

PATENT SPECIFICATION

(11) 1 559 194

1 559 194

- (21) Application No. 40025/76 (22) Filed 27 Sept. 1976
(31) Convention Application No. 29525
(32) Filed 21 Nov. 1975 in
(33) Italy (IT)
(44) Complete Specification published 16 Jan. 1980
(51) INT CL³ C08F 10/00, 4/64
(52) Index at acceptance

C3P 440 452 474 486 526 534 536 540 542 546 578 582 584
594 596 598 602 GA



(54) CATALYSTS FOR POLYMERIZING ALPHA-OLEFINS

- (71) We, MONTEDISON S.p.A., an Italian body corporate and MITSUI PETROCHEMICAL INDUSTRIES LTD., a Japanese body corporate of Foro Buonaparte, 31, Milan, Italy and Kasumigaseki Bldg., 2—5 Kasumigaseki, 3-chome, Chiyoda-ku, Tokyo, Japan respectively, 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:—
- This invention relates to a catalyst component useful in catalysts for homopolymers and co-polymerizing alpha-olefins having at least three carbon atoms and for polymerizing ethylene alone or in mixtures with said alpha-olefins, and to the catalysts containing the said component, their use and the products resulting therefrom.
- By virtue of their high activity and stereospecificity in the polymerization of the alpha-olefins, the catalysts of this invention are particularly suited to the preparation of crystalline polymers of the alpha-olefins containing at least 3 carbon atoms and of crystalline copolymers of the said alpha-olefins with ethylene. Thus the present invention is especially concerned with catalysts capable of stereospecifically polymerizing propylene and mixtures of same with ethylene, and to a process for preparing polypropylene having a high isotacticity index as well as crystalline copolymers of propylene with ethylene.
- Examples of catalysts exhibiting a high activity and stereospecificity in the polymerization of alpha-olefins and of propylene in particular are described in British Patent No. 1,387,890 and in German Patent Application DOS 2,504,036. The catalysts described in British Patent No. 1,387,890 are generally prepared by reacting an Al-trialkyl compound, partially complexed with an electron-donor compound, with the product obtained by finely grinding a Mg dihalide in mixture with an electron-donor compound and with a halogenated Ti compound. The activity of these catalysts, expressed in g of polymer/g of Ti, is sufficiently high when carried out in a liquid phase, in the absence of inert hydrocarbon diluents, but it decreases to unsatisfactory values and necessitates purification of the polymer from the catalyst residues when the polymerization is conducted in the presence of inert hydrocarbon solvents. Furthermore, the isotacticity index of the polymers obtained with these catalysts is remarkably reduced when the polymerization occurs in the presence of hydrogen as modifier of the polymer molecular weight.
- The catalysts according to DOS 2,504,036 are prepared by reacting an Al-alkyl compound with the product obtained by reacting a liquid Ti compound with a composition prepared by finely grinding a mixture of a Mg dihalide with an organic ester and with an organic Si compound. These catalysts exhibit a high stereospecificity when polymerization is conducted in the absence of hydrogen; conversely it decreases very markedly when hydrogen is used as molecular weight modifier. If one tries to improve the stereospecificity of the catalysts by adding an electron-donor compound to the Al-alkyl compound employed as co-catalyst, an improvement of the polymers' isotacticity index is attained, but the catalytic activity is considerably reduced.
- Japan Published Patent 50-126590 describes polymerization catalysts obtained from an Al-alkyl compound (Al-triethyl) and from a catalyst component prepared by grinding mixtures of MgCl₂ with an organic ester and by successively reacting the ground product with TiCl₄. The catalysts described in this patent application are provided with high activity and stereospecificity in the polymerization of

propylene carried out in the absence of hydrogen as molecular weight modifier, but again, if the polymerization is carried out in the presence of hydrogen, the isotacticity index (stereospecificity) is strongly reduced.

5 It has now surprisingly been found that it is possible to synthesize catalysts useful to polymerize alpha-olefins containing at least 3 carbon atoms and mixtures of same with ethylene, characterized by a high stereospecificity also when the polymerization is conducted in the presence of hydrogen, and capable of providing high yields of polymer even when polymerization is effected in the presence of an inert hydrocarbon diluent. 5

10 The present invention accordingly provides a solid catalyst component useful in the polymerization of alpha-olefins, comprising, at least on the surface, the reaction product of a halogenated Mg compound with a tetravalent Ti compound and with an electron-donor compound, the ratio g. moles electron-donor/g. atoms Ti in said product being higher than 0.2 and the ratio g.atoms halogen/g.atoms Ti being higher than 4, wherein at least 80% by weight of the Ti compounds contained therein is insoluble in boiling n-heptane and at least 50% by weight of the Ti compounds insoluble in boiling n-heptane is insoluble also in TiCl₄ at 80°C, and the surface area of the catalyst component as a whole is higher than 40 m²/g. 10 15

20 The catalyst component of the present invention can be used to form catalysts which comprise the products obtained by contacting the following starting components: 20

a) a metallorganic Al compound not containing halogen atoms directly bound to the Al atom;

25 b) an electron-donor compound employed in such an amount that 15% to 100% by weight of said metallorganic Al compound is combined with the electron-donor compound; 25

c) a solid catalyst component according to the present invention as defined above.

30 The catalysts of this invention are preferably prepared by contacting component c) with the product obtained by premixing, for a time-period generally shorter than 1 hour, component a) with component b). 30

35 High-performance catalysts may be also obtained by contemporaneously mixing the components or by contacting component c) at first with component a) and then with component b), and vice-versa. The amount of electron-donor compound employed as component b) is preferably such that the molar ratio between the electron-donor groups of the electron-donor compound, which are reacted with the metallorganic Al compound and the total of said Al compound is comprised between 0.2 and 0.4. This means that from 20 to 40 mol% of the metallorganic Al compound is combined with the electron-donor compound. 35

40 Any electron-donor compound (or Lewis base) capable of providing complexes with the metallorganic Al compound used as component a) or of bringing about a substitution reaction with such compound (such as, for example, in the following equation: 40

$2 \text{AlR}_3 + \text{RNH}_2 \rightarrow \text{R}_2\text{Al}-\underset{\text{R}}{\text{N}}-\text{AlR}_2 + 2\text{RH}$) may be utilized as component b).

45 Some examples of electron-donor compounds employable as component b) are amines, amides, ethers, ketones, nitriles, phosphines, stibines, arsines, phosphoramides, thioethers, thioesters, aldehydes, alcoholates, amides and salts of organic acids and of metals belonging to Groups I to IV of the Mendeleer Periodic Table. In the case of Al salts they can be formed *in situ* by reaction of an organic acid with the metallorganic Al compound used as component a). 45 50

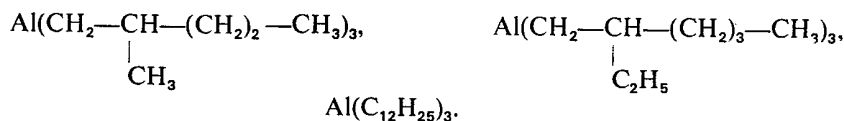
Suitable organic acids are the aromatic ones, for example benzoic acid, p-hydroxybenzoic acid.

55 Some examples of specific compounds are triethylamine, N,N'-dimethylpiperazine, diethylether, di-n.butylether, tetrahydrofuran, acetone, acetophenone, benzonitrile, tetramethylurea, nitrobenzene, Libutylate, dimethylaminophenyl-lithium, Na-dimethylamide. 55

60 The most interesting results as regards both activity and stereo-specificity of the catalysts have been achieved with the esters of the organic and inorganic oxygen containing acids and with ethers like di-n.butylether. Particularly suited esters are, for example, the alkyl esters of aromatic acids, such as benzoic, p-methoxy- or -ethoxybenzoic and p-toluic acids, such as, for instance, ethyl benzoate, ethyl p-methoxy-benzoate, methyl p-toluate, ethyl p-butoxybenzoate. 60

Further examples of useful esters are diethyl carbonate, triethylborate, ethyl pivalate, ethyl naphthoate, ethyl o-chlorobenzoate, ethyl acetate, dimethyl maleate, alkyl or aryl silicates, methylmethacrylate.

5 The metallorganic Al compounds employable as component a) preferably consist of Al-trialkyl compounds, such as, for example, Al-triethyl, Al-tripropyl, Al-triisobutyl, 5



10 It is possible to employ also metallorganic Al compounds containing two or more Al atoms through O or N atoms. They are generally obtained by reacting an Al-trialkyl compound with water, ammonia or with a primary amine according to known methods. 10

Examples of such compounds are:



15 The metallorganic Al compounds described in British Patent Specification No. 1,513,480 constitute further examples of utilizable compounds. Other employable compounds are, for example, the hydrides of aluminium dialkyl, the alkoxides of aluminium-dialkyl, such as: $\text{Al}(\text{C}_2\text{H}_5)_2(\text{OC}_2\text{H}_5)$, $\text{Al}(\text{C}_4\text{H}_9)_2(\text{OC}_4\text{H}_9)$ and the sesquialkoxides of Al-alkyl, such as sesquithoxy-aluminium-ethyl and sesquibutoxy-aluminium-butyl. 15 20

The electron-donor compound present in combined form in component c) may be the same compound employed in component b) or a different compound. In this case too, any electron-donor compound capable of forming complexes with the Mg halides may be used to prepare component c). Esters and ethers and diamines are preferably employed. Examples of esters are those already indicated as employable as component b) of the catalyst. A particularly efficacious diamine is N,N,N',N'-tetramethylethylenediamine. 25

Component c) of the present invention preferably comprises, at least on the surface, reaction products of halogenated Mg compounds selected from Mg dichloride and dibromide, and halogenated compounds of tetravalent Ti, in particular TiCl_4 , TiBr_4 , Ti halogen-alcoholates, with an electron-donor compound selected from amongst the organic esters, in particular from amongst the esters of the aromatic acids such as, for example, benzoic acid. Nature and composition of this component is further defined by the following parameters. 30

The Mg/Ti gram atomic ratio is preferably within the range from 3 to 40, more preferably between 10 and 30; the halogen gram atoms/Ti gram atoms ratio is preferably within the range from 10 to 90, more preferably between 20 and 80 and the ratio g. moles of electron-donor compound/g.atoms of Ti is higher than 0.2, e.g. within the range from 1 to 6, preferably 0.4 to 3, and more preferably from 1.2 to 3. 35

At least 80% and preferably 90% by weight of the Ti compounds contained in component c) is insoluble in boiling n-heptane, while at least 50% by weight, more particularly more than 70% by weight, of the Ti compounds insoluble in boiling heptane is also insoluble in Ti tetrachloride at 80°C. 40

The surface area of the component c) as well as the area of the product insoluble in Ti tetrachloride at 80°C is preferably larger than 100 m²/g, more preferably within the range from 100 to 200 m²/g. 45

Components c) particularly suited for preparing very active catalysts having a high stereospecificity are furthermore characterized by a shift in the most intense line appearing in the X-ray spectrum, compared with that of the Mg chloride and bromide of the normal type, as defined by standards ASTM 3—0854 and 15—836 for chloride and bromide respectively. 50

In the present components, the X-ray spectrum thereof shows a halo whose maximum intensity is shifted with respect to the distance *d* of the maximum intensity line which appears in the X-ray spectrum of the corresponding pure Mg-dihalide. 55

As regards MgCl_2 , the halo intensity peak is comprised between $d = 2.44$ and 2.97 Å.

Generally, the composition of component c) may be expressed as consisting for 70—80% by weight of Mg dichloride or dibromide, the difference to 100 consisting of the Ti compound and of the electron-donor compound.

5 Component c), however, may include, besides the above-cited components, also inert solid fillers in amounts that can reach 80% and above with respect to the weight of component c). Examples of such materials are: LiCl, CaCO₃, CaCl₂, Na₂SO₄, Na₂CO₃, Na₂B₄O₇, CaSO₄, AlCl₃, B₂O₃, Al₂O₃, SiO₂, and TiO₂. It has been noticed, in particular, that if component c) is prepared in the presence of inert solid matters, the surface area generally decreases. More particularly it has been observed that when component c) is homogeneously mixed with agglomerating substances, in particular B₂O₃, or AlCl₃, the product obtained usually has a surface area below 100 m²/g. The performance of the catalyst obtained from the so treated component c) are, however, still acceptable especially as regards the polymer yield. 10

In the preparation of component c) it is possible to support the active components of component c) on inert carriers such as, for example, SiO₂ and Al₂O₃ having a high porosity i.e. higher than 0.3 cc/g. In this case the Ti and Mg halogenated compounds and the electron-donor compound make up a reduced proportion with respect to the total amount, thus providing catalysts in which the amount of undesired matter, such as halogens, is at a minimum. 15

It is to be borne in mind that the Mg/Ti g. atomic ratio in component c) is generally higher than 1, but it is lower than 1 when TiO₂ and Ti salts of inorganic oxygen-containing acids, which do not react with the halogenated Mg compound, are used as fillers. 20

Component c) may be prepared according to various methods.

25 A general method consists in starting from a particular composition or carrier comprising a Mg halide (preferably dichloride or dibromide) and a complex between said Mg halide and an electron-donor compound, in which the ratio g. atoms Mg/g. moles of electron-donor compound is higher than 2 and preferably ranges from 2 to 15, and in treating said composition or carrier with a liquid tetravalent Ti compound under conditions in which a certain amount of Ti compounds is fixed on the carrier, and in subsequently separating the reaction solid product from the liquid phase under conditions in which practically no Ti compounds soluble in boiling n-heptane and extractable with Ti tetrachloride at 80°C remain on the product. 30

35 The peculiar feature of the Mg mixture to be treated with the liquid Ti compound is that of providing the X-ray spectrum previously mentioned as characteristic of component (c), in which the maximum intensity line appearing on the Mg halide spectrum of normal type exhibits a decreased relative intensity and appears asymmetrically broadened so as to form a halo in which the intensity peak is shifted with respect to the maximum intensity line, or the maximum intensity line is not present in the spectrum and instead of it a halo appears having an intensity peak shifted with respect to distance *d* of the maximum intensity line. This X-ray spectrum shift thus becomes characteristic of the component (c) itself. 40

45 This Mg mixture, which is the starting product for the preparation of component c), can be obtained in various manners. A preferred one consists in subjecting to grinding mixtures of a Mg halide, in particular dichloride and dibromide, with an electron-donor compound, preferably an organic ester or an aliphatic or aromatic ether, optionally operating in the presence of a Ti compound at an Mg/Ti ratio higher than 2 and/or of an inert co-carrier and/or of matters contributing to promote the grinding, such as silicone oils, until the above-described halos having the intensity peak shifted with respect to the maximum intensity line appear in the X-ray spectrum of the ground product. 50

55 The ground product is then treated with a liquid halogenated Ti compound, in particular TiCl₄, at such temperature (generally between room temperature and 200°C) and for such time-period as to fix the proper amount of Ti compound.

60 The solid product of the reaction is then separated from the liquid phase, for example by means of filtration, sedimentation etc., under such conditions of temperature and/or dilution with the liquid Ti compound, that in the solid product, after extraction at first with boiling n-heptane and then with TiCl₄ at 80°C, no amounts of extractable Ti compounds exceeding 20% and 50% by weight respectively are present any longer. 60

65 Other methods of preparing a Mg mixture suited to prepare component c) are those of reacting, in an inert hydrocarbon solvent, an anhydrous Mg halide with an organic compound containing active hydrogen in the presence of an organic ester and in successively treating the reaction product with a metallorganic Al 65

compound. It is possible also to invert the order of the reaction, i.e. to treat the complex between the Mg halide and the active hydrogen-containing compound with the metallorganic compound and then to react the resulting product with the organic ester.

5 These preparation methods are illustrated in French Patent No. 2.283,909. 5

The product so obtained is washed with an inert hydrocarbon solvent to remove any traces of free metallorganic compound, and is then reacted with a liquid Ti compound, in particular $TiCl_4$, at a temperature ranging from 20° to $200^\circ C$, and the solid reaction product is separated from the liquid phase under filtration or sedimentation conditions, as no Ti compounds extractable with boiling n-heptane and with Ti-tetrachloride at $80^\circ C$ remain on the solid component. 10 10

Another method of preparing a Mg mixture suitable for the preparation of component c) is illustrated in German Patent Specification 2,605,922. In this case too the mixture is reacted with a liquid Ti compound and the reaction product is separated from the liquid phase, under such conditions that no Ti compounds soluble in boiling heptane and in Ti-tetrachloride at $80^\circ C$ remain on the solid product. 15 15

According to the above-cited preparation methods, when a Mg halide is used, this is preferably as anhydrous as possible (H_2O content lower than 1% by weight), especially when the catalyst component is prepared by grinding. 20 20

It is possible, however, to employ as starting compounds for the preparation of component c) a hydrated Mg halide containing generally from 0.1 to 6 moles of H_2O per mole of halide. Furthermore, it is possible to use oxygen containing Mg compounds such as MgO , $Mg(OH)_2$, $Mg(OH)Cl$, Mg carbonate, Mg salts of organic acids, Mg silicate, Mg aluminates, Mg alcoholates and halogenated derivatives of same. Metallorganic Mg compounds containing at least a Mg-C linkage can also be used. Examples of such compounds are the Grignard's reagents and compounds MgR_2 in which R is an alkyl-, cycloalkyl- or aryl radical containing up to 20 carbon atoms. In all these cases, the Mg compound is reacted with Ti-tetrachloride in excess and is thus converted to the desired halogenated Mg compound of component (c), operating preferably at the tetrachloride boiling point and then hot-separating, preferably at the $TiCl_4$ boiling point, the solid product. 25 25 30 30

The resulting solid product is treated in suspension in an inert hydrocarbon with an organic ester, in particular with an ester of an aromatic carboxylic acid in amounts equal to 1—20 g moles per g-atom of Ti contained in the carrier, operating at temperatures ranging from room temperature to $200^\circ C$. The solid product treated in this way is accurately separated from the unreacted ester, and then reacted with a liquid halogenated Ti compound and separated from the reaction liquid phase under the conditions specified hereinbefore for the other preparations. 35 35 40 40

In all these preparation methods it is of essential importance that at least 80% by weight of the Ti compounds contained in component c) is insoluble in boiling n-heptane, and that less than 50% by weight of the Ti compounds insoluble in boiling heptane is extractable with Ti-tetrachloride at $80^\circ C$. In fact, the presence of soluble Ti compounds is detrimental in both activity and stereospecificity of the catalyst, particularly when polymerization is conducted in the presence of hydrogen. 45 45

The catalyst component c) according to the present invention is preferably employed in catalysts for the polymerization of alpha-olefins having at least three carbon atoms and in particular in the preparation of crystalline polymers and copolymers of propylene. It can be also used in catalysts for the polymerization of ethylene, in which case the component b) may be omitted. It has been found that it is possible to produce good catalysts using components c) in which the valence of the Ti has been reduced to values lower than 4 by treatments with reducing agents, before the contact of component c) with component a). Suitable reducing agents are metallorganic Al compounds, Al metal, hydrogen. 50 50 55 55

Polymerization is conducted according to conventional methods, operating in a liquid phase, either in the presence or in the absence of an inert hydrocarbon diluent, such as hexane, heptane, or cyclohexane, or in a gas phase. Polymerization temperature is generally comprised between 0° and $150^\circ C$, preferably between 40° and $90^\circ C$; it is operated at atmospheric pressure or at a higher pressure. 60 60

When crystalline copolymers of propylene are to be prepared, it is preferable to polymerize the propylene until obtaining a homopolymer amount equal to 60—90% of the total composition, followed by one or more polymerization steps of propylene-ethylene mixtures or of ethylene only, so that the polymerized ethylene content may range from 5 to 30% calculated on the weight of the final composition. 65 65

Also mixtures of propylene and ethylene are polymerized in order to obtain a copolymer containing at most 5% by weight of ethylene.

The following examples are given to illustrate the present invention.

Examples 1 to 11 and Comparative Examples 1—2.

- 5 **A) GRINDING** 5
- Anhydrous $MgCl_2$ (containing less than 1% by weight of water), ethyl benzoate (EB) and, optionally, a silicone were co-ground in two vibrating mills of the type VIBRATOM manufactured by N. V. TEMA'S, Gravenhage (Holland), having a total volume of one and six litres respectively and containing respectively 3 and 18 kg of stainless steel balls of 16 mm diameter. 10
- Grinding was effected employing a filling coefficient equal to 135 g/l of total volume (vacuum), at a temperature in the mill inside around 40°C and with grinding times, different from run to run, varying from 50 to 100 hours. 10
- Charging of the mill with the products to be ground, successive grinding and discharging of the co-ground product from the mill occurred in a nitrogen atmosphere. 15
- In Example 10, grinding was conducted in a rotary mill having a capacity of 1 litre, containing 120 stainless steel balls of 15.8 mm diameter and made to rotate at 50 r.p.m. 15
- The following Table 1 shows, for the various runs, the data relating to type and amount of the products to be ground, to the grinding conditions and to the characteristics of the products obtained. 20
- B) TREATMENT WITH $TiCl_4$**
- A portion (15—50 g) of the co-ground product was transferred, always in a nitrogen atmosphere, into a 500 cc reactor, wherein it was contacted with an excess of $TiCl_4$. The treatment with $TiCl_4$ took place at temperatures ranging from 80° to 135°C for a 2-hour period, whereupon the $TiCl_4$ in excess and the products soluble in same were removed by filtration at the temperatures specified in Table 1. Two or more washings with boiling hexane followed. 25
- The resulting solid product was dried in a nitrogen atmosphere and a portion thereof was analyzed to determine the per cent content of Ti and Cl. 30
- The data relating to the operative conditions employed in the various runs during the treatment with $TiCl_4$ as well as the characteristics of the solid products thus obtained are reported too on Table 1. 30
- The stereospecificity and activity of these solid products (catalyst components) were determined in runs for the polymerization of propylene in a hydrocarbon solvent or in liquid monomer, using, as co-catalysts, aluminium-trialkyls treated with electron-donor compounds. 35
- C) POLYMERIZATION IN A SOLVENT**
- This was conducted in a 2500 cc autoclave, equipped with a stirrer and previously purified with nitrogen at 60°C. Polymerization was conducted at 60°C, at a propylene (C_3^-) pressure of 5, 8 or 9 atmospheres (kept constant by addition of propylene during the polymerization runs) for a 4 or 5-hour time-period, using as hydrocarbon solvent technical grade dearomatized and dried (1000 cc) n-heptane (nC_7^+), hexane (C_6^+) or mixed heptanes (C_7^+), in the presence of hydrogen as molecular weight modifier. 40
- $Al(C_2H_5)_3$ (TEA) or $Al(iC_4H_9)_3$ (TIBAL) were used as aluminium trialkyls; p-ethylanisate (PEA) and ethyl p-toluate (EPT) were employed as electron-donor compounds. The molar ratio between Al-trialkyl and donor was comprised between 2.74 and 3.14. 45
- The autoclave was charged, in the order and in a propylene atmosphere, with the solvent (870 cc), a portion of Al-alkyl and of donor previously mixed for 10' in 150 cc of said solvent, and contemporaneously with the supported catalyst component in suspension in 80 cc of solvent containing the remaining portion of Al-alkyl and of donor. Hydrogen and propylene were then introduced into the autoclave until reaching the polymerization pressure, and the temperature was raised to the value required. 50
- At the conclusion of the polymerization run the solvent was removed by stripping with steam and the polymer so obtained was dried in a nitrogen atmosphere at 70°C. 55
- 60

D) POLYMERIZATION IN LIQUID MONOMER

This was conducted in 30—1 and 135—1 autoclaves equipped with stirrer, at a temperature of 65°C, with propylene at 26.5 eff. atmosph., for a 5-hour time, in the presence of hydrogen (15 Nl and 50 Nl) as molecular weight modifier.

5 $\text{Al}(\text{C}_2\text{H}_5)_3$ in an amount of 12.5 g (runs in a 30—1 autoclave) and $\text{Al}(\text{iC}_4\text{H}_9)_3$ in an amount of 36 g (runs in a 135—1 autoclave), both treated with electron-donor compounds such as p-ethylanisate or ethyl p-toluate in molar ratios of from 2.2 to 2.74, were employed as aluminium trialkyls. 5

10 The autoclave was charged in the order, in a propylene atmosphere, with Al-alkyl in a 12% by weight heptane solution, with liquid propylene and with the donor. 10

The autoclave was heated to the polymerization temperature and the catalyst component and the hydrogen were then introduced thereinto.

15 At the conclusion of the polymerization, the residual propylene was evaporated and the polymer was then dried in a nitrogen atmosphere at 70°C. 15

In both cases (polymerization in a solvent and in liquid monomer), the dry polymer was weighed to calculate the yield with respect to titanium present in the catalyst; moreover, the polymer was extracted with boiling n-heptane to determine the per cent amount of polymer insoluble in boiling n-heptane.

20 Apparent density and inherent viscosity (in tetraline at 135°C) of the polymer thus obtained were determined too. The following Table 2 reports the data relating to the various polymerization runs and to the characteristics of the polymers so obtained. In all cases except the comparative Examples, the essential requirements of the catalyst components according to the present invention were satisfied. 20

TABLE 1 - PREPARATION OF THE SUPPORTED CATALYST COMPONENT

	EXAMPLES:	1	2	3
	Measure units			
GRINDING				
Vibrating mill volume	l	6	6	6
Rotary mill volume	l			
MgCl ₂	g	530	651.5	651.5
EB amount	g	280	158.5	158.5
MgCl ₂ /EB molar ratio		3/1	6.5/1	6.5/1
Silicone oil and amount of	g			
TiCl ₄	g			
B ₂ O ₃	g			
Grinding time	h	100	50	50
CHARACTERISTICS OF THE GROUND PRODUCT				
X-ray Spectrum (*)			A	A
TREATMENT WITH TiCl₄				
TiCl ₄	g	375	375	375
Ground product	g	25	25	25
Ground product of comp. example 1	g			
Treatment temperature	°C	80	80	135
Filtration temperature	°C	80	80	135
Washing with boiling heptane (amount)	g			
CHARACTERISTICS OF THE PRODUCT TREATED WITH TiCl₄				
Elemental analysis: Ti	% by weight	1.30	1.60	1.80
Cl	% by weight	63.15	65.25	68.60
Surface area	m ² /g		150	190

(*) Spectrum A means a spectrum in which the maximum intensity line of magnesium chloride that appears at $d = 2.56 \text{ \AA}$ has decreased in relative intensity and broadens asymmetrically forming a halo, whose intensity peak is comprised between $d = 2.44 \text{ \AA}$ and $d = 2.97 \text{ \AA}$.

Spectrum B means a spectrum in which the above said maximum intensity line is absent and its place is taken by a halo having an intensity peak shifted with respect to such line, and comprised between $d = 2.44 \text{ \AA}$ and $d = 2.97 \text{ \AA}$.

(**) PDSM 500, PDSM 100 and PDSM 50 are polydimethylsiloxanes having a viscosity of 500, 100 and 50 centistokes respectively.

TABLE 1 - PREPARATION OF THE SUPPORTED CATALYST COMPONENT

	EXAMPLES:	4	5	Comp:	
	Measure units				
<u>GRINDING</u>					
Vibrating mill volume	l	6	6	6	
Rotary mill volume	l				
MgCl ₂	g	651.5	651.5	651.5	
EB amount	g	158.5	158.5	158.5	
MgCl ₂ /EB molar ratio		6.5/1	6.5/1	6.5/1	
Silicone oil and amount of TiCl ₄	g	-	-	-	
	g	-	-	200	
B ₂ O ₃	g	-	-	-	
Grinding time	h	100	100	100	
<u>CHARACTERISTICS OF THE GROUND PRODUCT</u>					
X-ray spectrum (*)		B	B	B	
<u>TREATMENT WITH TiCl₄</u>					
TiCl ₄	g	375	375		
Ground product	g	25	25		
Ground product of comp. example 1	g				
Treatment temperature	°C	80	130		
Filtration temperature	°C	80	135		
Washing with boiling heptane (amount)	g				
<u>CHARACTERISTICS OF THE PRODUCT TREATED WITH TiCl₄</u>					
Elemental analysis:	Ti	% by weight	1.95	2.15	5.1
	Cl	% by weight	67.30	67.7	61.6
Surface area		m ² /g	176	185	3

TABLE 1 - PREPARATION OF THE SUPPORTED CATALYST COMPONENT

	EXAMPLES:	6	Comp 2	7
<u>GRINDING</u>				
	<u>Measure units</u>			
Vibrating mill volume	l	*	*	1
Rotary mill volume	l	*	*	
MgCl ₂	g	*	*	96.5
EB amount	g	*	*	30.6
MgCl ₂ /EB molar ratio				5/1
Silicone oil and amount of	g	*	*	(**) PDMS 500/1
TiCl ₄	g	*	*	
B ₂ O ₃	g	*	*	
Grinding time	h	*	*	100
<u>CHARACTERISTICS OF THE GROUND PRODUCT</u>				
X-ray spectrum (*)				
<u>TREATMENT WITH TiCl₄</u>				
TiCl ₄	g	375		150
Ground product	g			18
Ground product of comp. example 1*	g	25	25	
Treatment temperature	°C	80		80
Filtration temperature	°C	80		80
Washing with boiling heptane (amount)	g		800	
<u>CHARACTERISTICS OF THE PRODUCT TREATED WITH TiCl₄</u>				
Elemental analysis: Ti	% by weight	2.6	1.65	1.55
	Cl		58.4	
Surface area	m ² /g		4	

TABLE 1 -- PREPARATION OF THE SUPPORTED CATALYST COMPONENT

	EXAMPLES:	8	9	10	
<u>GRINDING</u>					
	<u>Measure units</u>				
Vibrating mill volume	l	1	6	-	
Rotary mill volume	l			1	
MgCl ₂	g	96.5	651.5	20	
EB amount	g	30.6	157	6	
MgCl ₂ /EB molar ratio		5/1	6.5/1	5.2/1	
Silicone oil and amount of	g	(**) PDMS 100/13,9	(**) PDMS 50/3		
TiCl ₄	g	-	-	-	
B ₂ O ₃	g	-	-	-	
Grinding time	h	100	100	100	
<u>CHARACTERISTICS OF THE GROUND PRODUCT</u>					
X-ray spectrum (*)					
<u>TREATMENT WITH TiCl₄</u>					
TiCl ₄	g	375	375	150	
Ground product	g	25	25	28	
Ground product of comp. example 1	g				
Treatment temperature	°C	80	80	80	
Filtration temperature	°C	80	80	80	
Washing with boiling heptane (amount) g					
<u>CHARACTERISTICS OF THE PRODUCT TREATED WITH TiCl₄</u>					
Elemental analysis:	Ti	% by weight	1.65	2.00	1.1
	Cl	% by weight	62.05	62.55	66.1
Surface area		m ² /g	172		

TABLE 1 - PREPARATION OF THE SUPPORTED CATALYST COMPONENT

	EXAMPLES:	
	11	
<u>GRINDING</u>		
	<u>Measure units</u>	
Vibrating mill volume	l	1
Rotary mill volume	l	
MgCl ₂	g	45
EB amount	g	10.1
MgCl ₂ /EB molar ratio		6.8/1
Silicone oil and amount of	g	
TiCl ₄	g	
B ₂ O ₃	g	54
Grinding time	h	
<u>CHARACTERISTICS OF THE GROUND PRODUCT</u>		
X-ray spectrum (*)		
<u>TREATMENT WITH TiCl₄</u>		
TiCl ₄	g	135
Ground product	g	20
Ground product of comp. example 1	g	
Treatment temperature	°C	80
Filtration temperature	°C	80
Washing with boiling heptane (amount)	g	
<u>CHARACTERISTICS OF THE PRODUCT TREATED WITH TiCl₄</u>		
Elemental analysis: Ti	% by weight	1.4
Cl	% by weight	3.1
Surface area	m ² /g	80

TABLE II -- RESULTS OF THE PROPYLENE POLYMERIZATION

<u>CATALYST COMPONENT</u>		<u>Measure units</u>		
Reference-example in TABLE I		1	1	2
Catalyst component amount	mg	80	450	70
Ti	% by weight	1.30		1.60
Cl	% by weight	63.15		65.25
<u>POLYMERIZATION RUNS</u>				
Autoclave capacity	l	2.5	30	2.5
Polymerization medium and volume	cc	nC ₇ ⁺ /1000	C ₃ ⁻ /23000	nC ₇ ⁺ /1000
C ₃ ⁻ effective pressure	atm	5	26.5	5
Polymerization temperature	°C	60	65	60
Polymerization time	h	4	5	4
Type of Al-alkyl		TEA	TEA	TEA
Amount of Al-alkyl	g	1.135	12.5	1.135
Type of donor		PEA	PEA	PEA
Al alkyl/donor molar ratio		3.14	2.74	3.14
Hydrogen amount	Ncc	110	15000	110
<u>RESULTS OF POLYMERIZATION RUNS</u>				
Yield	g polymer/g Ti	113500	274000	103000
Isotacticity index	%	94.0	94.5	93.5
<u>CHARACTERISTICS OF THE POLYMER OBTAINED</u>				
Polymer apparent density	kg/l	0.47	0.45	0.44
Polymer intrinsic viscosity	dl/g	1.6	2.3	1.8

TABLE II – RESULTS OF THE PROPYLENE POLYMERIZATION

<u>CATALYST COMPONENT</u>		<u>Measure units</u>		
Reference example in TABLE I		3	4	4
Catalyst component amount	mg	127	66	310
Ti	% by weight	1.80	1.95	
Cl	% by weight	68.0	67.30	
<u>POLYMERIZATION RUNS</u>				
Autoclave capacity	l	2.5	2.5	30
Polymerization medium and volume	cc	nC ₇ ⁺ /1000	nC ₇ ⁺ /1000	C ₃ ⁻ /23000
C ₃ ⁻ effective pressure	atm	5	5	26.5
Polymerization temperature	°C	60	60	65
Polymerization time	h	4	4	5
Type of Al-alkyl		TEA	TEA	TEA
Amount of Al-alkyl	g	1.135	1.135	12.5
Type of donor		PEA	PEA	PEA
Al alkyl/donor molar ratio		3.14	3.14	2.74
Hydrogen amount	Ncc	110	110	15000
<u>RESULTS OF POLYMERIZATION RUNS</u>				
Yield	g polymer/g Ti	107000	155000	324000
Isotacticity index	%	91.5	93.0	93.5
<u>CHARACTERISTICS OF THE POLYMER OBTAINED</u>				
Polymer apparent density	kg/l	0.48	0.48	0.50
Polymer intrinsic viscosity	dl/g	2.0	1.8	2.1

TABLE II – RESULTS OF THE PROPYLENE POLYMERIZATION

<u>CATALYST COMPONENT</u>		<u>Measure units</u>		
Reference example in TABLE I		5	6	7
Catalyst component amount	mg	82	72	110
Ti	% by weight	2.15	2.6	1.55
Cl	% by weight	67.7		
<u>POLYMERIZATION RUNS</u>				
Autoclave capacity	l	2.5	2.5	2.5
Polymerization medium and volume	cc	$nC_7^+/1000$	$nC_7^+/1000$	$nC_7^+/1000$
C_3^- effective pressure	atm	5	5	5
Polymerization temperature	°C	60	60	60
Polymerization time	h	4	4	4
Type of Al-alkyl		TEA	TEA	TEA
Amount of Al-alkyl	g	1.135	1.135	1.135
Type of donor		PEA	PEA	PEA
Al alkyl/donor molar ratio		3.14	3.14	3.14
Hydrogen amount	Ncc	110	110	110
<u>RESULTS OF POLYMERIZATION RUNS</u>				
Yield	g polymer/g Ti	174000	164500	123000
Isotacticity index	%	90.5	91.5	94
<u>CHARACTERISTICS OF THE POLYMER OBTAINED</u>				
Polymer apparent density	kg/l	0.43	0.48	0.49
Polymer intrinsic viscosity	dl/g	2.0	1.8	

TABLE II – RESULTS OF THE PROPYLENE POLYMERIZATION

<u>CATALYST COMPONENT</u>		<u>Measure units</u>		
Reference example in TABLE I		8	9	10
Catalyst component amount	mg	63	65	110
Ti	% by weight	1.65	2.00	1.1
Cl	% by weight	62.05	65.00	66.1
<u>POLYMERIZATION RUNS</u>				
Autoclave capacity	l	2.5	2.5	2.5
Polymerization medium and volume	cc	C ₆ ⁺ /1000	C ₆ ⁺ /1000	C ₇ ⁺ /1000
C ₃ ⁻ effective pressure	atm	9	9	5
Polymerization temperature	°C	60	60	60
Polymerization time	h	4	4	4
Type of Al-alkyl		TIBAL	TIBAL	TEA
Amount of Al-alkyl	g	1.97	1.97	1.135
Type of donor		EPT	EPT	PEA
Al alkyl/donor molar ratio		3.14	3.14	3.14
Hydrogen amount	Ncc	190	190	110
<u>RESULTS OF POLYMERIZATION RUNS</u>				
Yield	g polymer/g Ti	333000	344000	141000
Isotacticity index	%	92.0	92.5	92
<u>CHARACTERISTICS OF THE POLYMER OBTAINED</u>				
Polymer apparent density	kg/l	0.50	0.43	0.48
Polymer intrinsic viscosity	dl/g	2.4	3.0	1.7

TABLE II – RESULTS OF THE PROPYLENE POLYMERIZATION

		<u>Measure units</u>		
<u>CATALYST COMPONENT</u>				
Reference example in TABLE I		11	Comp. 1	Comp. 2
Catalyst component amount	mg	100	105	105
Ti	% by weight	1.3	5.7	1.65
Cl	% by weight	31	61.0	58.4
<u>POLYMERIZATION RUNS</u>				
Autoclave capacity	l	2.5	2.5	2.5
Polymerization medium and volume	cc	$C_6^+/1000$	$C_7^+/1000$	$C_8^+/1000$
C_3^- effective pressure	atm	9	8	9
Polymerization temperature	°C	60	60	60
Polymerization time	h	4	5	4
Type of Al-alkyl		TIBA	TEA	TIBA
Amount of Al-alkyl	g	1.97	1.00	1.135
Type of donor		EPT	PEA	EPT
Al alkyl/donor molar ratio		3.14	2.9	3.14
Hydrogen amount	Ncc	190	170	190
<u>RESULTS OF POLYMERIZATION RUNS</u>				
Yield	g. polymer/g Ti	290000	70000	89500
Isotacticity index	%	90	90.5	88.5
<u>CHARACTERISTICS OF THE POLYMER OBTAINED</u>				
Polymer apparent density	kg/l	0.4	0.43	0.28
Polymer intrinsic viscosity	dl/g		1.9	

Example 12.

5 Anhydrous $MgCl_2$ (containing less than 1% by weight of H_2O) was co-ground with the electron-donor compounds listed in Table 3, under the conditions used in Example 4. The ground product was treated with $TiCl_4$ under the conditions of Example 4. The reaction product thus obtained exhibited the Cl and Ti contents indicated in Table 3. 5

The above said catalyst components were used in polymerization tests under the conditions set forth in Example 8 with the only difference that the C_3^- effective pressure was 5.4 atm. 10

The data concerning the yield of polymer and isotacticity index are reported in Table 3. 10

TABLE 3

electron-donor	EPT	PEA	MB	MMA	NBE
Ti % by weight	1.3	1.75	1.8	2.0	2.1
Cl % „ „	59.8	60.9	61	62	63.9
Yield (g polymer/g Ti)	250,000	183,000	170,000	167,000	185,000
isotacticity index	93	93	94	94.5	92

EPT = ethyl p-toluate

PEA = p.ethylanisate

MB = methylbenzoate

MMA = methylmetacrylate

NBE = di (n.butyl)-ether

Example 13.

500 ml of kerosene were introduced into a flask provided with a stirrer.

Propylene was introduced at a rate of 30 l/hr for 1 hour to expel air and moisture.

2,5 m Mol of Al-triethyl and 0.884 m Mol of the electron-donor compound indicated in Table 4 were introduced into the flask at room temperature. After 5 minutes there was introduced a catalyst component prepared according to Example 7 with the only difference that a silicon oil having a viscosity of 20 centistokes at 20°C was used. The molar ratio Al/Ti in the catalyst was 25.

The mixture was heated at 60°C. Propylene was polymerized for 1 hour at atmospheric pressure and was introduced at such a rate to maintain the pressure constant during the polymerization. Thereafter propylene was replaced by nitrogen and the reaction mixture cooled at room temperature. The solid product was filtered off, washed twice with methanol then dried at 70°C. The soluble polymer was recovered by evaporation of the kerosene layer in the filtrate. The data concerning the yield and the total isotacticity index of the polymer are reported in Table 4.

TABLE 4

electron-donor	BA	POBA	AAC	BAA	NBE
Yield (g.polymer/g Ti)	47,900	43,140	40,430	41,900	31,500
isotacticity index (on the total)	75.6	89.2	80.3	73.9	92.1

BA = benzoic acid

POBA = p.hydroxy-benzoic acid

AAC = alpha-aminoacetic acid

BAA = benzoic acid amide

NBE = di (n.butyl)-ether

Example 14.

10 g of the same catalyst component prepared as used in Example 13 and containing 2.1% by weight of Ti were suspended in 150 ml of kerosene. Diethylaluminium chloride 2.2 m.mol diluted with kerosene were added at room temperature and then 2.2 m.mol of ethylbenzoate were added and the mixture stirred for 1 hour. The solid product was filtered washed with hexane and dried in vacuum.

Into an autoclave of 2 l capacity and containing 750 ml of n.-hexane and 3.75 m.mol of $\text{Al}(\text{C}_2\text{H}_5)_3$ premixed with 1.25 m.mol of methyl p-toluate, there was introduced an amount of the dried product corresponding to 0.03 m.mol/l of Ti.

The polymerization test was carried out for 4 hours at 69°C at a pressure of propylene of 8 atm and in the presence of 400 N liter of hydrogen.

After removal of the solid by filtration and drying, 225.9 g of powder were obtained whose isotactic index was 94.2.

From the filtrate 5.9 g of polymer soluble in n-hexane were recovered.

Example 15.

10 g of MgCl_2 containing less than 1% by weight of water and suspended in kerosene (100 ml) were treated with 18.4 ml of ethyl alcohol at 20°C for 2 hours. The complex of MgCl_2 with ethanol was reacted with 2.5 ml of 2,6-dimethylphenol at 20°C for 1 hour, 11.7 ml of ethyl-benzoate at 80°C for 1 hour and 22.9 ml of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ at 20°C for 2 hours, in the above indicated order.

The solid product was separated by filtration, washed with n-hexane and dried in vacuum. 10 g of the product was treated with 100 ml of TiCl_4 at 100°C for 2 hours. The excess of TiCl_4 was separated by filtration. The solid product was washed repeatedly with n-hexane and then dried in vacuum.

The elemental analysis of the product gave the following results:

Ti = 3.60% by weight

Cl = 58.0% by weight

31 mg of the solid product were used in a polymerization test under the conditions employed in Example 14. After removal of the solvent by filtration and drying, 130 g of polymer were obtained. The isotactic index of this polymer was 95.4. The polymer soluble in hexane and recovered from the filtrate was 30 g.

Example 16.

CATALYST PREPARATION

One (1) kg of anhydrous MgCl_2 , 0.23 l of ethyl benzoate and 0.15 l of polydimethyl siloxane (viscosity 50 centistokes) were placed in a 100 l vibrating mill (containing therein 350 kg of stainless steel balls, each 15 mm in diameter), in which they were brought into mutual contact for 120 hr at 70°C.

Of the product of copulverization so obtained, 500 g was suspended in 5 l of TiCl_4 , and the resulting suspension was allowed to undergo reaction at 80°C for 2 hr. After completion of the reaction, the resulting system was filtrated at the same temperature for recovery of its solid component, which was then washed thoroughly with hexane until free TiCl_4 was no longer detected.

The resulting solid component contained 2.0, 23.0 and 64.0 wt% of Ti, Mg and Cl as atoms and 10.5 wt% of ethyl benzoate respectively, and exhibited a specific surface area of 200 m²/g.

Polymerization

An equipment was used comprising 4 reactors lined up in series, namely, reactors A, B, D and E (each with an effective volume of 190, 120, 140 and 200 l respectively) and a flash drum C (with an effective volume of 30 l) installed between the reactors B and D.

The reactor A was charged with 0.75 mmol-Ti/hr as hexane slurry of the solid CAT component prepared as described above, and a hexane solution of triethyl-Al and ethyl p-toluate (EPT) in such amounts that the Al/Ti and Al/EPT mol ratios will be 50 and 2.75 respectively, all together at a rate of 21 l/hr as the total hexane quantity.

Furthermore, the reactor was charged with 7 Nm³/hr of propylene and 13 Nl/hr of hydrogen, while maintaining the reactor pressure at 7 kg/cm² Gauge and the polymerization temperature at 60°C.

As the result, polypropylene (PP) having its isotacticity index and melt index (MI) at 92.8% and 0.36 respectively was produced in the reactor A at a rate of 240,000 g-PP/g-Ti.

The polymer slurry discharged from the reactor A was then forwarded to the reactor B, to which 4.5 mmol/hr of triethyl-Al and 5NI/hr of hexane were charged anew. Polymerization in the reactor B was then performed at a 3.0 kg/cm²G pressure and 60°C as the polymerization temperature.

5 PP having its isotacticity index at 92.2% and MI at 0.32 was produced in the reactors A and B collectively at a rate of 290,000 g-PP/g-Ti. 5

The polymer slurry discharged from the reactor B was then directed to the flash drum C, where unreacted propylene monomer was removed, and thereafter forwarded to the reactor D, to which 1,000 NI/hr of ethylene and 80 NI/hr of hydrogen were supplied additionally, together with nitrogen gas to maintain the reactor pressure at 2.5 kg/cm²G. 10

The composition of the gas held in the reactor D was: hydrogen 7.3%, nitrogen 45.5%, ethylene 25.8%, propylene 0.9% and hexane 20.4%.

15 As the result of polymerization in the reactor D at 60°C as the polymerization temperature, a polymer having its MI at 0.29 and bulk density at 0.350 was obtained at a rate of 27,000 g-polymer/g-Ti. 15

The polymer slurry discharged from the reactor D was then forwarded to the reactor E, to which ethylene was supplied at a rate of 1,700 NI/hr, hydrogen at a rate of 70 NI/hr, triethyl-Al 4.5 mmol/hr and hexane 10 l/hr additionally.

20 Polymerization was carried out under the polymerization pressure of 2.0 kg/cm²G and the polymerization temperature of 60°C, while the composition of the gas held in the reactor E was: hydrogen 38.2%, nitrogen 3.4%, ethylene 35.6%, propylene 0.1% and hexane 22.6%. 20

25 As the result of polymerization in reactor E, a polymer having its MI at 0.24 and bulk density at 0.350 was produced at a rate of 24,000 g-polymer/g-Ti. The polymer so produced contained 17.6 parts by weight of ethylene polymer per 100 parts by weight of PP. 25

WHAT WE CLAIM IS:—

30 1. A solid catalyst component useful in the polymerization of alpha-olefins, comprising, at least on the surface, the reaction product of a halogenated Mg compound with a tetravalent Ti compound and with an electron-donor compound, the ratio g. moles electron/donor/g. atoms Ti in said product being higher than 0.2 and the ratio g. atoms halogen/g. atoms Ti being higher than 4, wherein at least 80% by weight of the Ti compounds contained therein is insoluble in boiling n-heptane and at least 50% by weight of the Ti compounds insoluble in boiling n-heptane is insoluble also in TiCl₄ at 80°C, and the surface area of the catalyst component as a whole is higher than 40 m²/g. 35

2. A component according to claim 1, wherein the X-ray spectrum thereof shows a halo whose maximum intensity is shifted with respect to the distance *d* of the maximum intensity line which appears in the X-ray spectrum of the corresponding pure Mg-dihalide. 40

3. A component according to claim 1 or 2, wherein the halogenated Mg compound is selected from the dichloride and dibromide, and the tetravalent titanium compound is selected from TiCl₄ and Ti halogen-alcoholates, and the electron-donor compound is selected from organic esters and ethers. 45

4. A component according to claim 3, wherein the esters and ethers are esters of aromatic acids, aliphatic and aromatic ethers.

5. A component according to any of claims 1 to 4, wherein the Mg/Ti atomic ratio is within the range from 3 to 40, the halogen/Ti atomic ratio is within the range from 10 to 90, and the electron-donor compound/Ti molar ratio is within the range from 1 to 6. 50

6. A component according to claim 5, wherein the three ratios respectively are within the ranges from 10 to 30, from 20 to 80, and from 1.2 to 3.

7. A component according to any of claims 1 to 6, wherein the surface area of the catalyst component as a whole exceeds 100 m²/g. 55

8. A component according to claim 7, wherein the said surface area is within the range from 100 to 200 m²/g.

9. A component according to any of the preceding claims, which contains inert solid fillers other than Ti oxides and Ti salts of oxygen containing inorganic acids, in amounts up to 80% by weight based on the total amount. 60

10. A component according to any of claims 1 to 8, which contains inert fillers selected from amongst TiO₂ and Ti salts of inorganic oxygen containing acids, and in which the Mg/Ti atomic ratio is lower than 1.

11. A component according to any of the preceding claims, which is carried on SiO_2 or Al_2O_3 having a porosity higher than 0.3 cc/g.

12. A component according to any of the preceding claims, which is mixed with an agglomerating substance selected in particular from B_2O_3 and AlCl_3 .

5 13. A component according to any of the preceding claims, prepared by reacting a liquid halogenated tetravalent Ti compound with a solid composition comprising magnesium dichloride or dibromide and a complex between the Mg dihalide and an electron-donor compound and in which composition the ratio g.atoms Mg/moles of electron-donor compound is higher than 2, said solid composition being characterized in that in its X-ray spectrum the maximum intensity line appearing in the normal type halide spectrum, as defined in ASTM 3—0854 and 15—836 for dichloride and dibromide respectively, has decreased in relative intensity and asymmetrically broadens forming a halo that shows an intensity peak shifted with respect to interplanar distance d of the maximum intensity line, or the spectrum is characterized in that the maximum intensity line is absent and its place is taken by a halo having an intensity peak shifted with respect to distance d of the maximum intensity line. 10 15

14. A component according to claim 13, in which the said ratio g.atoms/Mg/moles of electron-donor compound is between 2 and 15.

20 15. A component according to claim 13 or 14, in which the intensity peak appearing in the X-ray spectrum of the composition reacted with the liquid halogenated Ti compound and comprising Mg dichloride, is comprised in the range from d 2.44 Å to d 2.97 Å.

25 16. A component according to any of claims 13 to 15, in which the composition to be reacted with the liquid halogenated tetravalent Ti compound is prepared by grinding a mixture of a Mg dichloride or dibromide, and an electron-donor compound which is an organic ester or an aliphatic or aromatic ether.

30 17. A component according to claim 16, in which the mixture to be subjected to grinding includes Ti compounds in a Mg/Ti atomic ratio higher than 2 and/or a grinding co-promoter which is a silicone oil and/or an inert solid substance.

35 18. A component according to claim 16 or 17, in which the reaction with the liquid Ti compound is conducted at a temperature from 20°C to 200°C, and the solid reaction product is separated from the liquid phase under conditions, in which less than 50% by weight of Ti compounds insoluble in boiling heptane but extractable with TiCl_4 at 80°C remains on the solid product. 35

19. A component according to any of the preceding claims, in which the valence of the Ti has been reduced to below 4 by treatment with a reducing agent.

20. A solid catalyst component according to claim 1 substantially as described in any one of the foregoing Examples 1 to 16.

40 21. A catalyst for the polymerization of alpha-olefins containing at least 3 carbon atoms and mixtures of same with ethylene, comprising the product obtained by contacting the following starting components: 40

a) a metallorganic Al compound free from halogen atoms directly bound to the Al atom;

45 b) an electron-donor compound in such an amount that 15% to 100% by weight of said metallorganic Al compound is combined with the electron-donor compound; 45

c) a solid component according to any one of the preceding claims.

50 22. A catalyst according to claim 21, in which the electron-donor compound is an organic ester, in an amount of 0.2—0.4 moles per mole of metallorganic Al compound. 50

23. A catalyst according to claim 21 substantially as described in any one of the foregoing Examples 1 to 16.

55 24. A catalyst for the polymerization of ethylene, comprising the product obtained by contacting a) a metallorganic Al compound free from halogen atoms directly bound to the Al atom; and b) a solid component according to any one of claims 1 to 20. 55

60 25. A process for preparing crystalline polymers and copolymers of α -olefins of at least 3 carbon atoms by polymerization thereof alone or in admixture with ethylene, wherein the polymerization is conducted in the presence of a catalyst as defined in any of claims 21 to 23. 60

26. A process for polymerization of ethylene, wherein the polymerization is conducted in the presence of a catalyst according to claim 24.

65 27. Process according to claim 25 or 26, in which the polymerization is conducted in the liquid phase in the presence or absence of an inert hydrocarbon solvent. 65

28. Process according to claim 25 or 26, in which the polymerization is conducted in a gas phase.

29. Process according to claim 25 substantially as described in any one of the foregoing Examples 1 to 16.

5 30. A polymer or copolymer or an alpha-olefin of at least 3 carbon atoms, obtained by the process of any of claims 25 and 27 to 29. 5

31. A polymer of ethylene obtained by a process according to claim 26.

J. A. KEMP & CO.,
Chartered Patent Agents,
14 South Square,
Gray's Inn,
London WC1R 5EU.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.