

[54] Title: COMPONENTS AND CATALYSTS FOR THE POLYMERIZATION OF OLEFINS

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## [56] Reference (s) Cited and/or Considered:

U.S. Pat. Nos.	4,246,383	Gessell	Jan. 1981
	4,298,718	Mayer, et al.	Nov. 1981
	4,400,303	Martin	Aug. 1983
[57]	4,522,930	Albisatti, et al.	June 1985
	4,762,398	Matsura, et al.	Aug. 1988

ABSTRACT

Solid catalyst components for the polymerization of olefins modified with electron-donor compounds, comprising a titanium halide supported on a magnesium dihalide in active form and containing as an electron-donor compound a di- or polyether having specific reactivity characteristics towards  $MCl_2$  and  $TiCl_4$ .

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OF OLEFINS

ABSTRACT

Solid catalyst components for the polymerization of olefins modified with electron-donor compounds, comprising a titanium halide supported on a magnesium dihalide in active form and containing as an electron-donor compound a di- or polyether having specific reactivity characteristics towards  $MgCl_2$  and  $TiCl_4$ .

The present invention relates to solid components of catalysts for the polymerization of olefins and the catalysts obtained therefrom. The catalysts including titanium compounds supported on magnesium halides in active form are well known in the art.

Catalysts of this type are described for the first time in the USA patent No. 4,298,718. Said catalysts are formed on titanium tetrahalides supported on halides of magnesium in active form.

Although the catalysts have high activity in the polymerization of ethylene as well as alpha olefins like propylene and butene-1, they are not very stereospecific.

Improvements to stereospecificity have been made by adding electron-donor compounds to the solid catalyst component (U.S. patent No. 4,544,717 ).

Substantial improvements were made using, in addition to the electron-donor present in the solid component, an electron-donor added to the Al-alkyl co-catalyst component (U.S. patent No. 4,107,414).

The catalysts modified in this manner although they are highly stereospecific (isotactic index about 94-95) still do not show sufficiently high levels of activity.

Significant improvements in activity and stereospecificity were obtained by preparing the solid catalytic component according to the technique described in U.S.

patent No. 4,226,741.

High level performance in catalyst activity as well as stereospecificity have been obtained with the catalysts described in European Patent No. 045977. Said catalysts have as a solid catalyst component, a magnesium halide in active form on which is supported a titanium halide preferably  $TiCl_4$  and an electron-donor compound selected from specific classes of carboxylic acid esters, of which the phthalates are typically examples, and, as a co-catalyst component, a system formed of an Al-trialkyl compound and a silicon compound containing at least one Si-OR bond (R hydrocarbyl radical). After the appearance of the above mentioned patents which mark the fundamental step for the development of the coordination catalysts supported on magnesium halides, many patents have been filed with the purpose of modifying and/or improving the performance of the above mentioned catalysts.

In the prolific patent and scientific literature available, however, there is no description of catalysts endowed with both high activity and stereospecificity in which the electron-donor of the solid catalyst component is the only donor present in the catalyst system. The catalysts known up to now that have both high activity and stereospecificity always include the use of an electron-donor in the solid catalyst component and in the co-



catalyst component.

Surprisingly, it has now been found that it is possible to prepare highly active and stereospecific catalysts where the only donor used is present in the solid catalyst component.

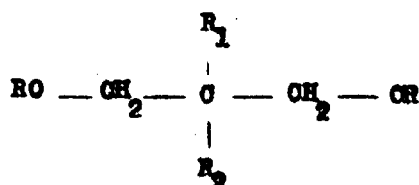
The donors used in the catalysts of this invention are ethers with one or more ether groups, which satisfy particular requisites of reactivity towards magnesium dichloride and titanium tetrachloride.

The ethers of the invention form complexes with magnesium dichloride but in a quantity of less than 60 mmoles per 100 g of  $MgCl_2$ ; with  $TiCl_4$  the ethers do not undergo at all substitution reactions or they react this way for less than 50% in moles.

Preferably the ethers form complexes with magnesium chloride in quantities comprised between 20 and 50 mmoles, and react with  $TiCl_4$  for less than 30%.

The procedures for the tests of magnesium chloride complexing and reaction with  $TiCl_4$  are reported below.

Examples of suitable ethers which satisfy the reactivity criterion set forth above are 1,3-diethers of formula:



where  $R$ ,  $R_1$  and  $R_2$  independently are linear or branched alkyl, cycloaliphatic, aryl, alkylaryl or arylalkyl radicals with 1-18 carbon atoms, and  $R_1$  or  $R_2$  may also be hydrogen.

- 5 In particular  $R$  is an alkyl radical with 1-6 carbon atoms, and more specifically it is methyl. In this case, when  $R_1$  is methyl, ethyl, propyl or isopropyl,  $R_2$  may be ethyl, propyl, isopropyl, butyl, isobutyl,  $t$ -butyl, 2-ethylhexyl, cyclohexyl methyl, phenyl, or benzyl; when  $R_1$  is hydrogen  $R_2$  can be ethyl, butyl,  $sec$ -butyl,  $t$ -butyl, 2-ethylhexyl, cyclohexylethyl, diphenylmethyl,  $p$ -chlorophenyl,  $n$ -naphthyl, 1-decahydronaphthyl;  $R_1$  and  $R_2$  can be the same and be ethyl, propyl, isopropyl, butyl, isobutyl,  $t$ -butyl, neopentyl, isopentyl, phenyl, benzyl or cyclohexyl.
- 10
- 15

- Examples of representative ethers that are included in the above formula are: 2-(2-ethylhexyl)-1,3-dimethoxypropane, 2-isopropyl-1,3-dimethoxypropane, 2-butyl-1,3-dimethoxypropane, 2- $sec$ -butyl-1,3-dimethoxypropane, 2-cyclohexyl-1,3-dimethoxypropane, 2-phenyl-1,3-dimethoxypropane, 2-cumyl-1,3-dimethoxypropane, 2-(2-phenylethyl)-1,3-dimethoxypropane, 2-(2-cyclohexylethyl)-1,3-dimethoxypropane, 2-( $p$ -chlorophenyl)-1,3-dimethoxypropane, 2-(diphenylmethyl)-1,3-dimethoxypropane, 2-(1-naphthyl)-1,3-dimethoxypropane, 2,2-fluorophenyl-1,3-dimethoxypro-
- 20
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pane, 2-(1-decahydronaphthyl)-1,3-dimethoxypropane, 2-(p-t-butylphenyl)-1,3-dimethoxypropane, 2,2-dicyclohexyl-1,3-dimethoxypropane, 2,2-diethyl-1,3-dimethoxypropane, 2,2-diisopropyl-1,3-dimethoxypropane, 2,2-dibutyl-1,3-dimethoxypropane, 2-methyl-2-propyl-1,3-dimethoxypropane, 2-methyl-2-benzyl-1,3-dimethoxypropane, 2-methyl-2-ethyl-1,3-dimethoxypropane, 2-methyl-2-propyl-1,3-dimethoxypropane, 2-methyl-2-benzyl-1,3-dimethoxypropane, 2-methyl-2-phenyl-1,3-dimethoxypropane, 2-methyl-2-cyclohexyl-1,3-dimethoxypropane, 2,2-bis(p-chlorophenyl)-1,3-dimethoxypropane, 2,2-bis(2-cyclohexylethyl)-1,3-dimethoxypropane, 2-methyl-2-isobutyl-1,3-dimethoxypropane, 2-methyl-2-(2-ethylhexyl)-1,3-dimethoxypropane, 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2,2-diphenyl-1,3-dimethoxypropane, 2,2-dibenzyl-1,3-dimethoxypropane, 2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-diethoxypropane, 2,2-diisobutyl-1,3-dibutoxypropane, 2-isobutyl-2-isopropyl-1,3-dimethoxypropane, 2,2-di-sec-butyl-1,3-dimethoxypropane, 2,2-di-tert-butyl-1,3-dimethoxypropane, 2,2-di-neopentyl-1,3-dimethoxypropane, 2-isopropyl-2-isopentyl-1,3-dimethoxypropane, 2-phenyl-2-benzyl-1,3-dimethoxypropane, 2-cyclohexyl-2-cyclohexylmethyl-1,3-dimethoxypropane."

Other suitable ethers are: 2,3-diphenyl-1,3-diethoxybutane, 2,3-dicyclohexyl-1,4-diethoxybutane, 2,2-di-

- benzyl-1,4-dieethoxybutane, 2,3-dibenzyl-1,4-dimethoxy-  
butane, 2,3-dicyclohexyl-1,4-dimethoxybutane, 2,3-diiso-  
propyl-1,4-dieethoxybutane, 2,2-bis(p-methylphenyl)-1,4-  
dimethoxybutane, 2,3-bis(p-chlorophenyl)-1,4-dimethoxy-  
butane, 2,3-bis(p-fluorophenyl)-1,4-dimethoxybutane, 2,4-  
diphenyl-1,5-dimethoxypentane, 2,3-diphenyl-1,6-dimethoxy-  
pentane, 2,4-diisopropyl-1,5-dimethoxypentane, 2,5-diphenyl-  
1,6-dimethoxypentane, 3-methoxymethyltetrahydrofuran, 3-  
methoxymethyldioxane, 1,1-dimethoxymethyl-decahydronaph-  
thalene, 1,1-dimethoxymethyl-indan, 2,2-dimethoxymethyl-  
indane, 1,1-dimethoxymethyl-2-isopropyl-3-methylcyclo-  
hexane, 1,3-diisobutoxypropene, 1,2-diisobutoxypropene,  
1,2-diisobutoxyethane, 1,3-diisobutoxypropene, 1,2-diiso-  
amuloxyethane, 1,3-dinopentoxypropene, 2,2-tetramethylene-  
1,3-dimethoxypropene, 1,2-dinopentoxylethane, 2,2-tetra-  
methylene-1,3-dimethoxypropene, 2,2-pentamethylene-1,3-  
dimethoxypropene, 2,2-pentamethylene-1,3-dimethoxypropene,  
2,2-hexamethylene-1,3-dimethoxypropene, 1,2-bis(methoxy-  
methyl)cyclohexane, 2,8-dioxaspiro[5,5]undecane, 3,7-di-  
oxabicyclo[3,3,1]nonane, 3,7-dioxabicyclo[5,3,0]octane,  
3,3-diisobutyl-1,3-dioxanonane, 6,6-diisobutylidioxyphe-  
tane, 1,1-dimethoxymethylcyclopropane, 1,1-bis[4-dimethoxy-  
methyl]cyclohexane, 1,1-bis[4-methoxymethyl]bicyclo[2,2,1]-  
heptane, 1,1-dimethoxymethyl cyclopentane, 2-methyl-2-  
methoxymethyl-1,3-dimethoxypropene.



The ethers preferred are the 1,3-diethers belonging to the general formula indicated above and in particular those where R is methyl and  $R_1$  and  $R_2$ , independently, are isopropyl, isobutyl, t-butyl, cyclohexyl, isopentyl, cyclohexylethyl. Ethers particularly preferred are 2,2-diisobutyl-1,3-dimethoxypropane; 2-isopropyl-2-isopentyl-1,3-dimethoxypropane; 2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane.

The ether complexing test with  $MgCl_2$  is conducted as follows.

In a 100 ml flask with fixed blades mechanical agitator are introduced in a nitrogen atmosphere, in order:

- 70 ml anhydrous n-heptane
- 12 mmoles anhydrous  $MgCl_2$  activated as described below
- 2 mmoles ether.

The ingredients are heated at  $60^\circ C$  for 4 hours (stirring speed 400 rpm), then filtered and washed at room temperature with 100 ml n-heptane and dried with mechanical pump.

The quantity of ether complexed is determined, after treatment of the solid with 100 ml of ethane, by quantitative gaschromatic analysis.

The data relative to the complexing test are shown in Table 1.

The test for reactivity with  $TiCl_4$  is conducted

as follows.

In a 25 ml test tube with a magnetic agitator are introduced, in a nitrogen atmosphere, in order:

- 10 ml anhydrous n-heptane
- 5    - 5 mmoles  $TiCl_4$
- 1 mmole ether donor

The ingredients are heated at  $70^\circ$  for 30 min. then cooled at  $25^\circ C$  and decomposed with 90 ml of ethanol.

10    The solution obtained is analysed gas chromatographically using a standard HIMONT method available upon request, with a Carlo Erba ERGO 5300 Mega Series gas chromatograph with a 25 meters Chrompack CP-SIL 5 CB capillary column. The data relative to the reactivity tests are shown in Table 1.

15    The magnesium dichloride used in the complexing test with the ethers is prepared as follows.

In a 1 l container of a vibrating mill (Siebtechnik's Vibratron) containing 1.8 kg of steel spheres 16 mm in diameter, are introduced under a nitrogen atmosphere, 50 g  
20    anhydrous  $MgCl_2$  and 6.8 ml 1,2 dichloroethane (DCE). The mixture is milled at room temperature for 96 hours, after which the solid obtained is dried at  $50^\circ C$  for 16 hours under vacuum of a mechanical pump.

Solid characterization.

25    In the X-ray powder spectrum:



- half peak breadth of 0110 reflection = 1.15 cm;
- presence of a halo with maximum intensity at angle  $2\theta = 32.1^\circ$ ;
- Surface area (B.E.T.) =  $125 \text{ m}^2/\text{g}$ ;
- 5 - Residual DCE = 2.5% by weight.

Table 1

	Ether	Complexing	Reaction
		with $\text{MgCl}_2$ (*)	with $\text{TiCl}_4$ (**)
10	2,2-dimethyl-1,3-dimethoxypropane	3,5	80
	2-methyl-2-isopropyl-1,3-dimethoxypropane	1,6	71
	2,2-diisobutyl-1,3-dimethoxypropane	3,3	98
15	2,2-diisobutyl-1,3-diethoxypropane	2,0	100
	2,2-diisobutyl-1,3-din-butoxypropane	0,5	97
	2,2-diphenyl-1,3-dimethoxypropane	0,7	75
20			

Table 1 (follow)

	2,2-bis(cyclohexylmethyl)-		
	1,3-dimethoxypropane	1,8	85
	1,3-diisobutoxypropane	2,6	99
5	2,2-pentamethylene-1,3-		
	dimethoxypropane	2,4	100
	1,1-bis(methoxymethyl)-		
	bicyclo-(2,2,2-heptane)	1,9	93
	1,3-dimethoxypropane	9,6	100
	<del>66666</del>		
10	1-isopropyl-2,2-dimethyl-		
	1,3-dimethoxypropane	1,3	0
	2-isopentyl-2-isopropyl		
	1,3-dimethoxypropane	2,5	98
	1,2-dimethoxyethane	9,4	76
15	(*) Moles of ether X 100 complexed by 100 g of MgO12		
	(**) Percentage in moles of ether recovered after reaction		
	with TiCl4		

The preparation of the solid catalyst component including the others of the invention is carried out according to various methods.

For example, the magnesium dihalide (used in anhydrous state containing less than 1% of water), the titanium compound and the di or polyether are ground together under conditions where activation of the magnesium dihalide occurs. The milled product is then treated one or more times with  $TiCl_4$  in excess at temperatures between 80 and 135°C and then washed repeatedly with a hydrocarbon i.e. hexane until all chlorine ions disappear.

According to another method, the anhydrous magnesium dihalide is preactivated according to known methods in the prior art and then reacted with an excess of  $TiCl_4$  which contains the ether compound in solution, at temperatures between 80 and 135°C. The treatment with  $TiCl_4$  is repeated and the solid is then washed with hexane to eliminate all traces of unreacted  $TiCl_4$ .

According to another method, an  $MgCl_2 \cdot nROH$  adduct (particularly in form of spheroidal particles) in which  $n$  is a number from 1 to 3, and ROH is ethanol, butanol, or isobutanol, is treated with an excess of  $TiCl_4$  containing the ether compound in solution at a temperature generally between 80 and 120°C. After the reaction, the so-

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lid is treated once more with  $TiCl_4$ , then separated and washed with a hydrocarbon until the chlorine ions are removed.

5 According to another method, alcoholates or chloroalcoholates of magnesium, the chloroalcoholates prepared according to U.S. patent No. 4,220,554 are treated with  $TiCl_4$  in excess containing the ether compound in solution, under reaction conditions described above.

10 According to another method complexes of magnesium halide with titanium alcoholates for example the complex  $MgCl_2 \cdot 2Ti(OC_4H_9)_4$  are treated, in a hydrocarbon solution, with  $TiCl_4$  in excess containing the ether compound in solution. The solid product is separated and further treated with an excess of  $TiCl_4$  and then separated and  
15 washed with hexane. The reaction with  $TiCl_4$  is conducted at temperatures between 80 and 120°C.

According to a variant of the above method, the complex between  $MgCl_2$  and the titanium alcoholate is reacted in hydrocarbon solution with hydroperoxyhexane. The  
20 separated solid product is reacted at 50°C with silicon tetrachloride containing the ether compound in solution and the solid is treated with  $TiCl_4$  in excess operating at 80-100°C. It is possible to react with  $TiCl_4$  in excess, containing the ether compound in solution, porous  
25 styrene-divinylbenzene resins in spherical particle form,



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impregnated with solutions of compounds or complexes of Mg soluble in organic solvents.

The resins and their method of impregnation are described in European Patent No. 344793.

5 The reaction with  $TiCl_4$  is carried out at 80-100°C. and after separating the  $TiCl_4$  excess, the reaction is repeated and the solid is then washed with a hydrocarbon.

The molar ratio  $MgCl_2$ /ether compound used in the reactions indicated above is generally between 4:1 and 12:1.

10 The ether compound is fixed on the magnesium halide containing component in quantities generally between 5 and 20% mole.

However, in the case of components supported on resins, the molar ratio between fixed ether compound and the magnesium present is generally between 0.5 and 0.8.

15 In the catalytic components of the invention the ratio Mg/Ti is generally between 30:1 and 4:1; in the components supported on resins the ratio is lower, generally from 2:1 to 3:1.

20 The titanium compounds that can be used for the preparation of catalytic components are the halides and halogen alcoholates. Titanium tetrachloride is the preferred compound. Satisfactory results are obtained also with trihalides, particularly  $TiCl_3$ ,  $HR$ ,  $TiCl_2$ ,  $ARA$ , and with haloalcoholates, such as  $TiCl_2OR$ , where R is a phenyl

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radical.

The above mentioned reactions result in the formation of magnesium dihalide in active form.

5 In addition to these reactions, other reactions that result in the formation of magnesium dihalide in active form starting with magnesium compounds different from halides are well known in literature.

10 The active magnesium dihalides present in the Me-  
lid catalyst components of the invention show in the X-ray powder spectrum of the catalyst component the replacement of the most intense diffraction present in the powder spectrum of the non-activated magnesium  
15 halides having a surface area of less than  $3 \text{ m}^2/\text{g}$  by a halo with the maximum intensity peak shifted with respect to the position of the most intense diffraction line, or a half peak breadth of the most intense diffraction line at least 30% greater than the half peak breadth of the corresponding line of the non-activated  
20 magnesium halide. The most active forms are those where in the X-ray powder spectrum of the catalyst component a halo appears.

25 Among the magnesium dihalides, the magnesium dichloride is the preferred compound. In the case of the most active forms of magnesium dichloride in the halo appears in place of the diffraction line that is present in the spectrum of the non-active magnesium chloride at



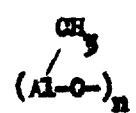
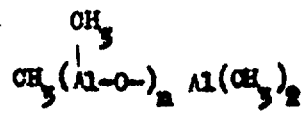
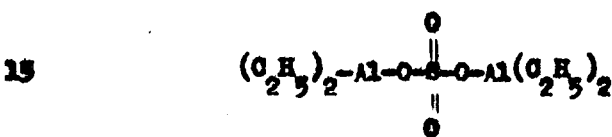
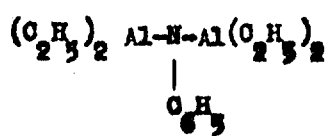
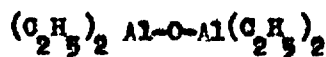
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an interplanar distance of 2.56Å.

The solid catalyst component of the invention  
 forms, by reaction with Al-alkyl compounds, catalysts for  
 the polymerization of olefins  $\text{CH}_2=\text{CHR}$ , where R is hydro-  
 5 gen, alkyl radical with 1-6C, or aryl radical, or mixtures  
 of said olefins mixed with each other with or without di-  
 olefins.

The Al-alkyl compounds include Al-trialkyl such as  
 Al-triethyl, Al-triisobutyl, Al-tri-n-butyl. Linear or  
 10 cyclic Al-alkyl compounds containing two or more Al atoms  
 linked to each other by O, N or S atoms may be used.

Examples of these compounds are:



where n is a number between 1 and 20.

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Also one can use  $AlR_2OR'$  compounds, where  $R'$  is an aryl radical substituted in position 2 and/or 6 and  $R$  is an alkyl radical with 1-6 carbon atoms, or  $AlR_2H$  compounds.

5 The Al-alkyl compound is used in Al/Ti ratios generally between 1 and 100.

The trialkyl compounds may be used in mixtures with Al-alkyl halides, such as  $AlEt_2Cl$ .

10 The polymerisation of olefins is carried out according to known methods in a liquid phase of the monomer(s) or a solution of monomer(s) in an aliphatic or aromatic hydrocarbon solvent, or in gas phase, or with techniques using a combination of liquid phase and gas phase.

15 The (co)polymerisation temperature is generally between  $0^\circ$  and  $150^\circ C$ , preferably between  $60^\circ$  and  $100^\circ C$ , while operating at atmospheric pressure or at a higher pressure.

20 The catalysts may be precontacted with small quantities of olefins (prepolymerisation). The prepolymerisation improves the catalyst performance as well as the polymer morphology.

25 The prepolymerisation is carried out by maintaining the catalyst in suspension in a hydrocarbon solvent (hexane, heptane, etc.) while contacting small amounts of the monomer with the catalyst and polymerising at a

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temperature between room temperature and 60°C. producing quantities of polymer included between 0.5 and 3 times the weight of the catalyst component. It may also be carried out in liquid or gaseous monomer, under the temperature conditions above, to produce quantities of polymer up to 1000 g per g of the catalyst component.

In case of stereoregular polymerisation of olefins, in particular of propylene, some times it is convenient to use together with the Al-alkyl compound an electron-donor selected from 2,2,6,6-tetramethylpiperidine and silicon compounds containing at least one Si-OR bond wherein R is a hydrocarbyl radical.

Preferably the silicon compounds have the formula



where  $R^I$  and  $R^{II}$  independently, are branched alkyl, cycloaliphatic or aryl radicals with 1-12 carbon atoms;  $R^{III}$  and  $R^{IV}$  independently are alkyl radicals with 1-6 carbon atoms.

Examples of such compounds are:

(t-butyl)<sub>2</sub> Si(OC<sub>3</sub>)<sub>2</sub>; (cyclohexyl)<sub>2</sub> Si(OCH<sub>3</sub>)<sub>2</sub>;  
(isopropyl)<sub>2</sub> Si(OCH<sub>3</sub>)<sub>2</sub>; (sec-butyl)<sub>2</sub> Si(OCH<sub>3</sub>)<sub>2</sub>.

The molar ratio between Al-alkyl compound and electron-donor is usually between 5:1 and 100:1.

As indicated above, the catalysts find particular

application in the polymerisation of  $\text{CH}_2=\text{CHR}$  olefins where R is an alkyl radical with 1-6 carbon atoms or an aryl radical.

5 They are also particularly suited for the polymerisation of ethylene and its mixtures with smaller proportions of alpha-olefins, such as butene-1, hexene-1 and octene-1 to form LLDPE, because the catalysts produce polymers with narrow molecular weight distribution.

10 In the copolymerisation of ethylene with propylene, or other alpha-olefins or mixtures thereof to form elastomeric products copolymers are obtained having low crystallinity suitable therefore for the production of elastomers with highly valued qualities.

The following examples illustrate the invention.

15 In the examples, unless otherwise indicated, the percentages are by weight.

The solubility in xylene is determined by thermo solubilising the polymer ( $130^\circ\text{C}$ ), cooling and then filtering it.

20 The solubility is determined by the fraction soluble at  $25^\circ\text{C}$ . The insoluble residue substantially corresponds to the isotacticity index determined by extraction with boiling n-heptane (4 hours). Melt index E and F for polyethylene and J for polypropylene are determined according to ASTM D1238. Melt index E and F are measured at  $190^\circ\text{C}$  with respective weights of 2.15 and 21.6 Kg. The one for polypre-

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propylene is measured at 230°C with a weight of 2.16 Kg.  
The intrinsic viscosity are determined in tetralin at  
135°C. Unless otherwise indicated, the isotacticity in-  
dex (I.I.) has been determined by extraction with boiling  
n-heptane (4 hours).

#### Polymerization Procedure

##### A. In liquid monomer

###### Procedure A.1.

In a 4 l stainless steel autoclave equipped with an  
anchor agitator and previously purged with nitrogen  
flux at 70°C for 1 hour, were introduced, under pro-  
pylene flow at 30°C, 80 ml anhydrous n-hexane con-  
taining an adequate quantity of solid catalyst com-  
ponent and 6.9 moles of  $Al(Et)_3$ . The autoclave  
was closed and 120 ml of hydrogen was introduced.  
The agitator was inserted and 1.2 Kg of liquid pro-  
pylene, or other alpha-olefin monomer capable of be-  
ing polymerized in liquid phase, was charged. The  
temperature was brought to 70°C in 5 minutes and the  
polymerization was carried out for 2 hours. At the  
end of the test the unreacted propylene is removed,  
the polymer recovered and dried in an oven at 70°C  
under nitrogen flow for 3 hours, and then charac-  
terized.



Procedure A.1.1.

The procedure of A.1 above were followed except that added to the hexane was an appropriate quantity of an electron-donor together with  $\text{Al}(\text{Et})_3$  corresponding to a molar ratio  $\text{Al}/\text{donor} \approx 20$ . The composition of the solid catalyst components and the ethers used, the polymerisation yields and the properties of the polymers obtained are described in tables 2 and 3.

In Table 3 the donor used together with  $\text{Al}(\text{Et})_3$  is indicated in parenthesis.

In solvent.Procedure B.2.

A 2.5 l stainless steel autoclave, equipped with a thermostat and magnetic agitator, which was previously purged with nitrogen flux at  $70^\circ \text{C}$  for 1 hour and washed 4 times successively with propylene, was heated to  $45^\circ \text{C}$  and, under a light nitrogen flow, 870 ml of anhydrous hexane was charged. The catalyst suspension (catalyst component and Al-alkyl premixed immediately before the test in 130 ml solvent) was then added. The autoclave was closed and 120 ml of hydrogen was fed from a calibrated cylinder. The agitator was inserted and the temperature was rapidly brought to  $75^\circ \text{C}$  (about 5 minutes). Gaseous propylene or other alpha-olefin monomer was then introduced up to a total pressure of 8 atm.

This condition was maintained for 4 hours continuously feeding propylene or other monomers to reintegrate the monomer polymerized. At the end of the polymerization the autoclave was rapidly degassed and cooled to 25-30°C. The polymer suspension was then filtered, the solid part was dried in an oven at 70°C in nitrogen for 4 hours and then weighed and analyzed. The filtrate was evaporated and the dry residue consisting of amorphous polymer was recovered and weighed. This was taken into consideration in calculating the total yield and the total isotactic index.

Procedure B.2.1

In a 2000 ml stainless steel autoclave, equipped with an anchor agitator, was introduced under a propylene flow at 25°C 1000 ml n-heptane, 2.5 mmoles of  $\text{Al}(\text{C}_2\text{H}_5)_3$  and an adequate quantity of the solid catalyst component. The autoclave was closed and the pressure brought to 1 atm. while feeding propylene, and an overpressure of hydrogen equal to 0.2 atm was introduced. The reaction mixture was heated to 70°C and the pressure brought to a total of 7 atm, by feeding propylene, and polymerized for 2 hours while continuing to feed the monomer to maintain the pressure at 7 atm. The polymer obtained was isolated by filtration and dried; the polymer remaining in the filtrate was precipitated in methanol, vacuum

dried and considered in determining the total insoluble residue of the extraction with n-heptane. The composition of the solid catalyst components and ethers used and the polymerization yields and the properties of the polymers obtained are described in tables 2 and 3.

#### Procedure B.2.2.

The polymerization methods described in procedure B.2.1. were followed except using 5 moles of  $\text{Al}(\text{C}_2\text{H}_5)_3$  together with an adequate quantity of electron donor such that the molar ratio  $\text{Al/donor} = 20/$ . The composition of the solid catalyst components, ether and electron donor (with the Al-alkyl compound) used and the polymerization yields and the properties of the polymers obtained are described in tables 2 and 3. In table 3 the donor used together with  $\text{Al}(\text{C}_2\text{H}_5)_3$  is indicated in parenthesis.

#### Example 1

In a 1 l flask equipped with condenser, mechanical agitator and thermometer was introduced 625 ml  $\text{TiCl}_4$  under nitrogen environment. 25 g of spherical  $\text{MgCl}_2 \cdot 2.1\text{C}_2\text{H}_5\text{OH}$  support, obtained according to the procedures and ingredients of example of U.S. patent 4 469 648, was fed at  $0^\circ\text{C}$ . with agitation and heated to  $100^\circ\text{C}$  over 1 hour. When the temperature reached  $40^\circ\text{C}$ , 4.1 ml of 2,2-diisobutyl-1,3-dimethoxypropane was introduced, and the contents maintained at  $100^\circ\text{C}$  for 2 hours, left to settle and the supernatant



siphoned off. 550 ml of  $\text{TiCl}_4$  was added to the solid and heated at  $120^\circ\text{C}$  for 1 hour with agitation. The agitation was stopped, the solid was allowed to settle and the supernatant was removed by siphon. The residual solid was then washed 6 times with 200 ml portions of anhydrous hexane at  $60^\circ\text{C}$  and 3 times at room temperature and dried under vacuum.

The catalyst solid component contained 3.4% Ti and 12.6% 2,2-diisobutyl-1,3-dimethoxypropane. Propylene was polymerized according to procedure A.1 above for the liquid monomer using 0.76 g of  $\text{Al}(\text{C}_2\text{H}_5)_3$ , 0.09 ml of hexane suspension containing 7.25 mg of solid catalyst component and 1000 ml hydrogen. 460 g of polymer was obtained. The polymer yield was 63.4 Kg/g of catalyst component. The polymer has a 95.3% insoluble residue in xylene at  $25^\circ\text{C}$ , a melt index of 10.0 g/10' and a tapped bulk density of 0.48 g/ml.

#### Example 2

In a 500 ml glass flask equipped with condenser, mechanical agitator and thermometer, was introduced, in an anhydrous nitrogen environment at  $20^\circ\text{C}$ , 285 ml of  $\text{TiCl}_4$  and 20 g of  $\text{C}_2\text{H}_5\text{OMgCl}$  support prepared according to the procedure of U.S. Patent No. 4,220,554. While agitating the contents were heated to  $70^\circ\text{C}$  in 30 minutes and then 4.7 ml 2,2-diisobutyl-1,3-dimethoxypropane was added and

heated to 120°C in 30 minutes. The temperature was maintained at 120°C. for 1 hour. The reaction mixture was allowed to settle and supernatant removed by siphon. Then another 285 ml  $\text{TiCl}_4$  were added and heated at 120°C for 1 hour. The reaction mixture was allowed to settle and the supernatant removed by siphon. The residual solids were washed 5 times with 150 ml portions of anhydrous heptane at 80°C, and again at room temperature with 150 ml portions of anhydrous hexane until  $\text{TiCl}_4$  there were no chlorine ions in the wash liquid.

The analysis of the vacuum dried solid catalyst component showed a content of 2.2% Ti and 12.2% 2,2-diisobutyl-1,3-dimethoxypropane.

Propylene was polymerized according to the Procedure A.1 above using 0.76 g  $\text{Al}(\text{C}_2\text{H}_5)_3$ , 0.12 ml hexane suspension containing 13 mg of solid catalyst component and 1000 ml hydrogen.

240 g of polymer was obtained with a polymer yield of 18.4 Kg/g catalyst component, a 95.2% insoluble residue in xylene, at 25°C, a melt index of 10.6 g/10' and a tamped bulk density of 0.50 g/ml.

### Example 3

In a 350 ml porcelain jar containing 4 porcelain spheres, was introduced, under an anhydrous nitrogen environment,

9.2 g of commercial anhydrous  $MgCl_2$  and 3.3 ml of 2,2-diisobutyl-1,3-dimethoxypropane. The jar is placed in a centrifugal mill operated at 350 rpm for 15 hours.

5 In a 250 ml glass flask fitted with a condenser, mechanical agitator and thermometer, under an anhydrous nitrogen environment at room temperature, were introduced 8 g of the above milled product and 115 ml of  $TiCl_4$ .

The contents were heated to  $120^\circ C$  in 20 minutes and maintained at  $120^\circ C$  for 2 hours.

10 The solids were allowed to settle and supernatant was siphoned off. Another 115 ml of  $TiCl_4$  was introduced, heated at  $120^\circ C$  for 2 hour. The solids were allowed to settle and the supernatant removed by siphons. The solid

15 residue was washed repeatedly at  $60^\circ C$  and at  $40^\circ C$  with 100 ml portions of anhydrous hexane, until there were no chlorine ions in the wash liquid. The solid residue, obtained by vacuum drying, contained 2.1% Ti and 10.2% 2,2-diisobutyl-1,3-dimethoxypropane. The polymerisation was

carried out according to procedure B.2, using 0.57 g  
20  $Al(C_2H_5)_3$  and 0.25 ml hexane suspension containing 15.0 mg of solid catalyst component. 284 g of polymer was obtained with a polymer yield of 18.9 Kg/g catalyst, a 96.1% residue insoluble in xylene at  $25^\circ C$ , a melt index of 4.2 g/10' and a tamped bulk density of 0.35 g/ml.

**Example 4**

In a 350 ml porcelain jar containing 4 porcelain spheres was introduced, under an anhydrous nitrogen environment, 7.63 of anhydrous  $MgCl_2$ , 2.76 ml 2,2-diisobutyl-1,3-dimethoxypropane, and 1.17 ml  $TiCl_4$ . The jar was placed in a centrifugal mill operated at 350 rpm for 20 hours. In a 350 ml glass reactor, equipped with porous disk for filtration, condenser, mechanical agitator and thermometer, was introduced at room temperature under an anhydrous nitrogen environment, 8 g of the above milled product and 32 ml 1,2-dichloroethane. The contents were heated at 85° C for 2 hours, then filtered and the solid residue washed 3 times with 50 ml portions of anhydrous hexane. The solid residue obtained by vacuum drying contained 1.5% Ti and 18.4% 2,2-diisobutyl-1,3-dimethoxypropane. Propylene was polymerized according to procedure B.2 using 0.57 g  $Al(C_2H_5)_3$  and 0.3 ml hexane suspension containing 61 mg solid catalyst component. 188 g of polymer was obtained with polymer yield of 2.3 Kg/g catalyst component, a 94.7% residue insoluble in xylene, at 25° C a melt index of 8.4 g/10', and tapped bulk density of 0.29 g/ml.

**Example 5**

In a 500 ml glass flask equipped with a condenser, mechanical agitator and thermometer, was introduced, at room

temperature under anhydrous nitrogen atmosphere, 750 ml of  $\text{TiCl}_4$  and 25 g of support in spherical particles comprising a styrene-divinylbenzene copolymer impregnated with the  $\text{MgO} \cdot 2\text{Ti}(\text{OC}_4\text{H}_9)_4$  complex, prepared according to procedure of example 1 of European Patent No. 344755.

While agitating, the contents were heated to  $100^\circ\text{C}$ . When the temperature reaches  $40^\circ\text{C}$ ., 1.52 ml of 2,2-diisobutyl-1,3-dimethoxypropane was introduced. The temperature maintained at  $100^\circ\text{C}$  for 1 hour, the solid allowed to settle and the supernatant was removed by siphon. An additional 250 ml  $\text{TiCl}_4$  was fed and heated at  $120^\circ\text{C}$  for 2 hours. After settlement of the solids and siphoning of the supernatant, the solid residue was washed 3 times with 150 ml portions of anhydrous heptane at  $85^\circ\text{C}$ , then 3 times with anhydrous hexane at room temperature, until no chlorine ions were formed in the wash liquid.

After vacuum drying, the solid catalytic component contained 0.77% Ti and 3.9% 2,2-diisobutyl-1,3-dimethoxypropane. Propylene was polymerized according to procedure A.1 using 0.79 g  $\text{Al}(\text{C}_2\text{H}_5)_3$ , 1.4 ml hexane suspension containing 49.5 mg solid catalyst component and 1300 ml hydrogen. 400 g of polymer was obtained with a polymer yield of 8.1 kg/g catalyst component, a 95.1% insoluble residue in xylene, at  $25^\circ\text{C}$ , a melt index of 11.2 g/10' and a tamped bulk density of 0.42 g/ml.

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Example 6

In a 500 ml glass flask equipped with condenser, mechanical agitator and thermometer was introduced 156.9 ml  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  and 20 g anhydrous  $\text{MgCl}_2$ . While agitating, the contents were heated to  $140^\circ\text{C}$  for 3 hours, cooled to  $40^\circ\text{C}$  and the resulting solution diluted with 157 ml anhydrous heptane. Then 31.5 ml polymethylhydrosiloxane was added ( $d=0.99$  g/ml,  $M_w=2236$ ). After allowing the solvents to settle and siphoning off the supernatant, the solid was washed 3 times with 150 ml portions of anhydrous heptane.

At  $50^\circ\text{C}$ , 18.4 ml of  $\text{SiCl}_4$  was added over a 15 minutes period, then treated with 2.7 ml 2,2-diisobutyl-1,3-dimethoxypropane and maintained at  $90^\circ\text{C}$  for 2 hours. The solids were allowed to settle and the supernatant removed by siphon and washed 4 times with 120 ml portions of anhydrous hexane. The residue was treated with 52.3 ml of  $\text{TiCl}_4$  and then heated at  $90^\circ\text{C}$  for 2 hours. The liquid was removed by siphon after the solids were allowed to settle, the solid residue was washed repeatedly with anhydrous heptane at  $60^\circ\text{C}$  and then 3 times at room temperature, until there were no chlorine ions in the wash liquid. After vacuum drying, the solid catalyst component contained 1.6% Ti and 14.9% 2,2-diisobutyl-1,3-dimethoxypropane.

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Propylene was polymerized according to procedure B.2 using 0.57 g  $\text{Al}(\text{C}_2\text{H}_5)_3$  and 0.4 ml hexane suspension containing 7.9 mg solid catalyst component. 229 g of polymer was obtained with a polymer yield of 29 kg per g of catalyst component 96.2% insoluble residue in xylene at 25°C and a tamped bulk density 10 AD of 0.42 g/cc.

#### Example 7

Into a 1 l glass flask equipped with condenser, mechanical agitator and thermometer, under anhydrous nitrogen atmosphere, was introduced 572 ml solution containing 11.4 g  $\text{Al}(\text{C}_2\text{H}_5)_3$  for each 100 ml hexane. While agitating at 5°C, 40 g spherical  $\text{MgCl}_2 \cdot 2.6\text{C}_2\text{H}_5\text{OH}$  support, prepared according to method of example 1 in U.S. patent No. 4,469,648 was added over 90 minutes, then heated to 60°C for 3.5 hours, the solids were allowed to settle and the supernatant removed by siphon. The solid residue was washed 10 times with 200 ml portions of anhydrous heptane.

To the product obtained, which was diluted to 100 ml with anhydrous heptane, was added over 2 hours at 80°C, 2.7 ml  $n\text{-C}_4\text{H}_9\text{OH}$  diluted with 1.5 ml anhydrous heptane. The solid were allowed to settle and the liquid siphoned off. The solid was washed repeatedly with 150 ml portions anhydrous hexane. After vacuum drying the solid showed a Mg content of 20.9% and  $\text{C}_2\text{H}_5\text{OH}$  of 3.6%.

In a 500 ml glass flask was introduced, under an anhy-

drous nitrogen environment, 342 ml  $\text{TiCl}_4$ , then while  
 agitating at  $0^\circ\text{C}$ , 14.5 g of the solid catalyst component  
 obtained above were added. Over a 1 hour period the con-  
 tents were heated to  $100^\circ\text{C}$ . When the temperature reached  
 5  $40^\circ\text{C}$ , 4.8 ml 2,2-diisobutyl-1,3-dimethoxypropane was  
 added. The contents were heated at  $100^\circ\text{C}$  for 2 hours.  
 The solids allowed to settle and the liquid was siphoned  
 off.

To the solid residue 319 ml of  $\text{TiCl}_4$  was added, heated to  
 10  $120^\circ\text{C}$  for 1 hour, and then the liquid was removed by  
 siphoning after settling. The solid was washed repeated-  
 ly with 150 ml portions anhydrous hexane first at  $60^\circ\text{C}$ .  
 and then at room temperature. After vacuum drying the  
 catalytic solid contains 2.45% Ti and 6.7% 2,2-diisobutyl-  
 15 1,3-dimethoxypropane.

Propylene was polymerized according to procedure A.1 using  
 0.76 g  $\text{Al}(\text{C}_2\text{H}_5)_3$ , 0.09 ml hexane solution containing 8.9  
 mg solid catalyst component and 1000 ml hydrogen. 430 g  
 of polymer was obtained with a polymer yield of 51.8 Kg/g  
 20 catalyst component, 90.4% insoluble residue in xylene at  
 $25^\circ\text{C}$ , a melt index of 8.9 g/10' and a tamped bulk density  
 of 0.49 g/ml.

#### Examples 8-12 and comparative examples 1-5

Into a 500 ml reactor equipped with filtering disk 223 ml  
 25  $\text{TiCl}_4$  was introduced at  $0^\circ\text{C}$ . While agitating 10.1 g (54





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mmoles) microspheroidal  $MgCl_2 \cdot 20 \frac{H}{2} OH$ , obtained according to the method of example 1 of U.S. patent 4,469,648, was added. Upon completing the addition, the temperature was brought to  $40^\circ C$  and 9 mmoles ether was introduced. The temperature was raised to  $100^\circ C$  over one hour period and allowed to react for 2 hours after which the unreacted  $TiCl_4$  was removed by filtration. Another 200 ml  $TiCl_4$  was added and allowed to react at  $120^\circ C$  for 1 hour, filtered and washed with n-heptane at  $60^\circ C$  until the chlorine ions disappeared from the filtrate.

The ethers used and the analytical data relative to the solid catalyst component obtained in this manner are reported in table 2.

Examples 19-36 and comparative examples 4-6

The polymerisation data with the catalysts obtained from the solid catalyst components prepared according to examples 6-18 and comparative examples 1-3 are reported in Table 3.



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Table 2

Ex. No.	Ether used	Composition of the solid catalyst component % by weight		
		Mg	Ti	Ether
8	2,2-dimethyl-1,3-dimethoxypropane		2.6	10.40
9	2-isopropyl-2-methyl-1,3-dimethoxypropane	21.7	3.24	10.44
10	2,2-diisobutyl-1,3-dimethoxypropane	16.64	3.1	15.5
11	2,2-diisobutyl-1,3-diethoxypropane		4.3	8.10
12	2,2-diisobutyl-1,3-di-n-butoxypropane	16.3	5.2	2.40
13	2,2-diphenyl-1,3-dimethoxypropane	14.3	5.59	11.10
14	2,2-bis(cyclohexylmethyl) 1,3-dimethoxypropane	14.87	4.43	11.4
15	1,3-diisobutoxypropane		4.7	0.005
16	2,2-pentamethylene 1,3-dimethoxypropane		2.9	15.1
17	1,1-bis(methoxymethyl) bicyclo-(2,2,1)-heptane		3.3	11.7

Table 2 (follow)

5	18	1,2-isopentyl-2-isopropyl- 1,3-dimethoxypropane		2.5	14.8
	Comp. 1	1,3-dimethoxypropane	18.0	1.7	10.6
	Comp. 2	1-isopropyl-2,2-dimethyl 1,3-dimethoxypropane	17.0	4.3	0
	Comp. 3	1,1-dimethoxyethane	20.8	3.0	4.0

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**Table 3**

Ex. No.	Ether Ex. No.	Polymer Yield g polymer/g Cat. comp.	I.I. %	dl/g	Polymerisation Method
19	8	3100	89.8	2.15	B.2.1.
20	9	8700	93.3	2.90	B.2.1.
21	10	9300	95.3		B.2.1.
22	11	14200	79.7		B.2.1.
23	12	13600	84.3	2.10	B.2.1.
24	13	9100	84.8	2.48	B.2.1.
25	14	19000	88.4	1.65	B.2.1.
26	15	20100	75.0		B.2.1.
27	16	7100	89.3		B.2.1.
28	17	8500	79.8		B.2.1.
29	18	11000	98.0		B.2.1.
Comp. 4	Comp. 1	1800	64.9		B.2.1.
Comp. 5	Comp. 2	2000	72.0	1.0	B.2.1.
Comp. 6	Comp. 3	4300	68.1	1.77	B.2.1.
30	10	8900	96.1	2.39	B.2.2.
(dimethyl dimethoxy- silane)					
31	10	7900	96.3	2.00	B.2.2.
(2,2-diisobutyl-1,3- dimethoxypropane)					
32	10	5100	97.5	2.15	B.2.2.
(phenyltriethoxysilane)					

Table 3 (follow)

5	33	10	33400	92.0	1.56	A.1.
	(2,2-diisobutyl-1,3-dimethoxypropene)					
	34	10	23200	96.0	1.71	A.1.1
	35	10	36600	93.8	1.83	A.1.1.
	(2,2,6,6-tetramethylpiperidine)					
	36	10	9600	96.6	1.94	A.1.1.
	(ethyl p. toluate)					

10

Example 37

A 1.4 stainless steel autoclave, equipped with a thermostat and mechanical agitator, was purged with gaseous propylene at room temperature for 1 hour. Then, while agitating, 66 g of butadiene, 230 g of liquid propylene and 300 ml of hydrogen were fed. Under propylene pressure a catalytic suspension of 0.6 Al(Et)<sub>3</sub>, TEAL and 0.048 g solid catalyst component of example 1. The temperature was rapidly brought to 70°C (in 3 min.) and the resulting pressure was 24.6 atm. These conditions were maintained for 4 hours reintegrating feeding propylene continuously to reintegrate the portion polymerized. The autoclave was then degassed and cooled at room temperature. 64 g. polymer, dried in an oven under nitrogen at 60°C for 4

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hours, was recovered, with a yield of 1333 g polymer per g catalyst. When analyzed, using standard methods, the polymer showed the following characteristics:

$[\eta]$  in tetrahydronaphthalene at 135°C = 1.8 dl/g.

9 MIL = 4 g/10'

Soluble in xylene at 25°C = 24.1% (weight).

Butadiene content (determined via IR):

- raw polymer = 0.6% 1,2; 3.7% 1,4 trans

- insoluble in xylene = 0.5% 1,2; 1.6% 1,4 trans

10 - soluble in xylene = < 0.25% 1,2; 8.2 1,4 trans.

#### Example 38

The autoclave and procedure of example 37 was used to polymerize propylene with the solid catalyst component of example 1, but using instead of Al-triethyl, a mixture of 3.3 mmoles Al-triethyl and 3.3 mmoles Al-diethylmonochloride and 0.018 g solid catalyst component.

15 380 g of a polymer with a polymer yield of 35.2 kg/g of catalyst component, a 94.1% insoluble residue in xylene at 25°C, and a melt index of 7.3 g/10'.

#### 20 Example 39

In the same autoclave used in example 1 was charged at 30°C. and without agitation, a catalyst suspension of 0.9 g Al-triethyl and 0.09 g of the solid catalyst component of example 37 in about 18 ml hexane. Then 800 g

- propane was introduced with agitation. The temperature was rapidly brought to 75° C, and then 2 atm hydrogen, 200 g butene-1 were introduced. Ethylene was then introduced until the pressure reached 33 atm. These conditions were maintained for 2 hours maintaining constant pressure by continuously feeding with a mixture of ethylene and butene-1 in a weight ratio of 10/1. The autoclave was degassed and cooled at room temperature. The amount of polymer, obtained after drying at 70° C under nitrogen for 4 hours, was 280 g, which corresponded to a yield of 31.1 kg per g of catalyst component. Analysed using standard methods, the product showed the following characteristics:
- MIB = 0.23 g/10' (P/E = 26.7)
  - MIF = 6.16 g/10'
  - Butene (determined via IR) = 6% (weight)
  - Density = 0.9211 g/cm<sup>3</sup>
  - Soluble in xylene at 25° C = 6.5% (weight)

#### Example 40

- In the same autoclave used in example 3 purged as described therein but using ethylene instead of propylene, was introduced at 45° C under hydrogen flow, a 900 ml solution of 0.5 g/l of Al-triisobutyl in anhydrous hexane and immediately after 0.015 g of solid catalyst component of example 1 suspended in 100 ml of the above mentioned solution. The contents were rapidly heated to a temperature of 75° C, then

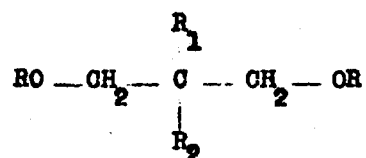


- hydrogen was fed until the pressure reached 4.5 atm. These conditions were maintained for 3 hours continuously replacing the ethylene polymerized. The autoclave was rapidly degassed and cooled at room temperature. The polymeric suspension was filtered and the solid was dried at 60°C under nitrogen for 8 hours. 300 g of polymer was obtained (corresponding to a yield of 20 kg/g of catalyst component) which had the following characteristics (determined by standard methods):
- MIE = 1.74 g/10<sup>3</sup> (MIF/MIE = 26.5)
  - MIF = 46 g/10<sup>3</sup>
  - $[\eta]$  135°C THN = 1.78 dl/g
  - tamped bulk density = 0.362 g/ml
- Other features, advantages and embodiments of the invention disclosed herein will be readily apparent to those exercising ordinary skill after reading the foregoing disclosures. In this regard, while specific embodiments of the invention have been described in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as described and claimed.



## CLAIMS:

1. A solid catalyst component for the polymerisation of olefins comprising a magnesium dihalide in active form and supported thereon a titanium compound containing at least one Ti-halogen bond and an electron-donor compound selected from ethers containing two or more ether groups and further characterized by the formation of complexes with anhydrous magnesium dichloride at less than 60 mmoles per 100 g of magnesium dichloride and the failure to enter into substitution reactions with  $TiCl_4$  or of reacting that way at less than 50% by moles.
2. The solid catalyst component of Claim 1 where the ethers are complexed in quantities between 20 and 90 mmoles per 100 g. of magnesium dichloride.
3. The solid catalyst component of Claim 1 wherein the ethers are selected from diethers with the following general formula:



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where  $R$ ,  $R_1$  and  $R_2$ , independently, are linear or branched alkyl, cycloaliphatic, aryl, alkylaryl or

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aryalkyl radicals with 1-18 carbon atoms and  $R_1$  or  $R_2$  may also be hydrogen.

- 3 4. The solid catalyst component of Claim 3 wherein R is methyl, and when  $R_1$  is methyl, ethyl, propyl or isopropyl,  $R_2$  is ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, 2-ethylhexyl, cyclohexyl, methylcyclohexyl, phenyl or benzyl, and when  $R_1$  and  $R_2$  are the same, they are ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, neopentyl, isopentyl, phenyl, benzyl or cyclohexyl.
- 10 5. The solid catalyst component of Claim 3 wherein R is methyl and  $R_1$  and  $R_2$  are different and are isopropyl, isobutyl, t-butyl, cyclohexyl, isopentyl or cyclohexylethyl.
- 15 6. The solid catalyst component of Claim 3 where the ethers are 2,2-diisobutyl-1,3-dimethoxypropane, 2-isopropyl-2-isopentyl-1,3-dimethoxypropane or 2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane.
- 20 7. The solid catalyst component of Claim 1 wherein the titanium compound is selected from the group consisting of the halo alcoholates and the halides of titanium and the magnesium dihalide is magnesium dichloride.
8. The solid catalytic component of Claim 7 wherein

the titanium compound is titanium tetrachloride.

- 5
9. The solid catalytic component of Claim 7 wherein the magnesium dichloride is present in active form characterized in that in the X-ray powder spectrum of the catalyst component a halo appears instead of the most intense diffraction line which appears at an interplanar distance of 2.56 Å in the non-activated magnesium dichloride and the maximum intensity of the halo is shifted with respect to said interplanar distance.
- 10
10. The solid catalyst component of Claim 1 wherein the ether is present in an amount from 5 and 20% moles with respect to the magnesium dihalide.
11. The solid catalyst component of Claim 1 wherein the Mg/Ti ratio is between 30:1 and 4:1.
- 15
12. The solid catalyst component of Claim 1 wherein the magnesium dichloride in active form is obtained from  $MgCl_2$  complexes with alcohols or titanium alcoholates, or from alcoholates and chloroalcoholates of magnesium.
- 20
13. The solid catalyst component of Claim 1 wherein the magnesium dichloride and the titanium compound are supported on resins and the Mg/Ti ratio is from 2:1 to 3:1.

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14. A catalyst for the polymerisation of olefins  $\text{CH}_2=\text{CHR}$ , wherein R is H, an alkyl radical with 1-6 carbon atoms or an aryl, or mixtures thereof with or without a diolefin, comprising the product obtained by reaction of a solid catalyst component of Claim 3 with an Al-trialkyl compound.
15. The catalyst of Claim 14 for the polymerisation of olefins  $\text{CH}_2=\text{CHR}$  wherein R is an alkyl radical with 1-6 carbon atoms, further comprising, in addition to the Al-trialkyl compound 2,2,6,6-tetramethylpiperidine or a silicon electron donor compound containing at least one Si-OR bond wherein R is a hydrocarbon radical.

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