

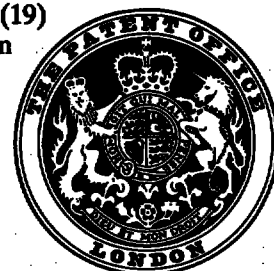
PATENT SPECIFICATION

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(54) CATALYSTS FOR α -OLEFIN POLYMERIZATION

(71) We, MONTEDISON S.p.A., and MITSUI PETROCHEMICAL INDUSTRIES LTD., a Italian Body Corporate and a Japanese Body Corporate of 31, Foro Buonaparte, Milan, Italy and Kasumigaseki Building, 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 new catalyst components for stereoregularly polymerizing α -olefins containing at least 3 carbon atoms, or mixtures of such α -olefins with one another and/or with ethylene; to a method of preparing the catalyst components; the catalysts incorporating said components; and to the use of said catalysts for producing crystalline polymers and copolymers of α -olefins.

It is known to produce a component of catalysts for polymerization of α -olefins by reacting halogen-containing titanium compounds with the product of the reaction of silicon compounds or metallorganic compounds of metals belonging to Groups I to III of the Periodic Table with addition products of magnesium halides and electron-donor compounds containing active hydrogen atoms (French Patents No. 2,200,291 and No. 2,206,339). When catalysts containing such components are employed in the polymerization of α -olefins containing 3 or more carbon atoms, polymers containing considerable amounts of atactic polymer are obtained.

Variations on these known catalysts are described in French Patents No. 2,283,909 and No. 2,300,772, the reaction between the silicon or metal compound and the addition product of magnesium halide being conducted in the presence of a further electron-donor compound not containing active hydrogen atoms. The resulting catalysts have satisfactory stereospecificity, but are not very active, particularly when polymerization is conducted in the presence of hydrogen as a molecular weight modifier and when an Al-alkyl partially complexed with an electron-donor compound is used as co-catalyst, and catalyst residues must be removed by purification after the polymerization.

It has now surprisingly been found that solid catalysts for polymerization with satisfactory stereospecificity and activity of α -olefins containing at least 3 carbon atoms can be produced by using a component made from Mg dihalide obtained by decomposition of an adduct of the Mg dihalide and an electron-donor compound when that decomposition product has an X-ray powder spectrum in which the usual Mg dihalide maximum intensity line is substantially no longer present and a halo line is present having its intensity maximum shifted with respect to said usual Mg dihalide line.

The present invention accordingly provides a solid catalyst component for polymerizing α -olefins containing at least three carbon atoms, comprising the product of reaction of:

- (a) a halogenated Ti compound soluble in hydrocarbons,
- (b) a product containing Mg dihalide selected from Mg dichloride and Mg dibromide obtained by decomposition of an adduct of the Mg dihalide and an electron-donor compound which is an organic electron-donor compound or ammonia, such electron-donor compound being present in the adduct in an amount of at least 0.5 moles per mole of Mg dihalide, the decomposition of the adduct having been carried out with substances, other than Ti compounds, capable of reacting with the electron-donor compound of the adduct, selected from amongst the metallo-organic compounds of metals belonging to groups I to III of the Periodic Table and, in the case of an electron-donor compound having active

hydrogen, also from amongst the halogen-containing compounds of Si, Sn and Sb, the halides of Al and B; and Si-tetra-alkyls and hydrides of Si-alkyls, and

(c) an electron-donor compound not containing active H atoms, which compound (c) may be pre-reacted with (a) or with (b) before the reaction of (a) with (b), or may be present in (b) with the provisos:

that in said catalyst component the content of titanium compounds soluble in TiCl_4 at 80°C is less than 20% by weight with respect to the total content of titanium compounds and reckoned as elemental titanium,

that the molar ratio Mg/Ti in the catalyst component is between 5 and 100;

that the proportion of compound (c) present in the catalyst component is within the range from 0.4 to 3.5 moles per g. atom of Ti;

and furthermore that in the X-ray spectrum of said decomposition product (b), the most intense line appearing in X-ray spectrum of Mg dichloride and Mg dibromide of normal type is substantially absent and there is present a halo line having its intensity maximum shifted with respect to the position of said most intense line. It is important to note that the catalyst component of the invention has an exceptionally low content of titanium compounds soluble in TiCl_4 at 80°C , viz. less than 20% by weight of total titanium compound content. Preferably the amount of tetravalent Ti compounds insoluble in TiCl_4 at 80°C is lower than 4% by weight, expressed as elemental titanium.

The catalyst component of the invention preferably contains, as compound (c) an alkyl benzoate, for example ethyl benzoate.

The solid catalyst component of the invention may be prepared by various methods, preferably starting from an Mg halide adduct prepared by dissolving an Mg dihalide in a liquid electron-donor compound and precipitating the adduct either by cooling the solution or by adding an inert liquid that does not dissolve the adduct. The resulting adduct has a homogeneous chemical composition and provides a decomposition product containing Mg dihalide that reveals, on X-ray analysis, a spectrum having the required characteristics.

In the decomposition products of the adducts of MgCl_2 , for example, the X-ray powder spectrum has a halo line whose intensity maximum is between 2.44 and 2.97 Å, and the line usually appearing at 2.56 Å in the case of rhombohedral MgCl_2 , and at 2.75 Å in the case of hexagonal MgCl_2 is substantially absent. In the corresponding decomposition products of the adducts of MgBr_2 , a halo line also appears and the line usually found at 2.93 Å is absent.

Organic electron-donor compounds suitable for the preparation of the decomposable adducts with the Mg dihalide include compounds with and without active hydrogen atoms. Some examples of such electron-donor compounds containing active hydrogen are aliphatic or aromatic alcohols and thioalcohols; phenols, primary and secondary amines, amides and aliphatic or aromatic carboxylic acids. Specific examples are the methyl, ethyl, n-butyl and hexyl alcohols, phenol, cresol. Ammonia is an electron-donor compound containing active hydrogen.

The amount of compounds containing active hydrogen generally ranges from 0.5 to 6 moles per mole of Mg dihalide. In the case of the adducts with alcohols, best results have been achieved with 2 to 6 moles of the alcohol per mole of Mg dihalide. The adducts may also contain, in a chemically combined form, water molecules in amounts generally lower than 2 moles per mole of Mg dihalide.

An electron-donor compound free from active hydrogen atoms, useful for the preparation of the adduct with the Mg dihalides, can be any substance capable of forming adducts with the Mg dihalides. Representative compounds are the following: - alkyl-, aryl-, cycloalkyl-esters of organic and inorganic acids, especially the alkyl esters of aromatic acids; - aliphatic or aromatic ethers, as for example di-n. butyl ether, diethylether, cyclic ethers as for example tetrahydrofurane, dioxane;

- ketones as acetone, benzophenone, cyclohexanone;

- anhydrides of carboxylic acids;

- aldehydes as benzaldehyde, anisaldehyde;

- nitriles as acetonitrile, benzonitrile;

- phosphines trisubstituted;

- azo compounds;

- chlorides of aliphatic acids;

- dialkylsubstituted amides;

- alkylamides;

- tertiary amines and oxides thereof;

- substituted lactams; and

- organic isocyanates;

The starting Mg halide adducts with the electron-donor compounds free from active hydrogen atoms contain in general up to 6 moles of said electron-donor.

The adduct may also contain, in a chemically combined form, metal compounds such as, for example, tetravalent Ti compounds, in particular the halogen-containing compounds and Si or Al compounds such as alkyl silicates and Al alcoholates. In fact it is possible to obtain the catalyst component of this invention by starting from adducts of Mg compounds, Ti halides and alcohols prepared, according to Belgian Patent No. 840,058 by dissolving the Mg halide in the alcohol and by adding a tetravalent Ti halide to the solution.

The adduct may also be prepared by grinding, for instance in a vibrating mill containing steel balls, for a time-period of 20-60 hours, a mixture of Mg dihalide with the desired amount of organic electron-donor compound containing active hydrogen atoms. By this technique, it is possible to obtain catalysts of a high activity even when the adduct contains a relatively low molar proportion of organic electron-donor compound containing active hydrogen atoms to Mg dihalide.

The adduct may be prepared in form of microspheres by spray-cooling or spray-drying according to known techniques, in which case the catalysts derived therefrom tend to produce polymers having a narrow particle size distribution.

The decomposition of the adducts with electron-donor compounds having active-hydrogen is effected with substances reactive with the active hydrogen atoms, other than the Ti compounds. Such substances include in particular the metallo-organic compounds of the metals belonging to any of Groups I to III of the Periodic Table, the compounds of Si, Sn and Sb, the halides of Al and B. Some typical examples of such substances are the halogen containing compounds of Si, Sn and Sb, such as for example tetra-halides of Sn or of Si, SnCl_4 , halides of Si-alkyls, halides of Sn-alkyls and hydro-halides of Sn, the preferred compounds being SnCl_4 and SiCl_4 ; other suitable substances are Si-tetra-alkyls and hydrides of Si-alkyls.

Catalyst components that have yielded particularly interesting results are obtained from decomposition of MgCl_2 adducts with aliphatic or aromatic alcohols, phenols, amines or ammonia, the decomposition being effected with halogen containing compounds of Si or Sn, such as SiCl_4 and SnCl_4 , or with metallo-organic compounds of Al, such as Al-trialkyls.

Some examples of suitable Al metallo-organic compounds include Al-alkyls, for instance $\text{Al}(\text{i-Bu})_3$ and AlEt_3 ; the halides of Al-alkyls such as AlR_2Cl , AlRCl_2 , $\text{Al}_2\text{Et}_3\text{Cl}_3$, AlEt_2Br , $\text{Al}(\text{OEt})\text{EtCl}$, $\text{Al}(\text{OEt})\text{Et}_2$, and $\text{Al}(\text{i-Bu})_2\text{H}$. The preferred compounds are Al-triisooalkyls such as, for example, Al-triisobutyl.

Further useful metallo-organic compounds are Mg, Ca or Zn compounds, such as Grignard reagents, Mg monoalkoxides, Mg-dialkyl or Mg-diphenyl compounds, and Zn-monoalkyl or Zn-dialkyl compounds.

The amount of such reactive substance used for the decomposition generally exceeds 1 mole per g-atom of active hydrogen present in the adduct, and the decomposition reaction is usually conducted in a liquid phase, optionally in the presence of an inert hydrocarbon solvent. When the reactive substance is volatile it can be used in vapour phase.

The decomposition of said adducts of electron-donor compounds free from active hydrogen may be carried out with the metallo-organic compounds of metals belonging to Groups I to III of the Periodic Table, especially the metallo-organic compounds of Al, Zn, Mg and B. Preferred such compounds are:

AlR_3 , $\text{AlR}_{3-n}\text{X}_n$, MgR_2 , MgRX (Grignard), ZnRX , ZnR_2 , $\text{Br}_{3-n}\text{X}_n$ wherein: R = alkyl-, cycloalkyl-, aryl-radicals containing 1-20 C atoms, n less than 3, X = halogen, OR, H. The decomposition conditions are the same as those indicated for the adducts of donors containing active hydrogen atoms.

It is possible that not all the electron-donor compound is removed from the adduct is the reaction resulting in decomposition of the adduct: in this case any residual electron-donor compound which is free from active hydrogens can be used as electron-donor compound reactant (c) for the reaction with the halogenated Ti compound (a).

Halogenated Ti compounds (a) to be utilized for preparing the catalyst components according to this invention are, for example, the halogen-containing compounds of tetravalent Ti, such as TiCl_4 , TiBr_4 and Ti halogen-alcoholates. The reaction with the Ti compound is preferably conducted in an excess of the Ti liquid compound and the unreacted compound is separated at a temperature such that the amount of Ti compounds in the reaction product extractable with TiCl_4 at 80°C is lower than 20% by weight.

If TiCl_4 is employed as reagent and reaction medium, the reaction temperature is generally between 50° and the TiCl_4 boiling point, in particular between 90° and 135°C . It is possible to employ also higher temperatures when operating under increased pressure. The separation of excess TiCl_4 is conducted at temperatures higher than 80°C , preferably from 90° to 135°C and normally comprises filtration or sedimentation.

Catalyst components particularly suited to prepare catalysts provided with high activity and stereospecificity are prepared starting from adducts of MgCl_2 with alcohols according to the following procedure. The MgCl_2 adduct is reacted, either simultaneously or

consecutively, with the compound of Si or Sn or Sb and with the electron-donor compound, the reaction being carried out in an inert gas atmosphere, at a temperature ranging from the room temperature to the mixture boiling point and optionally in the presence of an inert solvent such as n-heptane. The resulting solid product is filtered, washed with n-heptane, dried under vacuum and finally reacted with TiCl_4 at a temperature comprised between 100° and 150°C, usually between 100 and 135°C, preferably at 130°C; once substantially all the unreacted TiCl_4 has been removed at a temperature higher than 80°C, the catalyst component is washed with n-heptane, usually at a temperature of at least 90°C, and dried under vacuum.

When the adduct decomposition is carried out with an aluminium-organic compound, in particular with an Al-trialkyl, the electron-donor compound not containing active hydrogen should be suitably reacted after the decomposition reaction, in order to prevent possible reactions between the electron-donor compound and the Al-alkyl, which reactions would destroy the electron-donor compound.

The decomposition product obtained from the adducts of Mg dihalides with electron-donor compounds either free from active hydrogen atoms or containing the same, may be combined with the (further) electron-donor compound free from active hydrogen before or during the reaction with the halogenated Ti compound. The total amount of electron-donor compound free from active hydrogens is preferably at least 0.1 and less than 0.5 moles per mole of Mg dihalide in the decomposition product.

The solid catalyst component containing a tetravalent Ti compound can be treated with a substance capable of reducing the Ti valence to values lower than 4, before being mixed with an organic Al compound to form the polymerization catalyst. For example, the catalytic component may be reacted with an Al-alkyl compound; the reduction product so obtained is then used to form the polymerization catalyst.

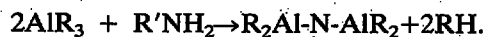
The electron-donor compounds c) can be any compounds free of active hydrogens which are capable of forming addition products with the Ti halogenated compounds. They can be the same as the ones used in the preparation of the adducts with Mg dihalides. Suitable compounds are for instance the alkyl, cycloalkyl or aryl esters of organic acids, in particular the esters of aromatic acids such as benzoic acid. Some examples of such esters are ethyl benzoate, ethyl *p*-methoxybenzoate, methyl *p*-toluate and ethyl *p*-butoxybenzoate. Other useful compounds are the ethers, such as for example di-*n*-butyl and diphenyl ether, or the ketones as benzophenone, the diamines as N,N,N',N'-tetramethylethylenediamine.

The catalysts for polymerizing alpha-olefins according to the present invention comprise the product obtained by mixing the following components:

- (A) an organic Al compound not containing halogen atoms directly bound to Al;
- (B) an organic electron-donor compound in such amount that from 10% to 95% of the compound (A) is combined with (B); and
- (C) the solid catalyst component containing Ti, as hereinbefore described.

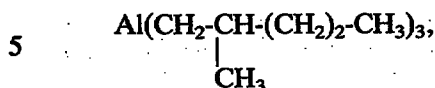
In such a polymerization catalyst, the Al/Ti molar ratio is higher than 10 and preferably ranges from 20 to 500. Compounds (A) and (B) are preferably mixed before contacting them with component (C). Components (A), (B) and (C) may also be combined simultaneously or component (A) may be added to component (C) before the reaction with (B).

The electron-donor compound used as component (B) can be any compound capable of reacting with the organic Al compound (A) to form complexes and/or substitution reaction products such as for example those obtained by reaction of an Al-trialkyl with an electron-donor compound containing active hydrogen atoms, as represented, for instance, by the following reaction:

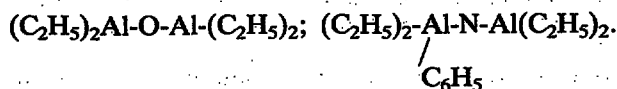


Some examples of electron-donor compounds employable as component (B) are amines, amides, ethers, thioethers, ketones, nitriles, phosphines, stibines, arsines, phosphoramides, aldehydes, esters, thioesters, alcoholates, amides and salts of organic acids and of metals of Groups I to IV of the Periodic Table. In the case of Al salts, they may be prepared in situ by reaction between component (A) and an organic acid. Preferred compounds are esters of organic and inorganic acids. Particularly suited are the esters of the aromatic acids, such as, for example, the alkyl esters of benzoic, *p*-methoxy benzoic, and *p*-toluic acids. Some examples of such esters are ethyl benzoate, ethyl *p*-methoxy benzoate, methyl and ethyl *p*-toluates and ethyl *p*-butoxy benzoate. Other examples of useful esters are: diethyl carbonate, ethyl pivalate, ethyl acetate, dimethyl maleate and alkyl or aryl silicates, in particular ethyl silicate $\text{Si}(\text{OC}_2\text{H}_5)_4$.

The Al organic compound employable as component (A) is preferably an Al-trialkyl compound such as, for example, Al-triethyl, Al-triisobutyl, Al-tripropyl,



or $\text{Al}(\text{C}_{12}\text{H}_{25})_3$. It is also possible to use Al organic compounds containing two or more Al atoms bound to one another through O-atoms or N-atoms. Some examples of such compounds are



The Al organic compounds described in Belgian Patent No. 842,866 represent further examples of useful compounds. Other employable compounds are Al-dialkyl hydrides, Al-dialkyl alkoxides and Al-alkyl sesquialkoxides such as sesquiethoxy Al-ethyl and sesquibutoxy Al-butyl. The organic Al compounds (A) can be used also in mixture with an Al alkylmonohalide used in quantity less than 1 mole per mole of compound (A).

The electron-donor compound not containing active hydrogen present in component (C) may be the same as or other than the compound not containing active hydrogen, employed as component (B).

The catalysts according to this invention are preferably employed in the polymerization of the alpha-olefins containing at least three carbon atoms or of mixtures of same with one another and/or with ethylene. They are particularly suited to prepare crystalline polymers and copolymers of propylene. Polymerization is conducted according to known methods either in the liquid phase, in the presence or absence of an inert hydrocarbon diluent such as hexane, heptane or cyclohexane, or in the gas phase. The polymerization is generally effected at a temperature within the range from 0°C to 150°C, preferably from 40° to 90°C, and at atmospheric pressure or above.

In the case of the preparation of crystalline copolymers of propylene it is preferable to polymerize the propylene until obtaining a homopolymer amount equal to 60-90% of the total polymeric composition. This polymerization step is then followed by one or more polymerization steps of ethylene-propylene mixtures or of ethylene alone, in such manner, that the polymerized ethylene content is comprised between 5 and 30% by weight, based on the composition. It is possible also to polymerize mixtures of propylene and ethylene in order to obtain copolymers containing less than 5% by weight of ethylene.

The following specific Examples are given to illustrate the present industrial invention. All of the solid catalyst components of the invention described in Examples 1 to 29 satisfy the requirements set out above in their definition for content of titanium compounds soluble in TiCl_4 , molar ratio Mg/Ti, proportion of electron donor compound (c) not containing active hydrogen and X-ray spectral characteristics.

Example 1

21.8 g of $\text{MgCl}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$ (58.7 millimoles), prepared by dissolving 1 mole of Mg chloride in 6 moles of ethanol at 70°C and by crystallizing the complex by cooling to 20°C, were reacted, in an inert gas atmosphere, with a solution containing 2.34 ml (15.6 m/moles) of ethyl benzoate in 200 ml of SiCl_4 for 18 hours at 60°C. The resulting white solid, after filtering, washing with 250 ml of anhydrous n-heptane and drying under vacuum, was treated with 100 ml of TiCl_4 at 130°C for 2 hours. After this time-period, TiCl_4 was removed by filtration at 130°C and an equal amount thereof was added again thereto, it was allowed to react for 2 hours at the same temperature, then it was filtered at 130°C to remove TiCl_4 and washed with n-heptane at 90°C until disappearance of the chloride ions in the filtrate. The solid dried under vacuum exhibited, on analysis, a titanium content of 1.43% by weight, a magnesium content of 18.70% by weight, a chlorine content of 65.2% by weight and ethyl benzoate content of 8% - 9% b.w.

The propylene polymerization test carried out by using such compound as catalytic component is reported in Table IV.

Examples 2, 3 and 4

The elemental analyses of the catalyst components prepared according to the procedure of example 1, but varying the molar ratio between MgCl_2 and ethyl benzoate, are reported on Table I.

The propylene polymerization tests effected by using such compounds as catalyst

12

components are reported in Table IV.

Examples 5 and 6

The elemental analyses of the catalyst components prepared according to the procedure of example 1, but varying the number of ethyl alcohol molecules coordinated with $MgCl_2$ in the starting adduct, are reported in Table II.

The propylene polymerization tests carried out by using such compounds as catalytic compounds are reported in Table IV.

Examples 7 and 8

The elemental analyses of the catalyst components prepared according to the procedure of example 1, but varying the type of alcohol coordinated with $MgCl_2$ in the starting adduct, are reported on Table III.

The propylene polymerization tests conducted by using such compounds as catalytic components are reported in Table IV.

TABLE I

Example	Mg/EB* molar ratio	% by weight of Ti	% by weight of Mg	% by weight of Cl
2	6	1.80	18.50	64.50
3	9	2.00	20.70	61.18
4	12	2.87	20.47	64.82

EB* = ethyl benzoate

TABLE II

Example	Starting complex	% b.wt. of Ti	% b.wt. of Mg	% b.wt. of Cl
5	$MgCl_2 \cdot 1.6$			
	EtOH*	1.00	23.60	63.12
6	$MgCl_2 \cdot 3.2$			
	EtOH*	1.87	18.53	64.56

EtOH* = ethanol.

TABLE III

Example	Starting complex	% b. wt. of Ti	% b. wt. of Mg	% b. wt. of Cl
7	$MgCl_2 \cdot 6CH_3OH$	2.08	20.32	63.50
8	$MgCl_2 \cdot 4C_4H_9OH$	0.96	22.17	64.97

Example 9

12.8 g of $MgCl_2 \cdot 6C_2H_5OH$ (34.5 m/moles), prepared as in example 1, were reacted in a nitrogen atmosphere with 95 ml of pure $SiCl_4$. The reaction mixture was heated to boiling and allowed to react for 16 hours.

Subsequently, 0.86 ml (5.75 m/moles) of ethyl benzoate were added and the whole was allowed to boil for further 2 hours. The resulting white solid, after having been filtered, repeatedly washed with n-heptane and dried under vacuum, was treated with 150 ml of

TiCl₄ at 130°C for 2 hours. TiCl₄ was then removed by hot filtration, an equal amount of fresh TiCl₄ was added once more thereto and the treatment was repeated for further 2 hours. After removal of TiCl₄, it was washed at 90°C with n-heptane until disappearance of the chloride ions in the filtrate.

5 The solid dried under vacuum exhibited the following composition: 5

Titanium = 2.39% by weight

10 Magnesium = 20.53% by weight 10

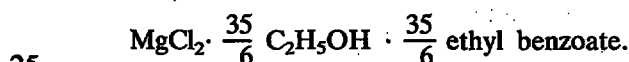
Chlorine = 62.2% by weight

Ethyl benzoate = 8% + 9% by weight

15 The propylene polymerization test carried out by using such compound as catalyst component is reported in Table IV. 15

Example 10

20 21.5 g of anhydrous MgCl₂ were dissolved in 200 ml of anhydrous ethanol. After addition of 5.65 ml of ethyl benzoate, the solution was reacted at 70°C for 1 hour. By evaporation under vacuum a white crystalline solid separated, which had the formula: 20



11.30 g of the compound described hereinbefore (30.5 m/moles) were reacted, in a nitrogen atmosphere, with 84 ml of pure SiCl₄.

The mixture was heated to boiling and left at such temperature for 18 hours.

30 The resulting white solid, after having been filtered, repeatedly washed with n-heptane and dried under vacuum, was treated with 150 ml of TiCl₄ at 130°C for 2 hours. 30

Successively TiCl₄ was removed by hot filtration, an equal amount of fresh TiCl₄ was added and the treatment was repeated for further 2 hours. After removal of TiCl₄, it was washed at 90°C with n-heptane until disappearance of the chloride ions in the filtrate.

35 The solid dried under vacuum had the following composition: 35

Titanium = 2.32 % by weight

40 Magnesium = 20.53 % by weight 40

Chlorine = 63.12 % by weight.

The propylene polymerization test carried out by using such compound as catalyst component is reported in Table IV.

Example 11

5.4 g of MgCl₂ · 3.8 C₂H₅OH (20 m/moles) were reacted in a nitrogen atmosphere with 120 ml of SiCl₄; it was heated at reflux for 16 hours.

50 The resulting white solid, after having been filtered, repeatedly washed with n-heptane and dried under vacuum, was treated with a solution containing 0.5 ml (3.3 m/moles) of ethyl benzoate at 150 ml of TiCl₄ preheated at 130°C. It was allowed to react at the same temperature for 4 hours. The solid was isolated by filtration, washed with n-heptane and dried under vacuum: on analysis it exhibited a per cent-content of Ti equal to 2.73, of Mg equal to 21.1 and of chlorine equal to 63.9. 50

55 The propylene polymerization test conducted by using such compound as catalyst component is reported in Table IV. 55

Example 12

60 7.3 g of MgCl₂ · 6C₂H₅OH were treated with SiCl₄ in vapour entrained by a nitrogen stream for 6 hours. The total amount of SiCl₄ employed corresponded to 400 ml. 2.2 g of the solid product so obtained were suspended in a solution containing, in 30 ml of n-heptane, 0.30 ml of ethyl benzoate, and were allowed to react under stirring for 3 hours at room temperature. 60

65 The liquid was removed and it was dried; then the isolated white solid was treated with 100 ml of TiCl₄ at 130°C for 2 hours. After removal of TiCl₄ by filtration, an equal amount 65

of fresh TiCl_4 was added and the treatment was repeated. After having removed the TiCl_4 , washing was carried out at 90°C with n-heptane until disappearance of the chloride ion in the filtrate.

The solid, once dried under vacuum, exhibited the following composition:

Ti = 3.96 % by weight

Mg = 18.90 % by weight

Cl = 59.08 % by weight.

The propylene polymerization test carried out by using such compound as catalyst component is reported in Table IV.

Example 13

15.7 g of $\text{MgCl}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$, prepared according to example 1, were introduced batchwise into a glass flask containing a boiling solution having the following composition : 200 ml of n-heptane, 177 ml of SiCl_4 , 1 ml of ethyl benzoate.

It was reacted to boiling for 16 hours.

The resulting white solid, after having been filtered, washed three times with 100 ml of n-heptane at 60°C and dried under vacuum, was treated twice with TiCl_4 according to the modalities illustrated in example 1.

The isolated product had the following composition:

Titanium = 1.39 %

Magnesium = 18.95 %

Chlorine = 64.80 %.

The propylene polymerization test carried out by using such compound as catalytic component is reported in Table IV.

Example 14

7.3 g of $\text{MgTiCl}_4(\text{OC}_2\text{H}_5)_2 \cdot 4\text{C}_2\text{H}_5\text{OH}$, prepared according to Belgian patent No. 840,058 (16.5 m/moles), were reacted in an inert gas atmosphere with a mixture of 50 ml of SiCl_4 and 0.83 ml (5.5 m/moles) of ethyl benzoate for 92 hours at 60°C .

The resulting solid, after having been filtered, washed with 200 ml of anhydrous n-heptane and dried under vacuum, was treated with 100 ml of TiCl_4 at 130°C for 2 hours.

After this time-period, TiCl_4 was removed by filtration and an equal amount of same was added again; it was allowed to react at the same temperature for 2 hours, then it was filtered in order to remove TiCl_4 and washed at 90°C with n-heptane until disappearance of the chloride ions in the filtrate. The solid dried under vacuum, exhibited on analysis a titanium content of 1.30 % by weight, a magnesium content of 21.20% by weight and a chlorine content of 62.90% by weight.

The propylene polymerization test carried out by using such compound as catalyst component is reported in Table IV.

Example 15

6.4 g of $\text{MgCl}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$ (24.6 m/moles) were allowed to react, in an inert gas atmosphere, with a solution containing 70 ml of SnCl_4 and 0.615 ml (4.1 m/moles) of ethyl benzoate for 20 hours at 70°C .

The resulting white solid, after having been filtered, washed with 250 ml of anhydrous n-heptane and dried under vacuum, was treated with 100 ml of TiCl_4 at 130°C for 2 hours. Successively, TiCl_4 was removed by hot filtration and an equal amount of same was added again; it was allowed to react at the same temperature for 2 hours, then it was filtered to remove TiCl_4 and washed at 90°C with n-heptane until disappearance of the chloride ions in the filtrate. The solid, dried under vacuum, exhibited on analysis a titanium content of 4.1 % by weight, a magnesium content of 19.05 % by weight and a chlorine content of 58.93% by weight.

The propylene polymerization test carried out by using such compound as catalyst component is reported on Table IV.

Example 16

5.3 g of $\text{MgCl}_2 \cdot 3.8 \text{C}_2\text{H}_5\text{OH}$ (19 m/moles) were reacted, in an inert gas atmosphere, with

a mixture consisting of 100 ml of antimony pentachloride and 0.49 ml (3.3 m/moles) of ethyl benzoate for 20 hours at 70°C.

The resulting white solid, after having been filtered, washed with 250 ml of anhydrous n-heptane and dried under vacuum, was treated with 100 ml of TiCl_4 at 130°C for 2 hours. After this time-period, TiCl_4 was removed by filtration and an equal amount of same was added again; it was reacted at the same temperature for 2 hours, then it was filtered to remove TiCl_4 and washed at 90°C with n-heptane until disappearance of the chloride ions in the filtrate. The solid dried under vacuum exhibited on analysis a titanium content of 2.30% by weight, a magnesium content of 20.47% by weight and a chlorine content of 63.10% by weight.

The propylene polymerization test carried out by using such compound as catalyst component is reported on Table IV.

Example 17

5.6 g of $\text{MgCl}_2 \cdot 3.8 \text{ C}_2\text{H}_5\text{OH}$ (21.4 m/moles) were added batchwise, at room temperature and under stirring, to 250 ml of a molar heptane solution of aluminium triisobutyl. After 1 hour it was heated to 80°C for 4 hours. It was filtered and washed with 200 ml of anhydrous n-heptane. The isolated solid was suspended in a solution of 0.54 ml (3.6 m/moles) of ethyl benzoate in 50 ml of n-heptane, and the resulting suspension was kept under stirring at room temperature for 2 hours.

The product was isolated by filtration and dried under vacuum. The resulting white solid was treated with 100 ml of TiCl_4 at 130°C for 2 hours. After this time-period, TiCl_4 was removed by filtration and an equal amount of same was added again; it was caused to react at the same temperature for 2 hours, then it was filtered to remove TiCl_4 and washed at 90°C with n-heptane until disappearance of the chloride ions in the filtrate. The solid, dried under vacuum, exhibited on analysis a titanium content of 2.05% by weight, a magnesium content of 21.25% by weight, a chlorine content of 59.3% by weight and ethyl benzoate about 7% b.w.

The propylene polymerization test carried out by using such compound as catalyst component is reported on Table IV.

Example 18

3.1 g of $\text{MgCl}_2 \cdot 6\text{NH}_3$ (15.7 m/moles) were added, at room temperature under stirring, to 270 ml of a molar heptane solution of aluminium triisobutyl.

After 1 hour it was heated to 80°C for 4 hours. It was filtered and the precipitate so obtained was washed with 200 ml of anhydrous n-heptane. The isolated solid was suspended in a solution of 0.39 ml of ethyl benzoate (2.6 m/moles) in 50 ml of n-heptane and the resulting suspension was kept under stirring at room temperature for 2 hours.

The insoluble product was isolated by filtration and dried under vacuum. The resulting white solid was treated with 100 ml of TiCl_4 at 130°C for 2 hours. After this time-period TiCl_4 was removed by filtration and an equal amount of same was added again; it was reacted at the same temperature for 2 hours, then it was filtered in order to remove TiCl_4 and it was washed at 90°C with n-heptane until disappearance of the chloride ions in the filtrate. The solid dried under vacuum exhibited on analysis a titanium content of 2.08% by weight, a magnesium content of 23.05% by weight and a chlorine content of 61.54% by weight.

The propylene polymerization test carried out by using such compound as catalyst component is reported in Table IV.

Example 19

2.93 g of $\text{MgCl}_2 \cdot 3.8 \text{ C}_2\text{H}_5\text{OH}$ (11 m/moles) were caused to react, in a nitrogen atmosphere, with a solution containing 10.5 ml (83 m/moles) of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ in 60 ml of n-heptane. It was reacted for 1 hour, then it was heated to 80°C for 3 hours; the precipitate obtained was filtered and washed with 200 ml of n-heptane.

The isolated solid was suspended in a solution of 0.27 ml of ethyl benzoate (1.8 m/moles) in 50 ml of n-heptane; and the resulting suspension was kept under stirring at room temperature for 2 hours. The insoluble product was isolated by filtration and dried under vacuum. The resulting white solid was treated with 100 ml of TiCl_4 at 130°C for 2 hours. After this time-period TiCl_4 was removed by filtration and an equal amount of same was added again; it was reacted at the same temperature for 2 hours, then it was filtered to remove TiCl_4 and washed at 90°C with n-heptane until disappearance of the chloride ions in the filtrate. The solid dried under vacuum exhibited on analysis a titanium content of 1.07% by weight, a magnesium content of 22.9% by weight and a chlorine content of 62.86% by weight.

The propylene polymerization test carried out by using such compound as catalyst

component is reported in Table IV.

Example 20

4.5 g of $\text{MgCl}_2 \cdot 2.5 \text{H}_2\text{O} \cdot 2.3 \text{C}_2\text{H}_5\text{OH}$ (18.3 m/moles) were added batchwise, at room temperature under stirring, to 200 ml of a molar heptane solution of $\text{Al}(\text{iso-C}_4\text{H}_9)_3$. After 1 hour it was heated to 80°C for 4 hours. It was filtered and washed with 200 ml of anhydrous n-heptane. The isolated solid was suspended in a solution of 0.46 ml (3.05 m/moles) of ethyl benzoate in 50 ml of n-heptane and the resulting suspension was kept under stirring at room temperature for 2 hours. The product was isolated by filtration and dried under vacuum. The resulting white solid was treated with 100 ml of TiCl_4 at 130°C for 2 hours. After this time-period TiCl_4 was removed by filtration and an equal amount of same was added again; it was reacted at the same temperature for 2 hours, then it was filtered to remove TiCl_4 and washed at 90°C with n-heptane until disappearance of the chloride ions in the filtrate. The solid dried under vacuum exhibited on analysis a titanium content of 2.06% by weight, a magnesium content of 16.39% by weight and a chlorine content of 60.4% by weight. The propylene polymerization test conducted by using such compound as catalyst component is reported in Table IV.

Example 21

The complex $\text{MgCl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ was prepared by co-grinding at 30°C for 40 hours in a steel cylindrical vibrating mill, having a height of 80 mm and a diameter of 125 mm, charged with 150 steel balls of 10 mm diameter, 92 g of anhydrous MgCl_2 (0.97 moles) and 56.5 ml of anhydrous ethyl alcohol (0.97 moles). 8.5 g of the complex so obtained were treated with a solution containing 1.5 ml of ethyl benzoate in 50 ml of SiCl_4 at 60°C for 40 hours. The filtered product, after washing with n-heptane and drying under vacuum, was treated with 150 ml of TiCl_4 at 130°C for 2 hours under stirring. After removal of TiCl_4 by filtration, the treatment was repeated with the same amount of TiCl_4 . The product, after filtration, -- washing at 90°C with n-heptane until disappearance of the chloride ions from the filtrate, and drying under vacuum, exhibited the following composition :

Ti	= 1.12%
Mg	= 20.82%
Cl	= 63.3%.

The polymerization test carried out by using such compound as catalyst component is reported in Table IV.

Example 22

19.6 g of $\text{MgCl}_2 \cdot (\text{C}_4\text{H}_9)_2\text{O}$ (82 m/moles) were added batchwise, at room temperature and under stirring, to 328 ml of a molar heptane solution of aluminum tri-isobutyl. After 1 hour it was heated to 80°C and kept at such temperature for 6 hours. It was filtered and washed with 300 ml of anhydrous n-heptane. The isolated solid was suspended in 137 ml of a heptane solution containing 0.1 mole of ethyl benzoate, and it was kept under stirring at room temperature for 2 hours. The product was isolated by filtration and dried under vacuum. The resulting white solid was treated with 200 ml of TiCl_4 at 130°C for 2 hours. After this time-period, TiCl_4 was removed by filtration and an equal amount of same was added again; it was allowed to react at the same temperature for 2 hours, whereupon it was filtered to remove TiCl_4 and washed at 90°C with n-heptane until disappearance of the chlorine ions in the filtrate. The solid, dried under vacuum, exhibited on analysis a titanium content of 1.54% by weight, a magnesium content of 21.35% by weight and a chlorine content of 67.9% by weight. The propylene polymerization test carried out by using such compound as catalytic component is reported in table IV.

Example 23

17.7 g of $\text{MgCl}_2 \cdot \text{CH}_3\text{COOC}_2\text{H}_5$ (97 m/moles) were added, in small batches, at room temperature and under stirring, to 290 ml of a molar heptane solution of aluminium tri-isobutyl. After 1 hour it was heated to 80°C and kept at such temperature for 6 hours. It was filtered and then washed with 300 ml of anhydrous n-heptane. The isolated solid was suspended in 162 ml of a heptane solution containing 0.1 mole of ethyl benzoate, and kept under stirring at room temperature for 2 hours. The product was isolated by filtration and dried under vacuum. The resulting white solid was treated with 200 ml of TiCl_4 at 130°C for 2 hours. After this time, TiCl_4 was removed by filtration and an equal amount thereof was added again; it was allowed to react at the same temperature for 2 hours, whereupon it was filtered to remove TiCl_4 and washed at 90°C

with n-heptane until disappearance of chlorine ions in the filtrate. The solid, dried under vacuum, exhibited on analysis a titanium content of 1.45% by weight, a magnesium content of 20.05% by weight and a chlorine content of 65.7% by weight.

The propylene polymerization test conducted by using such compound as catalyst component is reported in table IV.

Example 24

15.3 g of $\text{MgCl}_2 \cdot \text{CH}_3\text{COCH}_3$ (100 m/moles) were added, in small batches, to 250 ml of a molar heptane solution of aluminium triethyl, at room temperature and under stirring. After 1 hour it was heated to 80°C and kept at such temperature for 6 hours. It was filtered and washed with 300 ml of anhydrous n-heptane. The isolated solid was suspended in 170 ml of a heptane solution of 0.1 mole of ethyl benzoate, and kept under stirring at room temperature for 2 hours. The product was isolated by filtration and dried under vacuum. The resulting white solid was treated with 200 ml of TiCl_4 at 130°C for 2 hours. After this time TiCl_4 was removed by filtration and an equal amount thereof was added again; it was allowed to react at the same temperature for 2 hours, then it was filtered to remove TiCl_4 and washed at 90°C with n-heptane until disappearance of chlorine ions in the filtrate. The solid, dried under vacuum, exhibited on analysis a titanium content of 2.22% by weight, a magnesium content of 18.98% by weight and a chlorine content of 62.47% by weight.

The propylene polymerization test carried out by using such compound as catalytic component is reported in table IV.

Example 25

13.6 g of $\text{MgCl}_2 \cdot \text{CH}_3\text{CN}$ (100 m/moles) were added, in small batches to 250 ml of a molar heptane solution of aluminium tri-isobutyl, at room temperature and under stirring. After 1 hour it was heated to 80°C and kept at such temperature for 2 hours. It was filtered and washed with 300 ml of anhydrous n-heptane. The isolated solid was suspended in 170 ml of a heptane solution of 0.1 mole of ethyl benzoate and kept under stirring at room temperature for 2 hours.

The product was isolated by filtration and dried under vacuum. The resulting white solid was treated with 200 ml of TiCl_4 at 130°C for 2 hours. After this time, TiCl_4 was removed by filtration and an equal amount thereof was added again; it was allowed to react at the same temperature for 2 hours, whereupon it was filtered to remove TiCl_4 and washed at 90°C with n-heptane until disappearance of chlorine ions in the filtrate. The solid, dried under vacuum, exhibited on analysis a titanium content of 2.17% by weight, a magnesium content of 18.58% by weight and a chlorine content of 61.75 % by weight.

The propylene polymerization test carried out by using such compound as catalyst component is reported in table IV.

Example 26

10.6 g of $\text{MgCl}_2 \cdot 2\text{C}_2\text{H}_5\text{N}$ (42 m/moles) were added, in small batches to 200 ml of a molar heptane solution of aluminium tri-isobutyl, at room temperature and under stirring. After 1 hour it was heated to 80°C and kept at such temperature for 2 hours. It was filtered and washed with 300 ml of anhydrous n-heptane. The isolated solid was suspended in 70 ml of a heptane solution of 0.1 mole of ethyl benzoate and kept under stirring at room temperature for 2 hours.

The product was isolated by filtration and dried under vacuum. The resulting white solid was treated with 200 ml of TiCl_4 at 130°C for 2 hours. After this time, TiCl_4 was removed by filtration and an equal amount thereof was added again; it was allowed to react at the same temperature for 2 hours, whereupon it was filtered to remove TiCl_4 and washed at 90°C with n-heptane until disappearance of chlorine ions in the filtrate. The solid, dried under vacuum, exhibited on analysis a titanium content of 1.21% by weight, a magnesium content of 21.27% by weight and a chlorine content of 68.03 % by weight.

The propylene polymerization test carried out by using such compound as catalyst component is reported in table IV.

Example 27

49 m/moles of $\text{MgBr}_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ were added, in small batches to 110 ml of a molar heptane solution of aluminium tri-isobutyl, at room temperature and under stirring. After 1 hour it was heated to 80°C and kept at such temperature for 2 hours. It was filtered and washed with 300 ml of anhydrous n-heptane. The isolated solid was suspended in 80 ml of a heptane solution of 0.1 mole of ethyl benzoate and kept under stirring at room temperature for 2 hours.

The product was isolated by filtration and dried under vacuum. The resulting white solid was treated with 200 ml of TiCl_4 at 130°C for 2 hours. After this time, TiCl_4 was removed by

filtration and an equal amount thereof was added again; it was allowed to react at the same temperature for 2 hours, whereupon it was filtered to remove TiCl_4 and washed at 90°C with n-heptane until disappearance of chlorine ions in the filtrate. The solid, dried under vacuum, exhibited on analysis a titanium content of 0.72% by weight, a magnesium content of 15.93% by weight.

The propylene polymerization test carried out by using such compound as catalyst component is reported in table IV.

Example 28

44 m/moles of $\text{MgCl}_2 \cdot 2 \gamma$ -butyrolactone were added, in small batches to 250 ml of a molar heptane solution of aluminium tri-isobutyl, at room temperature and under stirring. After 1 hour it was heated to 80°C and kept at such temperature for 2 hours. It was filtered and washed with 300 ml of anhydrous n-heptane. The isolated solid was suspended in 73 ml of a heptane solution of 0.1 mole of ethyl benzoate and kept under stirring at room temperature for 2 hours.

The product was isolated by filtration and dried under vacuum. The resulting white solid was treated with 200 ml of TiCl_4 at 130°C for 2 hours. After this time, TiCl_4 was removed by filtration and an equal amount thereof was added again; it was allowed to react at the same temperature for 2 hours, whereupon it was filtered to remove TiCl_4 and washed at 90°C with n-heptane until disappearance of chlorine ions in the filtrate. The solid, dried under vacuum, exhibited on analysis a titanium content of 1.62% by weight, a magnesium content of 19.02% by weight and a chlorine content of 61.12 % by weight.

The propylene polymerization test carried out by using such compound as catalyst component is reported in table IV.

Example 29

8.3 g (30.4 m/moles) of $\text{MgCl}_2 \cdot 2\text{CH}_3\text{CON}(\text{CH}_3)_2$ were added, in small batches to 150 ml of a molar heptane solution of aluminium tri-isobutyl, at room temperature and under stirring. After 1 hour it was heated to 80°C and kept at such temperature for 2 hours. It was filtered and washed with 300 ml of anhydrous n-heptane. The isolated solid was suspended in 51 ml of a heptane solution of 0.1 mole of ethyl benzoate and kept under stirring at room temperature for 2 hours.

The product was isolated by filtration and dried under vacuum. The resulting white solid was treated with 200 ml of TiCl_4 at 130°C for 2 hours. After this time, TiCl_4 was removed by filtration and an equal amount thereof was added again; it was allowed to react at the same temperature for 2 hours, whereupon it was filtered to remove TiCl_4 and washed at 90°C with n-heptane until disappearance of chlorine ions in the filtrate. The solid, dried under vacuum, exhibited on analysis a titanium content of 3.95% by weight, a magnesium content of 13.29% by weight and a chlorine content of 57.16 % by weight.

The propylene polymerization test carried out by using such compound as catalyst component is reported in table IV.

Comparative Example

15.7 g of $\text{MgCl}_2 \cdot \frac{35}{6} \text{C}_2\text{H}_5\text{OH} \cdot \frac{1}{6}$ of ethyl benzoate,

prepared as described in example 10, were evaporated under vacuum at 50°C for 3 hours.

The product so obtained was treated with 150 ml of TiCl_4 at 130°C for 2 hours. TiCl_4 was then removed by hot filtration, and an equal amount of fresh TiCl_4 was added, repeating the treatment for further 2 hours.

Once TiCl_4 had been removed, the product was washed at 90°C with n-heptane until disappearance of the chloride ions in the filtrate. The solid, dried under vacuum, exhibited on analysis a titanium content equal to 8.2% by w. and an ethylbenzoate content of 3.8% by w.

The propylene polymerization test carried out by using such compound as catalyst component is reported in Table IV.

PROPYLENE POLYMERIZATION IN A SOLVENT

- Conditions A

5 millimoles of an aluminium trialkyls mixture, having the following composition of the gases (% by volume) after hydrolysis:

ethane	=	9
isobutane	=	49.4
n-butane	=	41.2
propane	=	0.16
isobutene	=	0.24

were reacted at room temperature with 1.25 millimoles of methyl *para*-toluate in 80 ml of n-heptane (anhydrous and desulphurized) for 5 minutes.

50 ml of such solution were contacted with a proper amount of the catalyst component prepared according to the examples described hereinbefore.

The remaining 30 ml were diluted to 1000 ml with n-heptane and introduced, under a nitrogen pressure, into a steel autoclave, having a capacity of 3000 ml, equipped with anchor magnetic stirrer and thermometer, thermoregulated at 40°C, whereinto propylene was made to flow.

In the same way, the catalytic component suspension was then introduced thereinto. After closing of the autoclave, hydrogen was added up to a partial pressure of 0.1 atm., then it was heated to 60°C under simultaneous feeding of propylene up to a total pressure of 5 atmospheres. Such pressure was kept constant throughout the polymerization by going on feeding the monomer.

After 4 hours polymerization was stopped and polypropylene was isolated by treatment with methanol and acetone.

The results of the polymerization tests conducted under these conditions are reported in Table IV.

- Conditions B

1.25 millimoles of the aluminium trialkyls mixture described under Conditions A were reacted for 5 minutes at room temperature with 0.37 millimoles of methyl *para*-toluate in 80 ml of (anhydrous desulphurized) n-hexane.

50 ml of such solution were contacted with a suitable amount of the catalyst component prepared according to the examples described hereinbefore.

The remaining 30 ml were diluted to 500 ml with n-hexane and introduced, under a nitrogen pressure, into a steel autoclave having a capacity of 1000 ml, equipped with anchor magnetic stirrer and thermometer, thermoregulated at 40°C, whereinto propylene was made to flow.

Successively, the catalyst component suspension was introduced thereinto and the subsequent polymerisation procedure was as described under Conditions A.

- Conditions C

1.25 millimoles of aluminium triisobutyl were reacted for 5 minutes at room temperature with 0.25 millimoles of methyl *para*-toluate in 80 ml of (anhydrous desulphurized) n-hexane. 50 ml of such solution were contacted with a proper amount of the catalyst component prepared according to the examples described hereinbefore.

The remaining 30 ml were diluted to 500 ml with n-hexane and introduced, under a nitrogen pressure, into a steel, 1-liter autoclave, equipped with anchor magnetic stirrer and thermometer, thermoregulated at 40°C, whereinto propylene was made to flow. Subsequently the catalyst component suspension was introduced thereinto and the subsequent polymerisation procedure was as described under Conditions A.

- Conditions D

2.15 millimoles of aluminium triethyl were reacted for 5 minutes at room temperature with 0.64 millimoles of methyl *para*-toluate in 80 ml of (anhydrous desulphurized) n-hexane.

50 ml of such solution were contacted with a suitable amount of the catalyst component prepared according to the examples described hereinbefore. The remaining 30 ml were diluted to 500 ml with n-hexane and introduced, under a nitrogen pressure, into a steel autoclave, having a 1 liter capacity, equipped with anchor magnetic stirrer and

thermometer, thermoregulated at 40°C, whereinto propylene was made to flow.

The catalyst component suspension was then introduced thereinto and the subsequent polymerisation procedure was as described under Conditions A.

5 - *Conditions E*

2.15 millimoles of aluminium triethyl were reacted for 5 minutes at room temperature with 0.64 millimoles of ethyl para-anisate in 80 ml of (anhydrous desulphurized) n-hexane.

50 ml of such solution were contacted with a suitable amount of the catalyst component prepared according to the examples described hereinbefore.

The remaining 30 ml were diluted to 500 ml with n-hexane and introduced, under a nitrogen pressure, into a steel autoclave equipped with anchor magnetic stirrer and thermometer, thermoregulated at 40°C, whereinto propylene was made to flow.

The catalyst component suspension was then introduced thereinto and the subsequent polymerisation procedure was as described under Conditions A.

- *Conditions F*

1.25 millimoles of the aluminium trialkyls mixture described under Conditions A were reacted for 5 minutes at room temperature with 0.37 millimoles of methyl para-toluate in 80 ml of (anhydrous desulphurized) n-hexane.

50 ml of such solution were contacted with a suitable amount of the catalyst component prepared according to the examples described hereinbefore.

The remaining 30 ml were diluted to 500 ml with n-hexane and were introduced, under a nitrogen pressure, into a steel autoclave having a capacity of 1000 ml, equipped with anchor magnetic stirrer and thermometer, thermoregulated at 40°C, whereinto propylene was made to flow.

In the same way the catalyst component suspension was then introduced thereinto. After closing of the autoclave, hydrogen was added up to a partial pressure of 0.2 atm., then it was heated to 60°C, feeding simultaneously propylene up to a total pressure of 9 atmospheres.

Such pressure was kept constant throughout the polymerization by going on feeding the monomer.

After 4 hours polymerization was stopped and polypropylene was isolated by treatment with methanol and acetone. The results of the polymerization tests conducted under these are reported in Table IV.

- *Conditions G*

1.25 millimoles of aluminium triisobutyl were reacted for 5 minutes at room temperature with 0.25 millimoles of methyl para-toluate in 80 ml of (anhydrous desulphurized) n-hexane. 50 ml of such solution were contacted with a suitable amount of the catalyst component prepared according to the examples described hereinbefore.

The remaining 30 ml were diluted to 500 ml with n-hexane and introduced, under a nitrogen pressure, into a steel 1000-ml autoclave, equipped with anchor magnetic stirrer and thermometer, thermoregulated at 40°C, whereinto propylene was made to flow.

In the same way the catalyst component suspension was then introduced thereinto. After closing of the autoclave, hydrogen was added up to a partial pressure of 0.1 atm., then it was heated to 50°C under simultaneous feeding of propylene up to a total pressure of 5 atmospheres. Such pressure was kept constant throughout the polymerization by going on feeding the monomer.

After 4 hours polymerization was stopped and polypropylene was isolated by means of treatment with methanol and acetone. The results of the polymerization tests conducted under these conditions are reported in Table IV.

- *Conditions H*

1.25 millimoles of aluminium triisobutyl were reacted for 5 minutes at room temperature with 0.25 millimoles of methyl para-toluate in 80 ml of (anhydrous desulphurized) n-hexane. 50 ml of such solution were contacted with a proper amount of the catalyst component prepared according to the examples described hereinbefore.

The remaining 30 ml were diluted to 500 ml with n-hexane and introduced, under a nitrogen pressure, into a steel autoclave having a 1000 ml capacity, equipped with anchor magnetic stirrer and thermometer, thermoregulated at 40°C, whereinto propylene was made to flow.

In the same way the catalyst component suspension was introduced thereinto. After having closed the autoclave, hydrogen was added up to a partial pressure of 0.1 atm., then it was heated to 70°C under simultaneous feeding of propylene up to a total pressure of 5 atmospheres. Such pressure was kept constant throughout the polymerization by going on

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feeding the monomer.

After 4 hours polymerization was stopped and polypropylene was isolated by treatment with methanol and acetone.

5 The results of the polymerization tests conducted under these conditions are reported in Table IV. 5

Propylene polymerization in liquid monomer

10 A suitable amount of the catalyst component prepared according to any of the examples hereinbefore was suspended in a solution containing, in 50 ml of n-heptane, 5 m/moles of aluminium trialkyl and 1.75 m/moles of methyl *para*-toluate. Said suspension was introduced, under an argon pressure, into a steel autoclave having a 3000 ml capacity, equipped with anchor magnetic stirrer and thermometer, thermoregulated at 60°C and containing 600 g of propylene and hydrogen for a partial pressure of 0.2 atmospheres. 10

15 After 4 hours the reaction was stopped by removal of not polymerized monomer, isolating the polypropylene obtained. The results of the polymerization tests conducted under these are reported in Table IV. 15

Propylene polymerization in the gas phase

20 50 g of thoroughly dry polyethylene in powder, along with a suspension containing, in 50 ml of n-pentane, a suitable amount of the catalyst component prepared according to the examples described hereinbefore, besides 5 millimoles of aluminium triisobutyl and 1.25 millimoles of methyl *para*-toluate were introduced into a stainless steel autoclave having a 2000 ml capacity, equipped with helical screw stirrer and thermoregulated at 60°C. After discharge of the n-pentane under vacuum, 0.2 atmospheres of hydrogen and propylene up to a total pressure of 15 atmospheres were added. Such pressure was kept constant throughout the polymerization by continuously feeding the monomer. After 4 hours the polymerization was stopped and the obtained polypropylene was isolated. 25

The results of the polymerization tests conducted under these are reported on Table IV.

TABLE IV

Catalyst Component		Polymerization Conditions		Polymer		Yield g of polymer/ g of Ti
Example	mg.	% of Ti		Product g.	η (dl/g.) Heptane re- sidue* (%)	
1	34	1.43	C	175	1.78	372,000
1	45	1.43	B	185	2.03	290,000
1	78	1.43	Gas Phase	195	2.34	175,000
2	32	1.87	C	123	1.79	200,000
3	29	2.00	C	180	2.21	310,000
4	41	2.87	C	160	1.77	136,000
5	100	1.00	C	175	1.65	175,000
6	39	1.80	C	141	1.80	200,000
7	40	2.08	C	130	1.75	156,000
8	82	0.96	C	100	1.80	127,000
9	38	2.39	C	205	2.27	225,000
9	45	2.39	G	110	2.13	102,000
9	43	2.39	H	125	2.28	123,000
9	23	2.39	F	195	1.85	360,000
9	43	2.39	D	130	1.88	126,000
9	35	2.39	E	124	1.90	147,000
9	25	2.39	Liquid Monomer	290	4.0	485,000

* Residue of the extraction with boiling n-heptane for 3 hours.

TABLE IV (Continuation)

Catalyst Component		Polymerization Conditions		Polymer		Heptane residue (%)	Yield g. of polymer/g. of Ti
Example	mg.	% of Ti		Product g.	η (dl/g.)		
10	32	2.32	C	173	2.06	90.1	234,000
11	86	2.73	A	200	2.31	93.5	85,000
12	96	3.96	A	510	2.09	87.5	134,000
13	43	1.39	C	70	2.28	90.7	117,000
14	94	1.30	A	165	1.80	89.4	135,000
15	95	4.10	A	680	2.51	89.5	173,000
16	72	2.30	A	135	2.12	88.3	82,000
17	95	2.05	A	730	2.86	93.7	375,000
18	94	2.08	A	550	2.45	90.4	282,000
19	47	1.07	C	48	2.20	89.0	96,000
20	84	2.06	A	150	2.28	92.5	87,000
21	93	1.12	A	85	2.06	92.0	84,000

TABLE IV (Continuation)

Catalyst Component		Polymerization		Polymer		Yield g. of polymer /g. of Ti	
Example	mg.	% of Ti		Product g.	Heptane re- sidue (%)		
22	42	1.54	A	160	1.78	88.4	246,000
23	55	1.45	A	175	1.92	89	220,000
24	102	2.22	A	320	1.64	86.2	145,000
25	70	2.17	A	80	1.50	88	53,000
26	58	1.21	A	140	1.73	87	200,000
27	108	0.72	A	150	1.52	83.2	193,000
28	69	1.62	A	135	1.55	86.2	120,000
29	95	3.95	A	155	1.68	91.5	41,000
compara- tive ex- ample	34	8.2	C	130	1.61	69.2	46,500



(28)

Attention is drawn to Patents 1,452,314, 1,433,537, 1,492,618, 1,505,315 and 1,502,886 all in the name of Mitsui Petrochemical Industries Ltd., all of which claim a catalyst composition suitable for use in the polymerisation of olefins and containing an organometallic compound of a metal of Groups I-III of the Periodic Table and a solid component which is obtained by reaction of (i) a magnesium dihalide, (ii) an electron donor compound, (iii) an organometallic compound of Groups I to III of the Periodic Table or a halogen or hydrocarbyl compound of tin or silicon and (iv) a titanium compound.

WHAT WE CLAIM IS:

1. A solid catalyst component for polymerizing alpha-olefins containing at least three carbon atoms, comprising the product of reaction of:

(a) a halogenated Ti compound soluble in hydrocarbons,

(b) a product containing Mg dihalide selected from Mg dichloride and Mg dibromide obtained by decomposition of an adduct of the Mg dihalide and an electron-donor compound which is an organic electron-donor compound or ammonia, such electron-donor compound being present in the adduct in an amount of at least 0.5 moles per mole of Mg dihalide, the decomposition of the adduct having been carried out with substances, other than Ti compounds, capable of reacting with the electron-donor compound of the adduct, selected from amongst the metallo-organic compounds of metals belonging to groups I to III of the Periodic Table and, in the case of an electron-donor compound having active hydrogen, also from amongst the halogen-containing compounds of Si, Sn and Sb, the halides of Al and B, and Si-tetra-alkyls and hydrides of Si-alkyls, and

(c) an electron-donor compound not containing active H atoms, which compound (c) may be pre-reacted with (a), or with (b) before reaction of (a) with (b), or may be present in (b) with the provisos:

that in said catalyst component the content of titanium compounds soluble in TiCl_4 at 80°C is less than 20% by weight with respect to the total content of titanium compounds and reckoned as elemental titanium;

that the molar ratio Mg/Ti in the catalyst component is between 5 and 100;

that the proportion of compound (c) present in the catalyst component is within the range from 0.4 to 3.5 moles per g. atom of Ti;

and furthermore that in the X-ray spectrum of said decomposition product (b), the most intense line appearing in X-ray spectrum of Mg dichloride and Mg dibromide of normal type is substantially absent and there is present a halo line having its intensity maximum shifted with respect to the position of said most intense line.

2. A catalyst component according to claim 1, in which the organic electron-donor compound of the Mg adduct is an aliphatic or aromatic alcohol a thio alcohol, a phenol, a primary or secondary amine, an amide, or an aliphatic or aromatic carboxylic acid.

3. A catalyst component according to claim 1 or 2, in which the decomposition of an adduct of the Mg dihalide with an electron donor compound having active hydrogen has been carried out with SiCl_4 or SnCl_4 .

4. A catalyst component according to claim 1 or 2 in which the decomposition of the adduct has been carried out by an Al-triisalkyl.

5. A catalyst component according to claim 1 or 2 in which the adduct of the Mg dihalide contains in chemically combined form a halogen-containing Ti compound, and alkyl silicate, or an Al alcoholate.

6. A catalyst component according to any one of the preceding claims, in which the electron-donor compound (c) not containing active hydrogen is an ester of an aromatic acid, or an aliphatic or aromatic ether.

7. A catalyst component according to claim 6, in which the electron-donor compound (c) is a benzoic acid ester.

8. A catalyst component according to any one of the preceding claims, wherein the total amount of electron-donor compound not containing active hydrogen present in the catalyst component is within the range from 0.1 to 0.5 moles per mole of the Mg dihalide in said decomposition product.

9. A catalyst component according to any one of the preceding claims, in which the amount of Ti compound insoluble in TiCl_4 at 80°C is lower than 4% by weight expressed as elemental titanium.

10. A catalyst component according to any one of the preceding claims in which the Ti compound (a) is TiCl_4 .

11. A catalyst component according to claim 1 substantially as described in any one of the foregoing Examples 1 to 22.

12. A catalyst component according to claim 1 substantially as described in any one of the foregoing Examples 23 to 31.

13. A process for preparing a catalyst component according to claim 1, which process

Attention is drawn to Patents 1,452,314; 1,433,537; 1,492,618; 1,505,315 and 1,502,886 all in the name of Mitsui Petrochemical Industries Ltd., all of which claim a catalyst composition suitable for use in the polymerisation of olefins and containing an organometallic compound of a metal of Groups I-III of the Periodic Table and a solid component which is obtained by reaction of (i) a magnesium dihalide, (ii) an electron donor compound, (iii) an organometallic compound of Groups I to III of the Periodic Table or a halogen or hydrocarbyl compound of tin or silicon and (iv) a titanium compound.

WHAT WE CLAIM IS:

1. A solid catalyst component for polymerizing alpha-olefins containing at least three carbon atoms, comprising the product of reaction of:
 - (a) a halogenated Ti compound soluble in hydrocarbons,
 - (b) a product containing Mg dihalide selected from Mg dichloride and Mg dibromide obtained by decomposition of an adduct of the Mg dihalide and an electron-donor compound which is an organic electron-donor compound or ammonia, such electron-donor compound being present in the adduct in an amount of at least 0.5 moles per mole of Mg dihalide, the decomposition of the adduct having been carried out with substances, other than Ti compounds, capable of reacting with the electron-donor compound of the adduct, selected from amongst the metallo-organic compounds of metals belonging to groups I to III of the Periodic Table and, in the case of an electron-donor compound having active hydrogen, also from amongst the halogen-containing compounds of Si, Sn and Sb, the halides of Al and B, and Si-tetra-alkyls and hydrides of Si-alkyls, and
 - (c) an electron-donor compound not containing active H atoms, which compound (c) may be pre-reacted with (a), or with (b) before reaction of (a) with (b), or may be present in (b) with the provisos:
 - that in said catalyst component the content of titanium compounds soluble in TiCl_4 at 80°C is less than 20% by weight with respect to the total content of titanium compounds and reckoned as elemental titanium;
 - that the molar ratio Mg/Ti in the catalyst component is between 5 and 100;
 - that the proportion of compound (c) present in the catalyst component is within the range from 0.4 to 3.5 moles per g. atom of Ti;
 - and furthermore that in the X-ray spectrum of said decomposition product (b), the most intense line appearing in X-ray spectrum of Mg dichloride and Mg dibromide of normal type is substantially absent and there is present a halo line having its intensity maximum shifted with respect to the position of said most intense line.
2. A catalyst component according to claim 1, in which the organic electron-donor compound of the Mg adduct is an aliphatic or aromatic alcohol a thio alcohol, a phenol, a primary or secondary amine, an amide, or an aliphatic or aromatic carboxylic acid.
3. A catalyst component according to claim 1 or 2, in which the decomposition of an adduct of the Mg dihalide with an electron donor compound having active hydrogen has been carried out with SiCl_4 or SnCl_4 .
4. A catalyst component according to claim 1 or 2 in which the decomposition of the adduct has been carried out by an Al-triisalkyl.
5. A catalyst component according to claim 1 or 2 in which the adduct of the Mg dihalide contains in chemically combined form a halogen-containing Ti compound, and alkyl silicate, or an Al alcoholate.
6. A catalyst component according to any one of the preceding claims, in which the electron-donor compound (c) not containing active hydrogen is an ester of an aromatic acid, or an aliphatic or aromatic ether.
7. A catalyst component according to claim 6, in which the electron-donor compound (c) is a benzoic acid ester.
8. A catalyst component according to any one of the preceding claims, wherein the total amount of electron-donor compound not containing active hydrogen present in the catalyst component is within the range from 0.1 to 0.5 moles per mole of the Mg dihalide in said decomposition product.
9. A catalyst component according to any one of the preceding claims, in which the amount of Ti compound insoluble in TiCl_4 at 80°C is lower than 4% by weight expressed as elemental titanium.
10. A catalyst component according to any one of the preceding claims in which the Ti compound (a) is TiCl_4 .
11. A catalyst component according to claim 1 substantially as described in any one of the foregoing Examples 1 to 22.
12. A catalyst component according to claim 1 substantially as described in any one of the foregoing Examples 23 to 31.
13. A process for preparing a catalyst component according to claim 1, which process

comprises reacting the adduct of the Mg dihalide with the substance reactive with the electron-donor compound, in suspension in a liquid phase, to decompose the adduct, separating the solid product from the liquid phase of the reaction product, reacting the solid product with the halogenated Ti compound (a), and separating the resultant solid product of this reaction between the halogenated Ti compound (a) and the decomposition product of the Mg dihalide adduct from the liquid phase of the reaction medium at a temperature higher than 80°C the decomposition reaction and/or the reaction with the Ti compound (a) being conducted in the presence of an electron-donor compound not containing active hydrogen when such compound is not present in the starting adduct.

14. A process according to claim 13 wherein the solid product of the reaction of the halogenated Ti compound (a) with the decomposition product of the Mg dihalide adduct is removed from substantially all the liquid phase at a temperature higher than 80°C, and the solid product is washed with n-heptane at a temperature of at least 90°C until the disappearance of chloride ions from the washings.

15. A process according to claim 13, in which an adduct of $MgCl_2$ with an aliphatic alcohol is reacted in suspension in the liquid phase with $SiCl_4$ or $SnCl_4$; the solid product is separated from the reaction liquid phase and reacted with $TiCl_4$ in excess at a temperature ranging from 100° to 135°C, the unreacted $TiCl_4$ being separated at a temperature higher than 80°C.

16. A process according to claim 13 substantially as described in any one of the foregoing Examples 1 to 21.

17. A process according to claim 13 substantially as described in any one of the foregoing Examples 22 to 29.

18. A catalyst component produced by a process according to any one of claims 13 to 15 and 17.

19. A catalyst component produced by a process claimed in claim 16.

20. A catalyst for polymerisation of alphaolefins containing at least three carbon atoms, comprising the product obtained by mixing the following components:

(A) an organic Al compound not containing halogen atoms directly bound to Al;
(B) an organic electron-donor compound in such amount that from 10% to 95% of the compound (A) is combined with the electron-donor compound (B); and
(C) a catalyst component as defined in any of claims 1 to 10, 12 and 18, the Al:Ti molar ratio in said catalyst being higher than 10:1.

21. A catalyst as defined in claim 20 except that component (C) is as defined in claim 11 or 19.

22. A catalyst according to claim 21 substantially as described in any one of the foregoing sets of polymerisation conditions A to H, "in liquid monomer", and "in gas phase".

23. A process for polymerizing alpha-olefins containing at least three carbon atoms or mixtures of said olefins with one another and/or with ethylene, wherein the polymerisation is conducted in the presence of a catalyst as defined in claim 20.

24. A process according to claim 23 wherein the catalyst is as defined in claim 21 or 22.

25. A process according to claim 23 or 24 substantially as described in any one of the foregoing sets of polymerisation conditions A to H, "in liquid monomer", and "in gas phase".

26. Crystalline polymers and copolymers of alpha-olefins prepared according to a process claimed in claim 23, 24 or 25.

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