

PATENT SPECIFICATION

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(54) OLEFIN POLYMERIZATION CATALYSTS

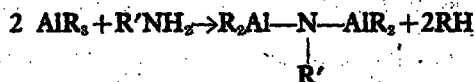
(71) We, MONTEDISON S.p.A., a Body Corporate organised and existing under the laws of Italy, of 31 Foro Buonaparte Milan, Italy, do hereby declare the invention for which we pray that a Patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The invention relates to olefin polymerization catalysts, that is to say components therefore comprising titanium, magnesium and halogen, catalysts obtained by reacting such components with an aluminio-organic compound, and processes for polymerizing olefins in which such catalysts are employed. Such catalysts have been found active and stereospecific. In the polymerization of ethylene, they have given polymers with a narrow particle-size distribution range.

A catalyst according to the invention comprises the reaction product of (A) an addition and/or substitution product of an electron donor compound (Lewis base) with an aluminium alkyl compound free of halogen with (B) a solid component comprising titanium, magnesium and halogen, in which the halogen:magnesium atomic ratio is not less than 1:1, the said solid component being a product of contacting a titanium compound with a solid halogenation product obtained from a halogenating agent and (a 1) an organic oxygen-containing magnesium compound containing a Mg—O—R linkage wherein R is an alkyl-, cycloalkyl-, aryl- or acyl-radical containing up to 20 carbon atoms, and/or (b 1) an organomagnesium compound containing a Mg—R' linkage wherein R' is an alkyl-, cycloalkyl- or aryl-radical containing up to 20 carbon atoms, the halogenation product containing an electron donor in a proportion of not more than 1 mol per g-atom of magnesium.

The term "addition and/or substitution product" for component (A) means products consisting of or comprising complexes of the electron donor compound with the aluminium

alkyl compound or with compounds resulting from the reaction of an aluminium trialkyl compound with an electron donor compound containing a mobile hydrogen atom or atoms capable of reacting with the aluminium trialkyl to bring about a substitution reaction such as:



In such reaction products, two or more aluminium atoms are bound together through oxygen or nitrogen atoms. In the said addition and/or substitution products, the amount of aluminium combined is generally from 0.01 to 1 mol per mol of that used as starting material.

Among electron donor compounds which can be used for preparing the addition and/or substitution products with aluminium alkyls are amines, amides, ethers, esters, ketones, nitriles, phosphines, stibines, arsines, phosphoramides, thioethers, aldehydes, alcoholates, amides and salts of organic acids of metals of the first four Groups of the Periodic System. The most interesting results, as regards both activity and stereospecificity, have been achieved using esters of carboxylic acids or diamines, and particularly esters of aromatic acids. Some examples of such compounds are: methyl and ethyl benzoate, methyl and ethyl *p*-methoxy-benzoate, diethyl carbonate, ethyl acetate, dimethyl maleate, triethyl borate, ethyl *o*-chloro-benzoate, ethyl naphthenate, ethyl toluate, ethyl *p*-butoxy-benzoate, ethyl cyclohexanoate, ethyl pivalate, N,N,N',N'-tetramethylene-diamine, 1,2,4-trimethyl-piperazine, and 2,5-dimethyl-piperazine.

The Lewis base:aluminium trialkyl ratio is generally lower than 1:1 and, in the case of esters or diamines, it is usually from 0.1:1 to 0.8:1, preferably from 0.2:1 to 0.4:1. Generally speaking, the activity and

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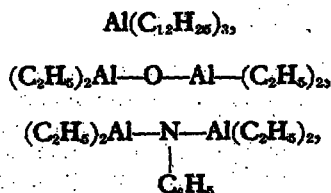
stereospecificity of the catalysts are affected, in opposite ways, by the Lewis base:aluminium alkyl molar ratio, in the sense that the higher the ratio, the lower the activity and vice-versa as regards stereospecificity.

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Suitable aluminium alkyl compounds include trialkyls having linear or branched chains containing up to 20 carbon atoms or products of their reaction with water, ammonia or a primary amine and containing therefore two or more aluminium atoms bound to one another by oxygen or nitrogen atoms. Examples of such compounds are the triethyl, trimethyl, tri-*n*-butyl, tri-*i*-butyl, tri-*n*-propyl, triisohexyl, triisooctyl, those of the formulae

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and isoprenyl aluminium. Aluminium alkyl compounds containing one alkoxy group can be used.

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Catalysts according to the invention may be prepared by reacting the Lewis base with the aluminium alkyl compound, generally for less than 1 hour, and then adding component A thus obtained to the component B. Alternatively the aluminium alkyl compound, the Lewis base and the component B can be mixed simultaneously. Another method comprises reacting the aluminium alkyl compound with the mixture of component (B) with the Lewis base.

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The Al:Ti atomic ratio in the catalyst is generally higher than 1:1 and can reach a value as high as 10,000:1, but is preferably from 10 to 200.

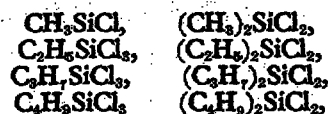
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Halogenating agents suitable for the preparation of a catalyst according to the invention are liquid or gaseous under the reaction conditions and able to react with the magnesium compound so that halogen atoms became bonded to magnesium atoms. Halogenating agents which are particularly suitable include hydrogen halides, for instance hydrogen chloride, phosphorous pentachloride, thionyl chloride, thionyl bromide, sulphuryl chloride, phosgene, nitrosyl chloride, and halides of organic and mineral acids. The halogens themselves may also be used successfully.

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Other suitable halogenating agents are silicon compounds of the formula X^1_mSiR_n , in which X is a halogen; R an alkyl, cycloalkyl, or aryl radical containing up to 20 carbon atoms; $n+m=4$, $1 \leq m \leq 4$ and $0 \leq n \leq 3$. Typical examples of these compounds are silicon tetrachloride, silicon tetrabromide and chloro-silanes of the formulae

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and trichlorovinylsilane. It is also possible to utilize products prepared by halogenating polysiloxane, for example, 1,3 - dichloro - tetramethyl - disiloxane, 1,5 - dichloro - hexamethyl - trisiloxane and 1,1 - dichloro - octamethyl - tetrasiloxane.

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There can also be used as halogenating agents compounds of the formula RX_n , wherein R is a hydrocarbon radical, X is halogen, preferably chlorine or bromine, and *n* is an integer from 1 to 10. Examples of such compounds are carbon tetrachloride, carbon tetrabromide, chloroform, ethylene dichloride, and 1,1,1 - trichloroethane. Good results are obtained also with halogen-containing aluminorganic compounds for example those of the formulae

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Examples of suitable halides of organic and inorganic acids are those of the formulae BCl_3 , SbCl_5 , benzoyl chloride and acetyl chloride. In the halogenation of a magnesium alcoholate with a halide of an organic acid, it is helpful to carry out the reaction in the presence of a halogen containing silicon compound.

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Magnesium compounds suitable for the preparation of the catalyst preferably have from 2 to 12 carbon atoms in R, and include: dialcoholates, for instance those of the formulae

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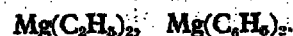
phenates and cresolates, monoalcoholates, for example $\text{Mg-alkyl}(\text{C}_1 \text{ to } \text{C}_{20})\text{-alcoholates}$, and compounds of the formula XMgOR in which X is a halogen, $(\text{SO}_4)_{1/2}$, OH^- , $(\text{CO}_3)_{1/2}$, $(\text{PO}_4)_{1/3}$ or carboxylate groups, for example acetate or benzoate, enolates, for example acetylacetonate, Grignard compounds (RMgX) for example those of the formulae

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and compounds of the formulae MgR_2 (R preferably from 4 to 12C) such as



The magnesium alcoholates can be used also in the form of complexes with different metal alcoholates, for example those of the formulae

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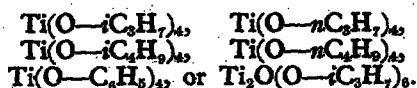
Mixtures of magnesium compounds with inert organic or inorganic substances can be employed.

Lewis bases for the preparation of component B are preferably esters or inorganic or organic oxygen-containing acids or polyamines. Typical examples of such compounds are the esters of aromatic carboxylic acids, such as benzoic acid, *p*-methoxy-benzoic acid or *p*-toluic acid, and particularly alkyl esters of such acids, alkylenediamines for example N',N'',N''',N'''' -tetramethyl-ethylene diamine. Also suitable are silicon compounds for instance, vinyl-tris(beta-methoxy-ethoxy)-silane or gamma-methacryloxypropyl-tris-methoxysilane.

The Lewis base can be formed in situ during the halogenation reaction. For example the halogenation reaction of a magnesium alcoholate with a halogen-containing silicon compound can be carried out in the presence of a halide of an organic acid, in particular of an aromatic acid such as benzoyl chloride, which forms a Lewis base by reaction with the magnesium or silicon compound.

Titanium compounds suitable for use according to the invention include the halides, and haloalcoholates. Non-halogen-containing titanium compounds can also be used. Examples are the tetra-alcoholates, the tetrachloride and tetramide.

The titanium compound may be added to or during the reaction of the magnesium compound with the halogenating agent when it is a titanium alcoholate such as one of the formulae



Preferably the titanium compound is contacted with the prehalogenated magnesium compound.

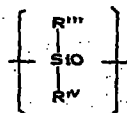
The reaction between the magnesium compound and the halogenating agent may be conducted in the presence or absence of a hydrocarbon solvent, at a temperature of from -15°C to 200°C , preferably from 50°C to 150°C . If operated in the presence of a solvent, it is preferable to use a high-boiling hydrocarbon (100 – 170°C), preferably an isoparaffin containing more than 10 carbon atoms. During the halogenation reaction, the halogen:magnesium atomic ratio is generally higher than 2:1. The Lewis base can be added to the magnesium compound before, during or after halogenation. The magnesium compound:Lewis base molar ratios are equal to or higher than 1:1 and preferably from 2:1 to 10:1.

The reaction of the halogen-containing magnesium compound with the titanium compound is generally conducted at from 20°C to 150°C . When titanium tetrachloride is

used, it is preferable to carry out the reaction by suspending the magnesium compound in the titanium tetrachloride and heating the suspension at from 20° to 136°C . The Ti:Mg atomic ratio is generally higher than 1:1 and preferably from 2:1 and 50:1.

The magnesium compound and the halogenating agent are preferably reacted in the presence of the Lewis base at from 50° to 170°C . The reaction product is then treated with a great excess of titanium tetrachloride operating at a temperature from 60° to the boiling point (136°C). After removal at room temperature of the excess titanium tetrachloride, and washing with a hydrocarbon solvent to eliminate the unreacted titanium tetrachloride, the solid catalyst component is obtained.

It is possible further to improve the activity of the catalysts according to the invention, if the preparation of component B is conducted in the presence of a silicon compound, either polymeric or not, containing the group



in which R^{III} and R^{IV} are each a hydrocarbon radical, either the same or different, preferably alkyl radicals containing from 1 to 6 carbon atoms or an aryl radical containing from 6 to 10 carbon atoms, or R^{III} is hydrogen. The silicon compound may be employed during the reaction between the magnesium compound and a halogen-containing silicon compound or after such reaction (before or after the reaction with the titanium compound). The magnesium:silicon atomic ratio is generally lower than 2:1, preferably from 0.1:1 to 1:1.

The catalysts according to the invention may be used to polymerize ethylene or an alpha-olefin containing at least three carbon atoms, such as propylene, butene-1, or 4-methylpentene-1, or to copolymerize propylene, or other higher olefins with one another and/or with generally smaller amounts of ethylene. When ethylene is to be polymerized, it is convenient to use, instead of component A, an aluminium trialkyl or an alkyl-aluminium halide not complexed with the Lewis base. The polymerization conditions comprise temperatures of from -80°C to $+150^\circ\text{C}$, preferably from 40°C to 100°C , at partial pressures of the alpha-olefins higher than atmospheric pressure. Polymerization may be conducted in a liquid phase, either in the presence or in the absence of an inert hydrocarbon diluent, or in a gas phase. Particularly good results have been achieved, in the polymerization of propylene, by operating in the presence of an aliphatic or aromatic

inert hydrocarbon diluent, liquid under the polymerization conditions, and by operating in liquid propylene as reaction medium.

The following Examples illustrate the invention. In the Examples, the melt-flow index (MIL) was determined according to ASTM D-1238/73; the flexural rigidity according to ASTM D-747/70 on specimens prepared by moulding in a plate press at 200°C and by annealing for 2 hours at 140°C; and the apparent density was determined on the polymer in powder form.

EXAMPLE 1

a) Preparation of the catalyst.

13.91 g of $Mg(OC_2H_5)_2$ were mixed with 29.8 g of gamma - methacryloxypropyl - trimethoxy - silane and 40.8 g of $SiCl_4$ at 62°C for 1.5 hours. The resulting product was treated with 240 ml of $TiCl_4$ at 136°C for 1.5 hours. The products dissolved in the $TiCl_4$ were removed in hot conditions by decantation and siphoning. The solid residue was treated again with 240 ml of fresh $TiCl_4$ at 136°C for 30 minutes. After hot-removal, by decantation and filtration, of all the $TiCl_4$, the solid residue was repeatedly washed with *n*-hexane to eliminate the excess $TiCl_4$. The residue was dried under vacuum at 55°C, and there was obtained a solid product, whose elemental weight percentage analysis was as follows: Mg=12.52%, Ti=3.6%, Cl=52.6%.

b) Polymerization of propylene in a solvent.

217 mg of the solid product of Example 1a were introduced into a 2.5 litre of *n*-heptane steel autoclave containing 1 litre of *n*-heptane and 1.135 g of $Al(C_2H_5)_3$ mixed with 572 mg of ethyl anisate. Polymerization was conducted at 60°C at a pressure of 5 kg/cm² gauge with propylene and hydrogen (1.5% by vol. of the gas phase) for 5 hours. The pressure was kept constant by continuous feeding of propylene. After removal of the solvent by stripping with steam, 314 g of dry polypropylene in particle form were obtained. The yield was 40,200 g of polymer/g of Ti, and the residue after extraction with boiling *n*-heptane 89.5%. The polymer also had the following properties:

bulk density 0.41 kg/l
intrinsic viscosity 2.3 dl/g
melt-flow index 1.3 g/10'
flexural rigidity 12,200 kg/cm².

c) Polymerization of propylene in liquid monomer.

10 kg of propylene, 12.5 g of $Al(C_2H_5)_3$, in 90 ml of *n*-heptane, 7.2 g of ethyl anisate in 120 ml of *n*-heptane, 720 mg of the solid product of Example 1a in 130 ml of *n*-heptane and 15 NI (normal litres) of hydrogen were introduced into a 30 litre stainless steel

autoclave. The polymerization temperature was brought to 65°C and the pressure to 26.5 kg/cm² gauge. After 5 hours, the propylene excess was removed, and 2.85 kg of polypropylene in particle form were obtained. The yield was 110,000 g of polymer/g of Ti, and the residue after extraction with boiling *n*-heptane 88.5%. The polymer had the following properties:

bulk apparent density 0.40 kg/l
intrinsic viscosity 1.9 dl/g
melt-flow index 3.2 g/10'
flexural rigidity 12,755 kg/cm².

The polymerization of Example 1c was repeated using 7.74 g of ethyl anisate and 730 mg of the solid product of Example 1a. The following results were obtained:

yield 72,300 g of polymer/g of Ti,
residue after extraction in boiling heptane 90.5%
bulk density 0.35 kg/l
intrinsic viscosity 1.7 dl/g
melt-flow index 5.7 g/10'
flexural rigidity 14,130 kg/cm².

d) Polymerization of ethylene in a solvent

20.3 mg of the solid product of Example 1a were introduced into a 2.5 litre stainless steel autoclave containing 1 litre of *n*-hexane and 2 g of $Al(i-C_4H_9)_3$. Polymerization was conducted at 85°C at a partial pressure of ethylene of 6 kg/cm² gauge and at a partial pressure of hydrogen of 7 kg/cm² gauge for 4 hours. After evaporation of the solvent in hot conditions and under vacuum, 284 g of polyethylene in particle form, free from powder, were obtained in a yield of 340,000 g of polymer/g of Ti. The polymer had the following properties:

bulk density 0.37 kg/l
particle average diameter 354 microns
E grade g/10' (melt flow characteristic: ASTM D 1238/70) 27.6

EXAMPLE 2

a) Preparation of the catalyst.

27.7 g of $Mg(OC_2H_5)_2$ were treated with 30.6 g of $SiCl_4$ and 3.37 g of C_6H_5COCl : the mixture was gradually heated to 155°C and kept at this temperature for 2.5 hours. The resulting semi-solid product was hot-treated, at 136°C, with 240 ml of $TiCl_4$ for 1.5 hours. The products dissolved in $TiCl_4$ were removed in hot conditions by filtering and washing with 200 ml of *n*-hexane. The residual solid product was treated again with 200 ml of boiling $TiCl_4$ for 1 hour. Subsequent operation was as in Example 1a. Ele-

mental analysis of the solid product yielded the following weight percentages: Mg=16.45%, Ti=2.70%, Cl=58.15%.

b) Polymerization of propylene in a solvent

Operation was as in Example 1b using 234 mg of the solid product of Example 2a, 1.135 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 572 mg of ethyl anisate. 245 g of dry polymer, having a residue of 92% after extraction with boiling *n*-heptane, were obtained in a yield of 38,800 g of polypropylene/g of Ti in 5 hours. The polymer also had the following properties:

bulk density	0.45 kg/l
intrinsic viscosity	2 dl/g
melt-flow index	5.1 g/10'
flexural rigidity	13,700 kg/cm ² .

c) Polymerization of propylene in liquid monomer.

Operation was as in Example 1c employing 12.5 g of $\text{Al}(\text{C}_2\text{H}_5)_3$, 7.2 g of ethyl anisate and 198 mg of the solid product of Example 2a. In this way 1.95 kg of polypropylene, having a residue after extraction with boiling *n*-heptane of 91%, were obtained in a yield of 90,500 g of polymer/g of Ti. The polymer also had the following properties:

bulk density	0.360 kg/l
intrinsic viscosity	1.7 dl/g
melt-flow index	4.9 g/10'
flexural rigidity	13,350 kg/cm ² .

EXAMPLE 3

a) Preparation of the catalyst

27.6 g of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ were mixed with 29 g of trichlorovinyl - silane ($\text{Cl}_3\text{SiCH}=\text{CH}_2$) and 7.2 g of ethyl benzoate. The mixture was gradually heated, and the temperature was kept at 158°C for 2 hours. The solid product obtained was treated with 240 ml of boiling TiCl_4 for 2 hours. Operation was then as in Example 1a. Elemental analysis of the product yield the following weight percentages:

Mg=18.13%; Ti=2.45%; Cl=64.4%.
Cl=64.4%.

b) Polymerization of propylene in a solvent

Operation was as in Example 1b, using 204 mg of the solid product of Example 3a, 1.135 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 572 mg of ethyl anisate. 275 g of dry polypropylene were obtained, having a residue after extraction with boiling *n*-heptane of 87.5%, in a yield of 55,000 g of polymer/g of Ti. The polymer also had the following properties:

bulk density	0.39 kg/l
intrinsic viscosity	1.9 dl/g
melt-flow index	3.2 g/10'
flexural rigidity	11,050 kg/cm ² .

c) Polymerization of propylene in liquid monomer.

Operation was as in Example 1c, employing 12.5 g of $\text{Al}(\text{C}_2\text{H}_5)_3$, 7.2 g of ethyl anisate and 730 mm of the solid product of Example 3a. 2.5 kg of polypropylene were obtained, having a residue after extraction with boiling *n*-heptane of 84%, an intrinsic viscosity of 1.8 dl/g, a melt-flow index of 4.7 g/10', a bulk density of 0.39 kg/l and a flexural rigidity of 10,530 kg/cm²; the yield being 140,000 g of polymer/g of Ti.

The polymerization of Example 3c was repeated employing 720 mg of solid component, 12.5 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 7.74 g of ethyl anisate. 1.6 kg of polypropylene, having a residue after extraction with boiling *n*-heptane of 85.5%, were obtained in a yield of 90,600 g of polymer/g of Ti. The polymer also had the following properties:

bulk density	0.40 kg/l
intrinsic viscosity	1.9 dl/g
melt-flow index	3.4 g/10'
flexural rigidity	11,370 kg/cm ² .

EXAMPLE 4

a) Preparation of the catalyst

240 ml of a solution in *n*-heptane containing 16.97 g of dissolved $\text{Mg}(n\text{-C}_4\text{H}_9)_2$ were added to 18.8 ml of a solution containing 22 g of SiCl_4 and 3.88 g of ethyl benzoate in 10 minutes at room temperature with stirring. The temperature was raised to 95°C and kept at 95°C for 2 hours. A further 22 g of SiCl_4 were gradually added. Heating and stirring were carried on for a further 2 hours. A white microcrystalline precipitate was separated by decantation in cold conditions. The supernatant solution was siphoned off, and the residue was washed with *n*-heptane to remove excess SiCl_4 . The solid residue was filtered and treated with 240 ml of boiling TiCl_4 for 2 hours. The solid residue was hot-filtered and treated again in hot conditions two consecutive times for 1 hour each time with the same amount of TiCl_4 . After the last hot-filtration, the solid residual product was repeatedly cold-washed with *n*-hexane to remove any trace of free TiCl_4 . The residue was then dried under vacuum at 50°C. Elemental analysis of the solid product yielded the following weight percentages: Mg=18.8%; Ti=3%; Cl=59.85%.

b) Polymerization of propylene in liquid monomer.

Operation was as Example 1c employing 970 mg of the solid product of Example 4a, 12.5 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 6.36 g of ethyl anisate. 1.12 kg of polypropylene in particle form, having a narrow particle size distribution, and a residue after extraction with boiling *n*-heptane of 79.5%, were thus obtained in a

yield of 38,400 g of polymer/g of Ti. The polymer also had the following properties:

	bulk density	0.31 kg/l
	intrinsic viscosity	1.7 dl/g
5	melt-flow index	5.4 g/10'
	flexural rigidity	10,000 kg/cm ² .

The polymerization of Example 4b was repeated using 1.1 g of solid product, 12.5 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 7.2 g of ethyl anisate. 650 g of polypropylene in particle form were thus obtained, having a narrow particle size distribution and a residue after extraction with boiling *n*-heptane of 82.5%. The yield was 19,700 g of polymer/g of Ti. The polymer also had the following properties:

	bulk density	0.30 kg/l
	intrinsic viscosity	1.5 dl/g
	melt-flow index	7.8 g/10'
	flexural rigidity	11,800 kg/cm ² .

c) Polymerization of ethylene in a solvent.
26.7 mg of the solid product of Example 4a were introduced into a 25 litre stainless steel autoclave containing 1 litre of *n*-hexane and 2 g of $\text{Al}(\text{i}-\text{C}_4\text{H}_9)_3$. Operation as in Example 1d. 255 g of particle form polyethylene free from powder were obtained in a yield of 318 kg of polymer/g of Ti. The polymer also had the following properties:

	bulk density	0.37 kg/l
30	average particle dia.	333 microns
	grade B (as above)	49.2.

EXAMPLE 5

a) Preparation of the catalyst

13.88 g of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ were mixed with 14.7 g of $\text{Cl}_3\text{SiC}_2\text{H}_5$ and 6.34 g of vinyl-tris - (beta - methoxy - ethoxy) - silane. The mixture was gradually heated to 155°C and kept at that temperature for 2 hours. After cooling, a semi-solid paste was obtained, which was treated with 240 ml of TiCl_4 at 136°C for 2 hours. The reacted TiCl_4 was decanted and siphoned off in hot conditions. The solid residue was re-treated twice with boiling TiCl_4 , each time for 1 hour and with the same amount. Operating according to Example 1a, a solid product was obtained, whose elemental analysis yielded the following weight percentages: Mg=19.6%; Ti=2.85%; Cl=68.15%.

b) Polymerization of propylene in a solvent
Operation followed Example 1b, employing 229 mg of the solid product of Example 5a, 1.135 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 572 mg of ethyl anisate. In 5 hours, there was obtained 135 g of polypropylene, having a residue after extraction with boiling heptane of 77.5%, and a yield of 20,700 g of polymer/g of Ti.

c) Polymerization of propylene in liquid monomer.

Operation followed Example 1c, employing 850 mg of the solid product of Example 5a, 12.5 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 7.2 g of ethyl anisate. 1.28 kg of polypropylene, having a residue after extraction with boiling *n*-heptane of 85%, were thus obtained in a yield of 52,800 g of polymer/g of Ti. The polymer also had the following properties:

	bulk density	0.39 kg/l
	intrinsic viscosity	1.2 dl/g
	melt-flow index	7.5 g/10'
	flexural rigidity	11,050 kg/cm ² .

EXAMPLE 6

a) Preparation of the catalyst

13.75 g of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ were mixed with 19.62 g of $\text{Cl}_3\text{SiC}_2\text{H}_5$, 3.38 g of benzoyl chloride and 3.38 g of polydimethylsiloxane (viscosity: 100 Cst). The mixture was gradually heated, with stirring, to 155°C and kept at this temperature for 2 hours. By operating according to Example 5a, a solid product was obtained, of which elemental analysis yielded the following weight percentages: Mg=21.6%; Ti=1.25%; Cl=68.95%.

b) Polymerization of propylene in a solvent

Operation was as in Example 1b, using 234 mg of the solid product of Example 6a, 1.135 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 572 mg of ethyl anisate. In 5 hours, 276 g of polypropylene in particle form, free from powder, were obtained, having a residue after extraction with boiling *n*-heptane of 86.5%, the yield being 94,500 g of polymer/g of Ti. The polymer also had the following properties:

	bulk density	0.42 kg/l
	intrinsic viscosity	1.9 dl/g
	melt-flow index	4.7 g/10'
	flexural rigidity	9,760 kg/cm ² .

c) Polymerization of propylene in liquid monomer.

Operation followed Example 1c, using 815 mg of the solid product of Example 6a, 12.5 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 7.2 g of ethyl anisate. Thus, there was obtained 2.35 kg of polypropylene in particle form free from powder, having a residue after extraction with boiling *n*-heptane of 86% in a yield of 230,000 g of polymer/g of Ti. The polymer also had the following properties:

	bulk density	0.47 kg/l
	intrinsic viscosity	1.8 dl/g
	melt-flow index	3 g/10'
	flexural rigidity	10,300 kg/cm ² .

EXAMPLE 7

a) Preparation of the catalyst

Example 6a was repeated using 1.68 g of benzoyl chloride and 13.73 g of polydimethyl

siloxane. A solid product was obtained, whose elemental analysis yielded the following weight percentages:

Mg=19.4%; Ti=1.55%; Cl=65%.

- 5 b) Polymerization of propylene in a solvent.
Operation was as in Example 1b, using 221 mg of the solid product of Example 7a, 1.135 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 572 mg of ethyl anisate. 270 g of particle-form polypropylene, free from powder, having a residue after extraction with boiling *n*-heptane of 81.5% were obtained in 5 hours in a yield of 78,800 g of polymer/g of Ti. The polymer also had the following properties:

15	bulk density	0.44 kg/l
	intrinsic viscosity	1.3 dl/g
	melt-flow index	13.2 g/10'
	flexural rigidity	13,500 kg/cm ² .

- 20 c) Polymerization of propylene in liquid monomer.
Operation followed Example 1c, employing 740 mg of solid product of Example 7a, 12.5 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 7.2 g of ethyl anisate. 1.67 kg of particle form polypropylene, free from powder, having a residue after extraction with boiling *n*-heptane of 87.5%, were obtained in a yield of 145,500 g of polymer/g of Ti. The polymer also had the following properties:

30	bulk density	0.41 kg/l
	intrinsic viscosity	1.5 dl/g
	melt-flow index	9 g/10'
	flexural rigidity	14,700 kg/cm ² .

EXAMPLE 8

- 35 a) Preparation of the catalyst
19.6 g of $\text{Cl}_3\text{SiC}_2\text{H}_5$ were mixed with 13.73 g of $\text{Mg}(\text{OC}_2\text{H}_5)_2$, gradually heated to 145°C, and kept at this temperature for 2 hours with stirring. The semi-fluid paste so obtained was repeatedly washed at 68°C with *n*-hexane by decantation. The solid, suspended in 50 ml of *n*-hexane, was added to 1.81 g of ethyl benzoate and 1.81 g of polydimethylsiloxane (viscosity=100 cst.). The mixture was heated to 70°C, kept at this temperature for 1 hour and evaporated under a moderate vacuum at 50°C. The solid residue obtained was treated with 240 ml of boiling TiCl_4 for 2 hours. After hot-filtration, the solid residue was subjected to a further treatment with boiling TiCl_4 for 1 hour. After several washings in hot conditions (68°C) with *n*-hexane, the residue was filtered under vacuum at 60°C. A solid product was obtained, of which elemental analysis yielded the following weight percentages:

Mg=17.16%; Ti=2.2%; Cl=60.65%.

- b) Polymerization of propylene in a solvent
Operation followed Example 1b, employing 187 mg of the solid product of Example 8a, 1.135 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 572 mg of ethyl anisate. 165 g of particle-form dry polypropylene was obtained, having a residue after extraction with boiling *n*-heptane of 86.5% and a yield of 40,200 g of polymer/g of Ti. The polymer also had the following properties:

	melt-flow index	0.40 kg/l
	bulk density	1.6 dl/g
	intrinsic viscosity	8.4 g/10'
	flexural rigidity	11,880 kg/cm ² .

- c) Polymerization of propylene in liquid monomer

Operation was as in Example 1c using 740 mg of the solid product of Example 8a, 12.5 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 7.2 g of ethyl anisate. 1.35 kg of particle-form polypropylene, having a residue after extraction with boiling *n*-heptane of 87%, were obtained in a yield of 82,800 g of polymer/g of Ti. The polymer also had the following properties:

	bulk density	0.41 kg/l
	intrinsic viscosity	2.4 dl/g
	melt-flow index	5.5 g/10'
	flexural rigidity	11,850 kg/cm ² .

EXAMPLE 9

Example 7b was repeated using 155 mg of the solid catalyst component prepared according to Example 7a, 1.135 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 640 mg of ethyl anisate. Polymerization was effected in *n*-heptane under a pressure of 10 kg/cm² gauge (1.5% by volume of hydrogen in the gas phase) for 6 hours. 260 g of polypropylene were obtained in particle form free from powder in a yield of 108,000 g of polymer/g of Ti, having a residue after extraction with boiling *n*-heptane of 85%, a bulk density of 0.45 kg/l, a melt-flow index of 13.7 g/10' and a flexural rigidity of 12,440 kg/cm².

EXAMPLE 10

- a) Preparation of the catalyst.
19.6 g of SnCl_4 were mixed with 13.73 g of $\text{Mg}(\text{OC}_2\text{H}_5)_2$, gradually heated to 145°C, and kept at this temperature for 2 hours with stirring. The semi-fluid paste obtained was repeatedly washed at 68°C with *n*-hexane by decantation. The solid, suspended in 50 ml of *n*-hexane, was added to 1.81 g of ethyl benzoate and 1.81 g of polydimethylsiloxane (viscosity=10 cst.). The mixture was heated to 70°C, kept at this temperature for 1 hour, and evaporated under a moderate vacuum at 50°C. The solid residue was treated with 240 ml of boiling TiCl_4 for 2 hours. After hot-filtration, a further treatment with boiling TiCl_4 was carried out for 1 hour on the solid

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residue. After several washings in hot conditions (68°C) with *n*-hexane, the residue was filtered under vacuum at 60°C.

b) Polymerization of propylene in a solvent.

- 5 Operation followed Example 1b employing 197 mg of the solid product of Example 10a, 1.135 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 572 mg of ethyl anisate. 170 g of dry polypropylene was obtained, having a residue after extraction with boiling *n*-heptane of 85%. The polymer also had the following properties:

15	bulk density	0.41 kg/l
	intrinsic viscosity	1.6 dl/g
	melt-flow index	8.4 g/10'
	flexural rigidity	11,880 kg/cm ² .

c) Polymerization of propylene in liquid monomer

- 20 Operation was as in Example 1c using 780 mg of the solid product of Example 10a, 12.5 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 7.2 g of ethyl anisate. 1.40 kg of polypropylene, having a residue after extraction with boiling *n*-heptane of 85%, were obtained. The polymer also had the following properties:

25	bulk density	0.42 kg/l
	intrinsic viscosity	1.4 dl/g
	melt-flow index	5.6 g/10'
	flexural rigidity	11,850 kg/cm ² .

EXAMPLE 11

30 a) Preparation of the catalyst.

- 119 g SOCl_2 were mixed with 11.45 g of $\text{Mg}(\text{OC}_2\text{H}_5)_2$, gradually heated to 60°C, and kept at that temperature for 2 hours with stirring. The excess SOCl_2 was removed and the solid product obtained was repeatedly washed at 68°C with *n*-hexane by decantation. The solid, suspended in 100 ml of *n*-hexane, was added to 3 g of ethyl benzoate and 1.81 g of polydimethylsiloxane (viscosity = 100 cst.). The mixture was heated to 70°C, kept at that temperature for 1 hour, and evaporated under a moderate vacuum at 50°C. The solid residue was treated with 240 ml of boiling TiCl_4 for 2 hours. After hot-filtration, a further treatment with boiling TiCl_4 was carried out for 1 hour on the solid residue. After several washings in hot conditions (68°C) with *n*-hexane, the residue was filtered under vacuum at 60°C.

50 b) Polymerization of propylene in a solvent

- Operation followed Example 1b employing 190 mg of the solid product of Example 11a, 1.135 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 572 mg of ethyl anisate. 168 g of polypropylene, having a residue after extraction with boiling *n*-heptane of 84%, was obtained. The polymer also had the following properties:

bulk density	0.39 kg/l
intrinsic viscosity	1.6 dl/g
melt-flow index	8.4 g/10'
flexural rigidity	11,880 kg/cm ² .

c) Polymerization of propylene in liquid monomer

- 65 Operation was as in Example 1c using 770 mg of the solid product of Example 11a, 12.5 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 7.2 g of ethyl anisate. 1.3 kg of particle form polypropylene, having a residue after extraction with boiling *n*-heptane of 85%, were obtained. The polymer also had the following properties:

bulk density	0.40 kg/l
intrinsic viscosity	1.4 dl/g
melt-flow index	5.6 g/10'
flexural rigidity	11,850 kg/cm ² .

EXAMPLE 12

a) Preparation of the catalyst

- 11.45 g of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ were mixed with 200 ml of *n*-hexane and 3 g of ethyl benzoate. Into the resulting mixture kept at 0°C gaseous anhydrous HCl was bubbled for 1 hour. The solid product obtained was filtered and repeatedly washed at 0°C with *n*-hexane until the HCl was completely removed, and then treated with 240 ml of boiling TiCl_4 for 2 hours. After hot-filtration, a new treatment with boiling TiCl_4 was carried out for 1 hour on the solid residue. After several washings in hot conditions (68°C) with *n*-hexane, the residue was filtered under vacuum at 60°C.

b) Polymerization of propylene in a solvent.

- 90 Operation followed Example 1b employing 185 mg of the solid product of Example 12a, 1.135 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 572 mg of ethyl anisate. 160 g of polypropylene, having a residue after extraction with boiling *n*-heptane of 86%, was obtained. The polymer also had the following properties:

bulk density	0.40 kg/l
intrinsic viscosity	1.6 dl/g
melt-flow index	8.4 g/10'
flexural rigidity	11,880 kg/cm ² .

c) Polymerization of propylene in liquid monomer.

- 105 Operation was as in Example 1c using 735 mg of the solid product of Example 12a, 12.5 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 7.2 g of ethyl anisate. 1.3 kg of polypropylene, having a residue after extraction with boiling *n*-heptane of 87%, were obtained. The polymer also had the following properties:

bulk density	0.41 kg/l
intrinsic viscosity	1.4 dl/g
melt-flow index	5.6 g/10'
flexural rigidity	11,850 kg/cm ² .

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WHAT WE CLAIM IS:—

1. A component for a catalyst for the polymerization of olefins comprising (B) a solid component comprising titanium, magnesium and halogen, in which the halogen:magnesium atomic ratio is not less than 1:1, the said solid component being a product of contacting a titanium compound with a solid halogenation product obtained from a halogenating agent and (a 1) an organic oxygen-containing magnesium compound containing a $\text{Mg}-\text{O}-\text{R}$ linkage wherein R is an alkyl-, cycloalkyl-, aryl- or acyl-radical containing up to 20 carbon atoms, and or (b 1) an organo magnesium compound containing a $\text{Mg}-\text{R}'$ linkage wherein R' is an alkyl-, cycloalkyl- or aryl-radical containing up to 20 carbon atoms, the halogenation product containing an electron donor in a proportion of not more than 1 mol per g-atom of magnesium.

2. A catalyst component according to claim 1 in which the magnesium compound is a dialcoholate having the formula $\text{Mg}(\text{OR})_2$.

3. A catalyst component according to claim 1 in which the magnesium compound is a monoalcoholate $\text{R}'\text{MgOR}$ in which R' is a C_1 to C_{20} alkyl group or a halogen.

4. A catalyst component according to claim 1 in which the magnesium compound is a Grignard compound RMgX in which X is bromine or chlorine.

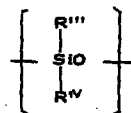
5. A catalyst component according to claim 1 in which the magnesium compound is of the formula MgR_2 .

6. A catalyst component according to any preceding claim in which the halogenating agent is a silicon compound of the formula $\text{X}_n\text{SiR}_m''$, in which X is a halogen; R'' is an alkyl, cycloalkyl or aryl radical containing up to 20 carbon atoms; $n+m=4$, $1 \leq m \leq 4$ and $0 < n < 3$, or a halogenation product of a polysiloxane.

7. A catalyst component according to any preceding claim in which the titanium compound is an alcoholate, haloalcoholate or halide.

8. A catalyst component according to claim 7 in which the titanium compound is the tetrachloride.

9. A catalyst component according to any preceding claim prepared in the presence of a silicon compound, either polymeric or not, containing a group



in which R^{III} and R^{IV} are each hydrocarbon radical, either the same or different or R^{III} is hydrogen.

10. A catalyst comprising a reaction product of a component according to any preceding claim with (A) an addition and/or substitution product (as herein defined) of an electron donor compound (Lewis base) with an aluminium alkyl compound free of halogen.

11. A catalyst according to claim 10 in which the Lewis base is an ester of an inorganic or organic oxygen-containing acid or is a compound containing at least two amine groups.

12. A catalyst according to claim 10 in which the Lewis base is vinyl - tris - (beta - methoxyethoxy)silane or gamma - methacryloxy - propyl - tris - (methoxy)silane.

13. A catalyst for the polymerization of ethylene comprising a reaction product of a component according to any of claims 1 to 9 with an aluminium alkyl compound.

14. A catalyst for the polymerization of olefins as herein described in any of the Examples.

15. A process comprising polymerizing an olefin in the presence of a catalyst according to any of claims 10 to 14.

16. An olefin polymer prepared by a process according to claim 15.

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