	MFI, g/ mmol	MFR 21.6/ 10 min 5	M_w/M_n	VN cm ³ / g	BD g/ cm ³
20	mmol Ti	mmol	kg/ mmol					
12	0.01	TiBA 5.0	11.200	3.44	11.24	6.8	215	0.28
13	0.01	TEA, 3.0	4.300	1.79	13.29	7.6	235	0.27



Table 7: Catalyst type D, washed

No.	Catalyst	Activator and amount	CP(Ti+V)	MFI ₅	MFR	M _w /M _n	VN	BD
5		mmol Ti+V	mmol	kg/ mmol	g/ 10 min	21.6/ 5	cm ³ / g	g/ cm ³
1.0 bar H ₂ , 5.0 bar C ₂ H ₄								
14	0.031	TIBA, 5.0	5.400	0.82	10.2	-	-	0.28
10 15	0.031	TIBA, 5.0	4.590	2.06	13.01	-	-	0.22
16	0.031	TEA, 3.0	3.980	1.26	13.41	8.8	250	-
17	0.031	TEA, 3.0	4.240	1.74	14.85	-	230	-
18	0.031	TIBA, 5.0						
		CHCl ₃ , 4.0	5.820	10.4	21.37	24.0	160	0.28
15 19	0.031	TIBA, 5.0						
		CHCl ₃ , 4.0	6.070	10.72	15.45	-	155	0.25
0.5 bar H ₂ , 5.5 bar C ₂ H ₄								
20	0.031	TEA, 3.0						
		CHCl ₃ , 3.0	5.210	3.13	18.2	-	210	0.26
20 21	0.031	TEA, 3.0						
		CHCl ₃ , 3.0	7.060	1.36	21.4	18.6	235	0.26
22	0.031	TIBA, 5.0						
		CHCl ₃ , 1.9	7.950	0.98	20.9	28.4	250	0.30
23	0.031	TIBA, 5.0						
25		CHCl ₃ , 4.0	6.380	2.04	22.12	-	220	0.22



Table 8: Catalyst type B

No.	Catalyst	Activator and amount	CP(Ti+Zr)	MFI ₂	MFR	M _w /M _n	VN	BD
	mmol Ti+Zr	mmol	kg/mmole	g/10 min	21.6/5		cm ³ /g	g/cm ³
1.0 bar H ₂ , 5.0 bar C ₂ H ₄								
24	0.016	TiBA, 5.0	4.730	1.08	11.9	-	270	0.28
0.5 bar H ₂ , 5.5 bar C ₂ H ₄								
25	0.016	TiBA, 5.0	5.820	0.42	9.8	-	-	0.28
1.5 bar H ₂ , 4.5 bar C ₂ H ₄								
26	0.016	TiBA, 5.0	3.420	2.52	10.3	-	-	0.24

Table 9: Catalyst type F

No.	Catalyst	Activator and amount	CP(Ti+Cr)	MFI ₂	MFR	M _w /M _n	VN	BD
	mmol Ti+Cr	mmol	kg/mmole	g/10 min	21.6/5		cm ³ /g	g/cm ³
27	0.02	DEALOX, 3.0	3.850	5.42	16.2	8.2	305	0.31
28	0.02	DEALOX, 3.0	4.900	3.01	14.0	-	260	0.28
29	0.02	DEALOX, 3.0	4.720	1.89	13.9	-	410	0.32

DEALOX = diethylaluminumoxane



WHAT IS CLAIMED IS:

1. A process for producing a polyolefin having an MFR value equal to or greater than 10 by polymerization of a 1-olefin of the formula $R^1CH=CH_2$, in which R^1 is hydrogen or an alkyl radical having from 1 to 10 carbon atoms, in suspension, in solution or in the gas phase, at a temperature of from 20 to 200°C and a pressure of from 0.5 to 50 bar, in the presence of a catalyst composed of the reaction product of a magnesium alkoxide dispersion having a particle size of from 100 to 3000 nm with a transition metal compound (component a) and an organometallic compound of a metal of group I, II or III of the Periodic Table (component b), which comprises carrying out the polymerization in the presence of a catalyst whose component a was prepared by reacting the magnesium alkoxide dispersion simultaneously with different compounds of a number of transition metals selected from the group comprising titanium, zirconium, vanadium and chromium and then reacting the mixture with a chlorine-containing organoaluminum compound.
2. The process as claimed in claim 1, wherein a magnesium alkoxide of the formula $Mg(OR^1)(OR^2)$, in which R^1 and R^2 are identical or different and are alkyl radicals having from 1 to 6 carbon atoms, was used.
3. The process as claimed in claim 1, wherein the magnesium alkoxide used was $Mg(CH_3)_2$, $Mg(OC_2H_5)_2$, $Mg(OnC_2H_5)_2$ or $Mg(OiC_2H_5)_2$.
4. The process as claimed in claim 1, wherein the chlorine-containing organoaluminum compound used for the preparation of component a was ethylaluminum sesquichloride.
5. The process as claimed in claim 1, wherein the



- 20 -

transition metal compounds used were TiCl_4 , VCl_4 , VOCl_3 , ZrCl_4 , CrCl_3 , or CrO_2Cl_2 .

6. The process as claimed in claim 5, wherein if VOCl_3 was used CHCl_3 was used in addition.
- 5 7. The process as claimed in claim 1, wherein the component b comprises an organometallic compound of a metal of group III of the Periodic Table and CHCl_3 .

This Sheet Has Been Replaced

