

PATENT SPECIFICATION

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(54) COMPONENTS AND CATALYSTS FOR THE POLYMERISATION OF ALPHA-OLEFINS

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

The present invention relates to components of catalysts useful for polymerizing olefins, to the catalysts obtained therefrom and to the use of same in the polymerization of olefins of formula: $\text{CH}_2=\text{CHR}$, where R is hydrogen or alkyl having 1 to 6 carbon atoms.

More particularly, this invention relates to components of catalysts suited to the stereospecific polymerization of alpha-olefins $\text{CH}_2=\text{CHR}$, in which R is an alkyl radical having 1 to 6 carbon atoms, such as propylene, butene-1, 4-methylpentene-1 and mixtures thereof with minor percentages of ethylene.

Polymerization catalysts exhibiting high activity and stereospecificity in the stereoregular polymerization of alpha-olefins are already known. Essential components, for the preparation of said catalysts are an alkyl aluminium compound partially complexed with an electron donor compound, and a halogenated titanium compound, preferably in the form of a complex with an electron donor compound, supported on a Mg dihalide. Some examples of these catalysts are described in British patent No. 1,387,890.

The highly stereospecific and highly active catalysts known so far do not permit, however, to obtain polymers having a controlled morphology, and in particular in the form of free-flowing particles with a narrow size distribution. Generally, the polymers prepared by means of such catalysts exhibit a rather broadened distribution curve and are not free-flowing.

Most of the particles have sizes comprised between 1000 and 100 μ . However, also significant fractions having dimensions above 1000 μ and below 100 μ are present.

It is very desirable to have available highly active and stereospecific catalysts, that permit to obtain polymers in the form of free-flowing particles with a narrow size distribution.

US patent No. 3,953,414 describes polymerization catalysts that allow to obtain olefin polymers in the form of spheroidal particles having a controlled particle size distribution. The activity and stereospecificity of such catalysts, however, is not sufficiently high.

Thus, it is an object of the present invention to prepare highly active and stereospecific catalysts, useful to prepare olefinic polymers in the form of particles having a controlled particle size distribution, and catalyst components for use therein.

The catalyst components of the present invention are spheroidal particles at least 80% of which have a size from 5 to 25 microns, a surface area between 90 and 700 m^2/g and a porosity between 0.1 and 0.3 cc/g , the said particles consisting of a magnesium dihalide carrier on which a titanium compound is chemically bound. They are preferably prepared by reacting a tetravalent titanium compound having at least one Ti-halogen bond with one or more magnesium compounds of the formula:

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 $X_nMg(OR)_{2-n}$

wherein $0 < n < 2$ and especially $0 < n < 1$; R is an alkyl, aryl, or cycloalkyl radical of 1 to 20, preferably 1 to 12, carbon atoms; X is a halogen atom preferably Cl or Br, or a group OR' in which R', which may be the same or different from R, is an alkyl, aryl or cycloalkyl radical of 1 to 20 carbon atoms, the said magnesium compound or compound being in the form of particles having a surface area between 90 and 700, preferably between 200 and 700, m^2/g and a porosity between 0.1 and 0.2 cc/g. At least 80% of the particles preferably have a size from 5 to 25 microns (as in the catalyst component itself), and especially from 8 to 20 microns.

Among the catalyst components of this invention, those suited to the stereospecific polymerization of alpha-olefins, are prepared by reaction between a Ti compound, and a magnesium compound as aforesaid and an electron donor compound (or a Lewis base) capable of forming addition compounds with the Ti compound, preferably an ester of an organic or inorganic oxygenated acid, in particular an ester of an aromatic acid.

Halogenated Ti compounds particularly suited to prepare the catalytic components are the Ti tetrahalides, in particular $TiCl_4$. However, halogen-alcoholates and halogen-phenolates, such as $Ti(O-nC_4H_9)_2Cl_2$, $TiOC_2H_5Cl_3$, $Ti(OC_6H_5)_2Cl_2$, can also be suitably employed. The compounds of formula $X_nMg(OR)_{2-n}$ containing at least a Mg-OR bond, are represented by magnesium dialcoholates and magnesium monohalogen-alcoholates. Some of these compounds are for example: $Mg(OC_2H_5)_2$, $Mg(O-i-C_4H_9)_2$, $Mg(OC_6H_5)_2$, $Mg(OC_6H_4CH_3)_2$, $Mg(OC_6H_4C_2H_5)_2$, $Mg(C_2H_5)(OCH_2C_6H_5)$, C_2H_5OMgCl , C_4H_9OMgCl , $CH_3C_6H_5O-MgCl$, $(CH_3)_2C_6H_5OMgCl$.

The Mg alcoholates can be employed also in the form of complexes with alcoholates of other metals, such as alcoholates of Al, B, Zn, Zr.

The carrier(s) may contain, besides the above-cited Mg compounds, also organic or inorganic solids co-supports which are inert with respect to the Mg compounds, selected in particular from amongst the compounds of the metals of groups III and IV of the Periodic Table, such as, for instance, SiO_2 , Al_2O_3 , B_2O_3 , ZrO_2 , TiO_2 ; or from amongst those of the metals of groups I and II, such as, for example, Na_2CO_3 , $NaCl$, Na_2SO_4 , MgO , $MgCO_3$, $Mg(OH)Cl$, $CaCl_2$.

Compounds $X_nMg(OR)_{2-n}$, wherein n is 2, are represented by the Mg dihalides, in particular by $MgCl_2$.

Carrier(s) are generally characterized, not only by the characteristics of surface area and porosity indicated hereinbefore, but also by a resistance to ultra-sonic vibrations higher than 3 Watt h/l, and in particular higher than 30 and comprised between 30 and 70 Watt h/l. As regards the definition of the resistance to ultra-sonic vibrations and the determination of same, reference is made to US patent No. 3,953,414.

Electron donor compounds suited to the purpose may be besides the esters of oxygenated acids, also ketones, aldehydes, ethers, amides, and phosphorous compounds such as phosphines and phosphoramides. The preferred compounds are the alkyl esters of the aromatic acids. Some typical examples of these esters are the alkyl benzoates, alkyl toluates and alkyl anisates. Ethyl benzoate, methyl toluate and methyl anisate are representative compounds. The esters can be used also in the form of adducts with Lewis acid halides different from the Mg halides. The Al and Sn halides and in particular $AlCl_3$ are examples of the Lewis acid halides. The aromatic esters can be prepared in situ by an exchange reaction between OR groups of carrier(s) containing compounds $X_nMg(OR)_{2-n}$, wherein n is lower than 2, in particular $n=1$, and atoms of halogen of a halide of an aromatic acid. Benzoyl chloride, for example, can be employed to this purpose.

With a view to improving the catalysts, stereospecificity it is advisable to employ the aromatic ester admixed with minor amounts of a phenol, in particular an ortho-substituted phenol. Preferably, the electron donor compound is reacted with carrier(s) prior to the reaction with the Ti compound. It is possible, however, to react both the Ti compound and carrier(s) and the electron donor compound simultaneously. It is also possible to react the Ti compound with carrier(s) and then to treat the solid product of the reaction with the electron donor compound. The Ti compound can be also reacted in the form of an addition compound with the electron donor compound.

The reaction is conducted under such conditions, that the amount of electron donor compound present in combined form in the solid product separated from the

reaction mixture is lower than 1 mole per gram atom of Mg, in particular it is comprised between 0.1 and 0.3 moles per gram atom of Mg.

The molar ratio between the electron donor compound and the Ti compound ranges from 0.2 to 2, preferably from 0.5 to 1.5.

To secure high catalyst activity and stereospecificity it is important that less than 50% by weight of the tetravalent Ti compounds contained in the catalytic component should be extractable with TiCl_4 at 80°C . Preferably, the extractable Ti compounds should be less than 20% by weight.

The reaction between the compounds including Mg-OR bonds of carrier(s) and the halogenated Ti compound leads to a Mg dihalide containing a Ti compound chemically fixed on it. It is operated under such conditions, as to cause such conversion to be as complete as possible.

The reaction between carrier(s), a halogenated Ti compound, such as TiCl_4 , and the electron donor compound leads to a Mg dihalide comprising a Ti compound and an electron donor compound chemically bonded on the Mg halide. The fact that the Ti compound and the electron donor compound are chemically bound to the Mg dihalide can be shown by various methods, e.g. infrared and Raman analysis, and extraction with solvents.

It has been found, and this is another aspect of the present invention, that the product of the reaction between the Ti compound and carrier(s), whether or not containing the electron donor compound, retains the morphology of the carrier(s) and a surface area comprised between 90 and $700\text{ m}^2/\text{g}$.

Porosity is usually between 0.2 and 0.3 cc/g. Analogously, and this is a further feature of this invention, it is possible to obtain products retaining morphology and characteristics of starting carrier(s) if, prior to reaction with the Ti compound, carrier(s) containing at least a Mg compound with a Mg-OR bond is reacted with a halogenating substance capable of substituting OR groups of the carrier with halogen atoms. Some examples of such halogenating substances are: halogenated Si compounds such as, for instance, SiCl_4 , benzoyl chloride, AlCl_3 , Al-alkylmonohalides or Al-alkyldihalides, BCl_3 , PCl_3 . The compound that is obtained in this case is a Mg dihalide. In particular, Mg dichloride is formed when both halogenating substance and carrier(s) contain chlorine atoms. The halogenating compound is used in such an amount that the molar ratio between OR groups of compound $\text{X}_n\text{Mg(OR)}_{2-n}$ and the active halogen atoms of the halogenating agent is in general lower than 1.

An example of reactions leading to the formation of Mg dichloride that retains the morphological characteristics, including the surface area and the porosity of the starting carrier, is the reaction of $\text{ClMgOC}_2\text{H}_5$ with SiCl_4 , AlCl_3 and similar halogenating compounds.

As is better explained later on herein, compounds $\text{X}_n\text{Mg(RO)}_{2-n}$, in which n is <2 , in particular is equal to 1, can be decomposed in situ to a Mg dihalide by causing the reaction yielding $\text{X}_n\text{Mg(OR)}_{2-n}$ to occur in the presence of a halogenating substance, i.e. a substance capable of forming Mg-halogen bonds.

In both the case of the final catalytic component (after reaction with the Ti compound) and the case of the product resulting from the treatment with the halogenating substance, the particle size distribution is in a narrow range of values. At least 80% of the particles have sizes ranging from 5 to $25\text{ }\mu$, in particular from 8 to $20\text{ }\mu$.

When the halogenating substance is a hydrogen halide, e.g. anhydrous gaseous HCl, the resulting product is an adduct between the Mg dihalide and the alcohol or phenol that is formed during the reaction. In the case of components suited to prepare catalysts for the stereospecific polymerization of alpha-olefins, the adduct, before the reaction with the halogenated Ti compound, can be treated with a compound capable of reacting and removing the alcohol or phenol from the adduct, for instance an Al-trialkyl, SiCl_4 , AlCl_3 , benzoyl chloride.

However it is also possible and this is a preferred procedure, to cause the adducts to directly react with the Ti compound in the presence of an electron-donor compound free from active hydrogen, or the electron-donor compound being introduced in a combined form with the adduct itself, provided that the amount of electron-donor compound that remains fixed on the catalyst component after extraction with TiCl_4 at 80°C for 2 hours is of at least 0.5 and up to 3 moles/gram atom of Ti. It is furthermore of importance that the catalyst component should contain less than 50%, preferably less than 20%, of Ti compounds extractable with TiCl_4 at 80°C .

The pre-treatment of carrier(s) with a hydrogen halide permits to obtain

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catalyst components which, besides retaining the morphological properties of the starting carrier, have a higher content of Ti compounds not extractable with TiCl_4 at 80°C . This is an advantage, because it permits to lower the halogen/Ti ratio of the catalyst and to obtain, by consequence, polymers having a lower halogen content, the catalytic activity being the same.

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Prior to the reaction with the halogenating substance, the carrier(s) can be treated with the electron donor compound, or the electron donor compound can be present during the halogenation reaction or it can be reacted at the conclusion of such reaction.

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The preparation of the adducts starting from compounds $\text{X}_n\text{Mg}(\text{OR})_{2-n}$ can be effected according to various conventional methods: a preferred one consisting in reacting an anhydrous hydrogen halide or a mixture thereof with an alcohol or phenol with compounds $\text{X}_n\text{Mg}(\text{OR})_{2-n}$ (in which $0 \leq n < 2$, and X and R have the meanings already specified) already formed or during the preparation of same.

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The reaction is generally carried out in suspension in an inert hydrocarbon medium (hexane, heptane, etc.) at a temperature ranging from the room temperature, or even from a lower temperature, to the boiling point of the hydrocarbon solvent. The reaction with anhydrous hydrogen halide is preferably carried out at temperatures lower than room temperature, for example at 0°C .

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Preferably 1 mole of anhydrous hydrogen halide is used for each mole of OR groups of the $\text{X}_n\text{Mg}(\text{OR})_{2-n}$ compound.

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The reaction of the Ti compound with the adduct of the Mg dihalide with the alcohol or phenol can be effected in the presence of the electron-donor compound, or this compound can be prereacted with the adduct or introduced into such adduct during the formation of same, or it can be reacted with compound $\text{X}_n\text{Mg}(\text{OR})_{2-n}$ prior to its being transformed into adduct. The amount of electron-donor compound present in a combined form in the adduct is generally comprised between 0.05 and 1 mole per mole of alcohol or phenol in the adduct.

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The reaction between the Ti compound and carrier(s) or the adduct thereof with an alcohol or a phenol is conducted by suspending the carrier in a liquid reaction medium, that may consist of said liquid Ti compound or of a solution of same in an inert hydrocarbon diluent.

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The reaction is preferably conducted by using the liquid Ti compound as reaction medium. The temperature is generally comprised between room temperature and 150°C . In the case of TiCl_4 , it can be operated at its boiling temperature or at lower temperatures for example between 80 and 120°C . In general, it is preferable to operate between 110 and 135°C .

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The reaction solid product is separated from the liquid medium or from the excess of Ti compounds, at temperatures at which the undesired Ti compounds extractable with TiCl_4 at 80°C remain dissolved in the reaction medium and are removed together with it.

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When TiCl_4 is employed as reaction medium, separation of the solid is carried out at temperatures generally exceeding 80°C . It is also possible, however, to operate at lower temperatures, provided TiCl_4 amounts sufficient to dissolve the undesired Ti compounds are used. It is also convenient to repeat the treatment with TiCl_4 one or several times.

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The solid is separated from the reaction mixture and washed with an inert hydrocarbon diluent (e.g. hexane or heptane) to remove the last traces of the unreacted Ti compound.

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The reaction between the electron donor compound and carrier(s) when the (electron donor compound is reacted with the carrier before the reaction with Ti compounds) is generally carried out by suspending the carrier in a hydrocarbon solution containing the electron donor and by conducting the reaction at temperatures ranging from room temperature to 100°C , preferably from 40 to 80°C .

The reaction solid product separated from the liquid phase is first washed with a hydrocarbon diluent and then reacted with the Ti compound.

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The reaction between carrier(s) and halogenating agents is also effected by suspending the carrier in a liquid medium consisting of said halogenating agent or of a solution thereof, and by conducting the reaction at temperatures generally ranging from room temperature to 150°C .

The solid product is separated from the reaction mixture, it is washed and then reacted with the electron donor compound and/or with the Ti compound.

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As already explained hereinbefore, the electron donor compound may be added also during the halogenation reaction.

The preparation of compounds $X_nMg(OR)_{2-n}$, in which n is <2 and that may coincide, in practice, with the preparation of carrier(s), can be effected by an exchange reaction of a Mg metallorganic compound of formula X_nMgR_{2-n} , wherein $0 < n < 2$, R is an alkyl, aryl or cycloalkyl radical having 1 to 20 carbon atoms and X is a halogen or an alkyl, aryl or cycloalkyl radical having 1 to 20 C, either like or unlike R , with an ester of the orthosilicic acid.

Metallorganic compound X_nMgR_{2-n} may be preformed or may be formed in the nascent state by reaction between Mg metal and an organic halide RX , in which X is a halogen and R is a hydrocarbon radical having the meaning specified hereinbefore.

During the exchange reaction at least one radical R of metallorganic compound X_nMgR_{2-n} is transferred to the ester of the orthosilicic acid, and at least one group OR of such ester is linked to the magnesium atom.

Results similar to those obtained with the orthosilicic acid esters can be achieved with the esters of other oxygenated inorganic acids including, for instance the alkyl borates, alkyl carbonates and phosphates.

The preferred preparation method consists in reacting—in one step only—Mg metal, the organic halide and the orthosilicic acid ester.

RX compounds in which X is a halogen, preferably Cl or Br, R is an alkyl, alkenyl, aryl or cycloalkyl radical having 1 to 20 C, preferably 1 to 8 C, are employed as organic halides.

These compounds are, for example, methyl, ethyl, n-butyl, n-amyl, n-octyl, t-butyl, isobutyl and cyclohexyl chlorides and bromides, chlorobenzene, o-chlorotoluene, 2-chloroethylbenzene, vinyl chloride, benzyl chloride.

The silicic acid esters have the formula



wherein R has the meaning specified hereinbefore for the XR compounds, X is a halogen or an alkyl, aryl or cycloalkyl radical containing 1 to 20 C and m is a number from 0 to 3.

The preferred Si compound is ethyl silicate $Si(OC_2H_5)_4$. Examples of other Si compounds are: $Si(OCH_3)_4$, $CH_3Si(OCH_3)_3$, $(CH_3)_2Si(OCH_3)_2$, $Si(OnC_4H_9)_4$, $Si(OC_6H_5)_4$.

The Si compound is generally employed in such amount, that the ratio between OR groups and gram atoms of Mg is equal to or higher than 1 and preferably comprised between 3:1 and 5:1.

It is advisable to employ 1—2 moles of organic halide per gram atom of Mg.

It is operated at temperatures ranging from 50° to $250^\circ C$, preferably from 60° to $100^\circ C$. The order in which the reagents are added is not critical, still, it is preferable to add magnesium and organic halide to the Si compound either liquid or in solution.

The preferred reaction medium is the Si compound itself or a mixture thereof with the organic halide; the reaction may be carried out also in the presence of an inert diluent such as, for example, an aliphatic, cycloaliphatic or aromatic hydrocarbon (e.g. hexane, heptane, benzene, or toluene).

Iodine, alkyl iodides, or inorganic halides such as $CaCl_2$, $CuCl$, $AgCl$, and $MnCl_2$, may be used as reaction promoters. Magnesium is employed in the form of powder or chips.

According to another preparation method, the Si compound can be reacted with a Grignard reagent of formula $R Mg X$, or with a compound MgR_2 , where R is an alkyl, aryl or cycloalkyl radical having 1 to 20 C. Some Grignard reagents are for example: $ClMg-n-C_4H_9$; $ClMg-i-C_4H_9$; $ClMgC_5H_{11}$; C_6H_5MgCl ; $C_6H_5CH_2MgCl$; $CH_2=CHMgCl$.

Grignard reagents and compounds MgR_2 are prepared according to conventional methods. It is possible to utilize Grignard reagents prepared either with ethers or in apolar solvents, such as hydrocarbons. For instance, Grignard reagents prepared in hydrocarbons/ethers mixtures, such as e.g. the toluene/n-butyl ether mixture, may be employed.

The conditions of the reaction between silicic acid ester and Mg metallorganic compound are the same as indicated for the simultaneous reaction among Mg, RX and organic silicate.

Examples of conventional preparation methods leading to the formation of compounds $X Mg OR$, in which X is a halogen, and that can be utilized for

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preparing the components according to this invention, are described in US patents Nos. 2,380,057; 2,442,053 and in GB patent No. 591,440.

As already explained hereinbefore, both the reaction in one step among Mg, RX, and silicate, and the one between silicate and compound X_nMgR_{2-n} can be conducted in the presence of a halogenating compound. In such case the reaction final product consists essentially of a Mg dihalide, in the form of spheroidal particles exhibiting the morphological, area and porosity characteristics already specified.

If a hydrogen halide is employed as halogenating agent, the reaction final product is an adduct between the Mg dihalide and the alcohol that is formed during the reaction.

The catalytic components of the present invention form, by reaction with metallorganic compounds of the metal belonging to groups II and III of the Periodic Table, catalysts particularly active in the polymerization of olefins. The polymers obtained therefrom are in form of free-flowing particles with a flow index of less than 25 seconds and particularly comprised between 12 and 20 seconds (index measured according to ASTM 1895-69 Method A).

In particular, when the catalytic component contains an electron donor and when an Al metallorganic compound partially complexed with an electron donor is employed as co-catalyst, it is possible to obtain catalysts suited to polymerize alpha-olefins, exhibiting a high activity and stereospecificity, which, furthermore, provide polymers, such as polypropylene, in the form of free-flowing particles having a narrow particles size distribution.

The electron donor compounds suitable for being complexed with the Al metallorganic compounds belong to the same classes as the electron donor compounds previously described.

The amount of electron donor compound is preferably such that at least 10% and more specifically 20—80% of the Al metallorganic compound is in the form of a complex. The alkyl esters of the aromatic acids such as, for example, the esters of benzoic or toluic acid and the like are preferably employed.

Al-trialkyls, such as e.g. Al-triethyl, Al-triisobutyl etc. are preferably employed as Al compounds. Further examples of useful Al-alkyl compounds are described in GB patent 1,387,890. Al-trialkyls are employable also in admixture with Al-dialkyl halides.

The Al/Ti ratio in the catalysts suitable for stereospecifically polymerizing alpha-olefins is generally comprised between 10 and 1000. Al/Ti ratio lower than 10 can be used provided that no electron-donor compound is used or less than 20% by mols with respect to the Al-alkyl compound.

The polymerization conditions of the alpha-olefins with the catalysts according to this invention are those already known from the Art.

Polymerization may be conducted in a liquid phase either or not in the presence of an inert hydrocarbon solvent (hexane, heptane, etc.), or in a gas phase.

Temperature is generally comprised between 40° and 150°C, in particular between 50° and 90°C.

Propylene or a mixture thereof with minor amounts of ethylene is particularly polymerized with the stereospecific catalysts of the invention.

The polymers obtained by using the catalysts of this invention are characterized by a high flow index (generally comprised between 12 and 20 sec.) and by a very narrow granulometric distribution. The flow index is determined according to ASTM 1895-69/A. In general, more than 50% of the particles exhibits sizes ranging from 100 to 500 μ . The percentage of particles having mean sizes below 50 μ and above 100 μ is negligible.

The following examples illustrate the present industrial invention. The catalyst components described in the Examples are all in the form of spheroidal particles of at least 80% of which have a size from 5 to 25 microns a surface area between 90 and 700 m^2/g and a porosity between 0.1 and 0.3 cc/g .

EXAMPLE I

a) Preparation of the catalyst component

12.2 g of Mg metal in 35—50-mesh flakes were washed with 250 ml of n-hexane at 68°C for 1 hour in a 1000-ml flask and then dried in anhydrous nitrogen. 104.5 g of tetraethyl orthosilicate were successively charged, bringing the suspension to 65°C, and 0.2 ml of a solution of 2 g of iodine in 10 ml of methyl iodide were introduced as a promoter, a solution consisting of 50.9 g of n-BuCl in 100 ml of n-hexane being dropwise introduced in 45 minutes. Temperature was

kept at 70°C by removing the heat evolved by the reaction. It was then operated at 70°C for 6 hours. Washings with n-hexane at 50°C were carried out by decantation, employing an amount of 200 ml of n-hexane each time, for 6 consecutive times. The resulting solid product was dried at 50°C under vacuum; 60 g of a solid product were recovered, whose elemental analysis gave the following results (the percentages are by weight):

Mg=18.65%, Cl=27.05%.

The surface area (determined according to method B.E.T.—SORPTOMATIC 1860 apparatus—C. Erba) was 550 m²/g, the porosity 0.156 ml/g. 13.1 g of the dry product obtained were suspended in a solution containing 4.67 g of benzoyl chloride (33.3 m-moles) in 200 ml of anhydrous n-hexane, and were reacted 2 hours at 60°C. The solid obtained after filtering at room temperature was washed with n-hexane two times, employing 200 ml of n-hexane each time. The resulting solid product was treated with 110 ml of TiCl₄ at 120°C for 2 hours. After this time-period, TiCl₄ was removed by filtration at 120°C and the solid was then washed with n-hexane at 65°C until disappearing of the chlorine ion.

Analysis: Ti=1.85%; Mg=20.7%; Cl=70%.

b) Polymerization of propylene

5.05 m-moles of a mixture of Al-butyls (54.4 mol-% of Al-i-Bu₃ and 45.5 mol-% of Al-n-Bu₃) were reacted, at room temperature, with 1.69 m-moles (254 mg) of methyl p-toluate in 80 ml of (anhydrous) n-heptane for 5 minutes. 30 ml of this solution, diluted with 50 ml of anhydrous n-hexane, were contacted with an amount of the catalytic component prepared as described hereinabove, equal to 79 mg (equivalent to 1.43 mg of Ti), for a time-period of 5 minutes. This suspension was introduced, in nitrogen atmosphere, into a stainless steel autoclave having a total volume of 2.5 l, equipped with a screw magnetic stirrer and a thermocouple, and containing 870 ml of n-hexane saturated with propylene at 40°C; successively, the remaining 50 ml of the solution of Al-butyl and methyl p-toluate were introduced thereinto in a propylene flow. After closing of the autoclave, 300 Ncc of hydrogen were introduced, temperature was brought to 60°C and, simultaneously, propylene was introduced up to a total pressure of 9 atmospheres. During the polymerization the pressure was kept constant by continuous feeding of the monomer. After 4 hours, polymerization was stopped by quick cooling and degassing of the polymeric slurry. The polymer was separated from the solvent by stripping with steam and it was dried in a hot nitrogen flow at 70°C. 427 g of dry polymer in flakes were thus obtained, the yield was equal to 292,000 g of polypropylene/g of Ti, and the residue to the extraction with boiling n-heptane was 90% by weight. The obtained polypropylene was characterized by the following properties:

intrinsic viscosity	1.6 dl/g
melt-flow index	4.4 g/10 min.

Particle size distribution of the polymer
(Method ASTM D 1921—63):

Screen	(micron)	% (by weight)
above 2000	"	0.2
above 1000	"	1
above 500	"	5.2
above 177	"	80.6
above 105	"	7.8
above 55	"	4
below 55	"	0.8

The polymer apparent density was of 0.485 kg/l (Method DIN 53194) with a flow index of 16 seconds (ASTM 1895-69/Method A).

EXAMPLE 2

a) Preparation of the catalyst component

13.1 g of the dry product obtained by reacting Mg, Si(OEt)₄ and n-BuCl with one another according to example 1 a) were suspended in a solution containing 3 g

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of ethyl benzoate (20 m-moles) in 200 ml of anhydrous n-hexane, whereupon they were reacted 2 hours at 60°C. It was operated according to example 1a). The dry product obtained after two treatments with TiCl_4 was subjected to analysis, the following results having been obtained:

Ti=2%; Mg=18.65%; Cl=62.40%;

surface area=345 m^2/g ; porosity=0.291 ml/g .

b) Polymerization of propylene in n-hexane solvent

It was operated according to example 1b), introducing 71 mg of the catalytic component (1.42 mg of Ti) prepared as described in part a) of the present example. At the conclusion of the polymerization 493 g of dry polymer in flakes were obtained, with a yield of 347.000 g of polypropylene/g of Ti and a residue to the extraction with boiling n-heptane of 91% by weight. The polymer was characterized by the following properties:

intrinsic viscosity
melt-flow index

1.8 dl/g
2.9 $\text{g}/10 \text{ min.}$

Particle size distribution of the polymer	
(micron)	(% by weight)
over 2000	0.1
over 1000	0.6
over 500	1
over 177	89.1
over 105	5.5
over 53	2.7
below 53	0.8

The apparent density was of 0.505 kg/l and the flow index of 15 seconds.

EXAMPLE 3

a) Preparation of the catalytic component

53.5 g of Mg metal (2.2 gram atoms) and a solution consisting of 224 g of n-BuCl (2.42 moles) and of 459 g of $\text{Si}(\text{OEt})_4$ diluted in 400 ml of hexane were employed. Unlike what described in example 1a), the solution containing n-BuCl and $\text{Si}(\text{OEt})_4$ was added to magnesium, pre-activated in the presence of a iodine crystal, in a total time of 45 minutes, at a temperature of 70°C. The temperature was kept at 70°C for further 6 hours. After washings with hexane at 50°C and drying at 50°C under vacuum, 264 g of a solid product having the following centesimal composition were obtained:

Mg=16.7%; Cl=33.9%; Si=0.55%.

The area was 450 m^2/g ; the porosity was 0.157 ml/g . 12.35 g of the obtained dry product were reacted with 4.67 g of benzoyl chloride (33.3 mmoles) and with 200 ml of TiCl_4 at 130°C for 2 hours. After hot filtering, an analogous treatment with TiCl_4 was carried out. It was hot filtered again and washings with hot hexane were effected until disappearance of the chlorine ion in the filtrate. The resulting product was dried at 40°C; the elemental analysis of the dry product gave the following results:

Ti=1.4%; Mg=20.65%; Cl=70.65%.

The area was 385 m^2/g ; the porosity was 0.280 ml/g .

b) Polymerization of propylene

78 mg of the catalytic component prepared as described hereinbefore under the same polymerization conditions as illustrated in example 1b) were used. 360 g of polymer in flakes, with a yield of 330.000 g of polypropylene/g of Ti, having a residue to the extraction with boiling heptane equal to 89.5% by weight were obtained. The polymer was characterized by the following properties:

intrinsic viscosity
melt-flow index

1.9 dl/g
2.3 g/10 minutes.

Particle size distribution of the polymer
(micron) (% by weight)

5	over 2000	1.4	5
	over 1000	10	
	over 500	17.2	
	over 177	34.6	
	over 105	27.4	
10	over 53	8	10
	below 53	0.9	

The apparent density was of 0.50 kg/l, the flow index was equal to 18 second.

EXAMPLE 4

a) Preparation of the catalyst component

12.2 g of Mg metal (0.5 gram atoms) along with 104.5 g of tetraethyl orthosilicate (0.5 moles) and 150 mg of CuCl, acting as a promoter, were brought to 130°C. 0.2 ml of a solution of 2 g of iodine in 10 ml of CH₃I were introduced thereinto, whereupon 84.5 g (0.75 moles) of chlorobenzene were added dropwise in a total time of 2 hours. In this way the inside temperature rose to 160°C. At the conclusion of such operation, it was reacted still for 5 hours at a temperature of 160°C. The obtained solid product was washed three times at 50°C with toluene, employing 300 ml thereof each time, and then 4 times with 200 ml of hexane each time. The solid so separated was dried at 50°C under vacuum; 50.7 g of a dry product were thus recovered, whose centesimal composition was as follows:

Mg=21.95%; Cl=29.95%; Si=0.6%.

11.1 g of the solid dry product were reacted with 4.67 g of benzoyl chloride (33.3 m-moles) and with 110 ml of TiCl₄ for 2 hours at 130°C. It was hot filtered, and washings with hexane at 65°C were effected until disappearance of the chlorine ion in the filtrate. The solid product dried at 40°C under vacuum exhibited the following centesimal composition:

Ti=1.25%; Mg=18.8%; Cl=62.9%; Si=0.22%.

The area was 94 m²/g and the porosity 0.24 ml/g.

b) Polymerization of propylene

70 mg of the dry product prepared as described in part a) of this example were utilized to polymerize propylene under the same conditions of the test of example 1b). 217 g of a polymer in flakes with a yield of 248,000 g of polypropylene/g of Ti, and a residue to the extraction with boiling heptane equal to 90% by weight, were obtained. The polymer exhibited also the following properties:

intrinsic viscosity
melt-flow index

1.7 dl/g
9.3 g/10 min.

EXAMPLE 5

a) Preparation of the catalyst component

42.2 g of n-BuCl (0.45 moles) and 52 g of Si(OEt)₄ diluted in 100 ml of toluene were added, in 45 minutes and at a temperature of 60°C, to 10.95 g of Mg metal (0.45 gram atoms). It was reacted for 6 hours at 60°C. Washings with cold hexane were carried out. The residual solid product was dried under vacuum at 50°C, thus obtaining 49.4 g of a solid dry product having the following centesimal composition:

Mg=18.2%; Cl=31.2%; Si=0.42%.

12.35 g of such solid product were reacted at 60°C for 24 hours with 169.8 g (1 mole) of SiCl₄ and 3 g (20 m-moles) of ethyl benzoate. After removal of SiCl₄ by filtration at 60°C and after consecutive washings with hexane at 65°C, the residual solid product was twice treated with TiCl₄, using 200 ml thereof each time, at 135°C

and for 1 hour per treatment; further washings with hexane at 65°C were then carried out until disappearance of the chlorine ion in the filtrate. The dry solid product had the following centesimal composition:

Ti=1.05%; Cl=66.75%; Mg=20.3%; Si=0.21%.

The area was =302 m²/g; the porosity=0.27 ml/g.

b) Polymerization of propylene

Operating under the same polymerization conditions as described in example 1b), 66 mg of a solid product prepared as in example 5a) were employed. 220 g of a polymer in the form of irregular and not homogeneous flakes, with a yield of 318,000 g of polypropylene/g of Ti, having a residue to the extraction with boiling heptane equal to 87% by weight, were thus obtained. The polymer was furthermore characterized by the following properties:

apparent density	0.4 kg/l
intrinsic viscosity	1.7 dl/g
melt-flow index	5.2 g/10 minutes.

EXAMPLE 6

a) Preparation of the catalyst component

32.5 g of the product (MgClOEt-flakes) prepared according to example 3a) were suspended in 200 ml of anhydrous hexane, the temperature was brought to 0°C and anhydrous gaseous HCl was bubbled thereinto at a rate of 14.1 NI/hour for 2 hours altogether. After having stopped feeding HCl, the suspension was brought to a temperature of 60°C for 1 hour. It was washed with hexane at room temperature until disappearance of the chlorine ion. The solid was dried under vacuum (20 mm Hg of residual pressure) at 30°C, whereupon 34.8 g of dry product were obtained, the analysis of which gave the following results:

Mg=15.65%; Cl=50.55%; Si=0.07%.

14.2 g of the obtained solid product were reacted, for 24 hours at 60°C, with 340 g of SiCl₄ (2 moles) and 3 g of ethyl benzoate (20 m-moles). It was filtered at 25°C under removal of SiCl₄, successively the residual solid was repeatedly washed with cold hexane, then it was suspended in 200 ml of TiCl₄ and reacted at 120°C for 2 hours; after hot filtering, a similar treatment was carried out. After repeated washings with cold hexane, until disappearance of the chlorine ion, the solid product was dried under vacuum at 40°C. The analysis of the dry solid gave the following results:

Ti=2.25%; Cl=66.45%; Mg=16.35%.

Area=410 m²/g; porosity=0.185 ml/g.

b) Polymerization of propylene

Operating according to example 1b), 60 mg of the catalytic component (1.35 mg of Ti) prepared as described hereinabove were employed; 412 g of a polymer in flakes were obtained, the yield was equal to 305,000 g of polypropylene/g of Ti, and the residue to the extraction with boiling heptane was of 89% by weight. The polymer was characterized by the following properties:

intrinsic viscosity	2.1 dl/g
melt-flow index	2.5 g/10 min.

Particle size distribution of the polymer

(micron)	(% by weight)
over 2000	1.2
over 1000	11.1
over 500	14
over 177	44
over 105	27.3
over 53	1.7
below 53	0.6

apparent density	0.515 kg/l
flow index	16 seconds.

EXAMPLE 7

a) Preparation of the catalyst component

32.5 g of the product (MgClOEt-flakes) prepared as described in example 4a), were suspended in a solution containing 11.52 g of anhydrous ethyl alcohol (0.25 moles) in 150 ml of hexane; the suspension was brought to 0°C, whereupon anhydrous gaseous HCl was introduced at a rate of 14.1 NI/hour, for 2 hours. After having stopped introducing hydrochloric acid, the suspension was heated for 1 hour to 60°C. The solid product was washed with cold hexane and successively dried at 30°C under vacuum at a partial pressure of 20 mm Hg; 45.6 g of dry product were thus obtained, whose centesimal composition was as follows:

Mg=11%; Cl=37.65%; Si=0.1%.

20.3 g of such solid product were reacted with 340 g of SiCl₄ (2 moles) and with 3 g of ethyl benzoate (20 m-moles) for 24 hours at 60°C. After this time-period, SiCl₄ was removed by filtration at 60°C and the residual solid product was repeatedly washed with hexane at 60°C; it was then suspended in 200 ml of TiCl₄ and reacted for 2 hours at 130°C; after hot filtering, an analogous treatment was carried out, followed by washings with hexane at 65°C. After drying at 40°C under vacuum, the analysis carried out on the product yielded the following results:

Ti=2.15%; Cl=63.4%; Mg=18.05%; Si=0.23%.

b) Polymerization of propylene

Under the same polymerization conditions described in example 1b), 58 mg of the catalyst component prepared as described under a) hereof were employed. 400 g of a polymer in flakes, with a yield of 320,000 g of polypropylene/g of Ti, having a residue to the extraction with boiling heptane of 89.5% by weight, were so obtained. The polymer exhibited also the following characteristics:

intrinsic viscosity	2.1 dl/g
melt-flow index	2.2 g/10 min.

EXAMPLE 8

a) Preparation of the catalyst component

65.3 g of the product (MgClOEt-flakes) prepared as described in example 3a) were suspended in 400 ml of hexane; the temperature was brought to 0°C, then gaseous HCl was introduced at a rate of 14.1 NI/hour, for 4 hours. After having stopped the HCl feeding, the suspension was heated for 1 hour to 60°C. Washings with hexane at room temperature were carried out. After drying, effected as described in example 6a), 70.6 g of a solid dry product were obtained, whose analysis gave the following results:

Mg=15.85%; Cl=48.5%.

15.4 g of the product so prepared were reacted with 340 g of SiCl₄ (2 moles) and 4.05 g of ethyl benzoate (27 m-moles) for 2 hours at 25°C; then the mixture was heated for 18 hours at 60°C. After this treatment it was filtered at 50°C and repeatedly washed with heptane at 50°C. The residual solid was dried, suspended in TiCl₄ and reacted for 2 hours at 130°C; after hot filtering, the treatment with TiCl₄ was repeated. After some washings with heptane at 80°C and drying, the dry solid exhibited the following composition:

Ti=1.65%; Cl=66.15%; Mg=19.80%; Si=0.19%.

The area was 288 m²/g and the porosity 0.27 ml/g.

b) Polymerization of Propylene

64 mg of the catalytic component, prepared as described under a), were employed to conduct polymerization under the same conditions of example 1b). 296 g of polymer in flakes, with a yield of 280,000 g of polypropylene/g of Ti, having a residue to the extraction with boiling heptane of 87% were obtained. The polymer was characterized by an intrinsic viscosity equal to 2.1 dl/g and by a melt-flow index of 2.5 g/10 minutes.

EXAMPLE 9

a) Preparation of the catalytic component

12.2 g of Mg metal pre-activated as described in example 1a) were mixed with

104.5 g of $\text{Si}(\text{OEt})_4$ at a temperature of 65°C and in the presence of 0.2 ml of a solution consisting of 2 g of iodine dissolved in 10 ml of CH_2I_2 ; a solution consisting of 51 g of n-BuCl in 100 ml of hexane was introduced therein dropwise, simultaneously with gaseous HCl at a rate of 11.2 Nl/hour, at a temperature of 70°C ; n-BuCl in hexane was dropped for 1 hour, while hydrochloric acid was introduced for 6 hours altogether. After having stopped the HCl flow, the suspension was left under stirring 1 hour more at 70°C , after having diluted it with 100 ml of hexane; at the conclusions, washings were effected with hexane at 50°C . After drying, 76.3 g of a solid dry product were recovered, whose analysis yielded the following results:

Mg=14.5%; Cl=40.85%; Si=0.16%.

16.8 g of the solid product so obtained were reacted with a mixture of 340 g of SiCl_4 (2 moles) and 3 g of ethyl benzoate (20 m-moles), at a temperature of 60°C for 24 hours. After filtration at 55°C , the solid residue was repeatedly washed with hexane at room temperature and then reacted with 110 ml of TiCl_4 at 118°C for 2 hours; it was hot filtered and a new amount of TiCl_4 was introduced and reacted for 2 hours at 130°C . After hot filtering, it was repeatedly washed with hexane at 65°C . The solid residue was dried and analyzed. Its composition was the following:

Ti=2.2%; Cl=55.1%; Mg=22%; Si=0.21%.

b) Polymerization of propylene

65 mg of the catalyst component prepared as described under a) hereinbefore were employed to conduct polymerization under the same conditions of example 1b). 287 g of polymer, with a yield of 201,000 g of polypropylene/g of Ti, having a residue to the extraction with boiling heptane of 87% by weight were obtained. The polymer was characterized by an intrinsic viscosity of 1.4 dl/g and by a melt-flow index of 11.6 g/10 min.

EXAMPLE 10

a) Preparation of the catalyst component

13.1 g of the dry solid product prepared according to example 1a) were suspended in a solution containing 3 g of ethyl benzoate (20 m-moles) and 1.22 g of 2,6-dimethylphenol (10 m-moles) dissolved in 200 ml of anhydrous hexane. The suspension was brought to 60°C and kept at this temperature for 2 hours. The solid was then separated by filtration at room temperature and then washed twice with hexane (200 ml each time). The solid product was treated with TiCl_4 under the same conditions as described in example 1a). The solid product was then repeatedly washed with hexane at 65°C and successively dried under vacuum. From an analysis of same the following results were obtained:

Ti=2.5%; Cl=63.25%; Mg=20%; Si=0.21%.

b) Polymerization of propylene

It was operated under the same conditions of example 1b), employing 61 mg of the catalyst component (1.525 mg of Ti) prepared as illustrated under a) hereinbefore. At the conclusion of polymerization, 456 g of dry polymer in flakes were obtained; the yield was of 299,000 g of polypropylene/g of Ti, and the residue to the extraction with boiling heptane was equal to 91.5% by weight. The polymer exhibited furthermore the following characteristics:

intrinsic viscosity	2 dl/g
melt-flow index	2.4 g/10 min.

Particle size distribution of the polymer

(micron)	(% by weight)
over 2000	0.1
over 1000	0.2
over 500	0.7
over 177	90.2
over 105	4.6
over 53	3.1
below 53	1.1

apparent density	0.51 kg/l
flow index	16 seconds

c) Polymerization in liquid propylene

Into a 150-liter autoclave, thermoregulated by means of water and steam, in the absence of air, the following was introduced: 36 g of the mixture of Al-butyls as per example 1b), diluted with 55.5 ml of hexane, in a liquid propylene flow equal to 15 kg, and successively—under stirring—10.9 g of methyl p-toluate dissolved in 52 ml of hexane along with further 25 kg of liquid propylene (total amount of propylene introduced: 40 kg). The temperature was brought to 60°C in 20 minutes, and 0.7 g of the catalyst component (17.5 mg of Ti), prepared as per a) hereinbefore, suspended in 200 ml of hexane, were introduced at said temperature, under pressure of hydrogen introduced in an amount of 100 Nl. Temperature rapidly rose to 70°C (pressure=30 atmospheres) and was kept at such value for a total time of 3 hours. Polymerization was then stopped, the polymeric slurry was discharged into water and the unconverted monomer was removed by flashing. 5 kg of dry polymer in flakes were so obtained; the yield was of 286,000 g of polypropylene/g of Ti, and the residue of the extraction with boiling heptane was of 93.5% by weight. The polymer exhibited the following characteristics:

intrinsic viscosity	1.3 dl/g
melt-flow index	18.7 g/10 min.

The analysis of the catalyst residues in the polymer revealed the presence of: Ti=3.5 ppm; Mg=26 ppm; Cl=105 ppm.

Particle size distribution of the polymer

(micron)	(% by weight)
over 2000	—
over 1000	0.1
over 500	0.8
over 177	90.9
over 105	4.8
over 53	1.9
below 53	1.1

apparent density	0.48 kg/l
flow index	16 seconds.

EXAMPLE 11

a) The preparation of the catalyst component is described in example 2a).

b) Polymerization of ethylene in hexane

14.3 mg of the catalyst component, prepared as in example 2a), in suspension in 1000 ml of hexane containing 2 g of Al-tri-isobutyl were introduced, in a slight ethylene flow, into the same 2.5-liter autoclave described in example 1b). Temperature was rapidly brought to 85°C, while hydrogen was introduced at a partial pressure of 7.4 atmospheres, whereupon ethylene was introduced up to 6.6 atm. Polymerization was conducted at a total pressure of 15 atmospheres, introducing ethylene at 85°C for 4 hour. At the conclusion, 214 g of dry polymer in flakes were obtained; the yield was of 748,000 g of polyethylene/g of Ti; the E degree was equal to 7.8 g/10 min. and the N degree was equal to 81.6.

Particles size distribution of the polymer

(micron)	(% by weight)
over 2000	0.1
over 1000	0.3
over 500	30.1
over 177	65.3
over 105	2.1
over 53	1.7
below 53	0.4

apparent density	0.46 kg/l
flow index	23 seconds.

EXAMPLE 12

a) Preparation of the catalyst component

14.2 g of the solid product having the following composition: Mg=15.65%; Cl=50.55%; Si=0.07%, prepared according to example 6a) were reacted with 3 g of

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ethyl benzoate in 60 cc of n-octane at 60°C for 2 hours. The suspension was added to 200 ml of TiCl_4 and reacted at 120°C for 2 hours; after filtration, an analogous treatment was carried out. After repeated washings with heptane at 80°C until disappearance of the chlorine ions, a portion of the solid product was suspended in heptane, while the remaining portion was dried under vacuum at 40°C. From an analysis of the solid product the following results were obtained:

Ti=2.2%; Cl=60.8%; Si=0.13%; Ethyl benzoate=9%.

The surface area was equal to 410 m^2/g and the porosity to 0.190 ml/g .

b) Polymerization of propylene

It was operated as in example 1b) with the exception that there were employed 0.6 ml of the suspension of the catalyst component prepared as per a) and containing 1.72 mg of Ti. 430 g of polymer were obtained, corresponding to a yield of 250,000 g of polymer/g of Ti. The residue after extraction with boiling n-heptane was equal to 91.5%. Granulometric distribution of the polymer (method ASTM D 1921—63):

micron	% by weight
over 2000	0.2
over 1000	0.2
over 500	55.6
over 177	43.4
over 105	0.3
over 53	0.3

Apparent density: 0.5 kg/l .

EXAMPLE 13

a) Preparation of the catalyst component

It was operated as in example 12, with the exception that there were employed 2.8 g of benzoyl chloride, that was reacted for 1 hour at 60°C. After reaction with TiCl_4 , the dry product was subjected to analysis, from which the following results were obtained:

Ti=2.05%; Cl=62.2%; Si=0.04%; ethyl benzoate=10%.

b) Polymerization of propylene

It was operated as in example 12b). There were obtained 473 g of polymer equal to a yield of 222,220 g of polymer/g of Ti, with a residue after extraction with boiling n-heptane of 93%. The intrinsic viscosity $[\eta]$ was 2.5 dl/g . Granulometric distribution of the polymer:

micron	% by weight
over 2000	0.9
over 1000	1.8
over 500	31.6
over 177	64.6
over 105	0.7
over 53	0.3

Apparent density=0.52; flowability=16 seconds.

EXAMPLE 14

a) Preparation of the catalyst component

32.5 g of compound Cl Mg OEt, prepared according to example 3a were reacted with HCl under the same conditions as those of example 6a with the exception that it was operated in the presence of 3 g of ethyl benzoate. On analysis, the obtained product gave the following results:

Mg=14.02%; Cl=38.98%; ethyl benzoate=17%.

The product so obtained was reacted with TiCl_4 under the same conditions of example 12, except that it was operated at 110°C. From an analysis of the dry product the following was obtained:

Ti=2.65% Cl=59.8%; Si=0.1%; ethyl benzoate=9%.

b) Polymerization of propylene

The polymerization was conducted under the same conditions of example 12b) and 321 g of polymer were obtained, the yield being of 222,100 g of polymer/g of Ti.

EXAMPLE 15

a) Preparation of the catalyst component

16.8 g of the solid product prepared according to example 9a) and containing Mg=14.5%, Cl=40.83%, Si=0.16%, were reacted with 3 g of ethyl benzoate in 60 cc of n-octane for 1 hour at 60°C. The suspension was added to 200 ml of TiCl₄ and reacted at 120°C for 2 hours; after filtration, an analogous treatment was carried out. After repeated washings with heptane at 80°C, a part of the product was suspended in heptane, while the other part was dried under vacuum at 40°C. From an analysis of the dry product the following results were obtained:

Ti=2.2%; Cl=55.1%; Si=0.2%; ethyl benzoate=8%.

b) Polymerization of propylene

This test was conducted under the same conditions of example 12b). There were obtained 287 g of polymer, corresponding to a yield of 201,000 g of polymer/g of Ti.

EXAMPLE 16

a) Preparation of the catalyst component

37.7 g of the product prepared according to example 7a) and containing Mg=11%, Cl=37.65%, Si=0.1%, were reacted with 3 g of ethyl benzoate in 60 cc of n-octane for 1 hour at 60°C. The resulting suspension was reacted with TiCl₄ under the same conditions of example 12. On analysis, the dry product gave the following results;

Ti=1.8%; Cl=68.9%.

b) Polymerization of propylene

This test was carried out under the same conditions of example 12b). 350 g of polymer were obtained, corresponding to a yield of 296,000 g of polymer/g of Ti. The residue after extraction with boiling n-heptane was equal to 91.5%.

WHAT WE CLAIM IS:—

1. A component of a catalyst for the polymerization of olefins, in the form of spheroidal particles at least 80% of which have a size from 5 to 25 microns, a surface area between 90 and 700 m²/g and a porosity between 0.1 and 0.3 cc/g, the said particles consisting of a magnesium dihalide carrier on which a titanium compound is chemically bound.

2. A catalyst component according to claim 1, in which an electron donor compound is also chemically bound to the carrier, and the electron donor compound/titanium compound molar ratio is between 0.2 and 2.

3. A catalyst component according to claim 2, in which the electron donor compound is an alkyl benzoate, toluate, or anisate.

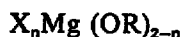
4. A catalyst component according to claim 1, 2 or 3, in which the titanium compound is a tetravalent titanium compound having at least one Ti-halogen bond.

5. A catalyst component according to claim 4, in which the content of tetravalent titanium compound extractable with TiCl₄ at 80°C is lower than 50% by weight of the tetravalent titanium compounds that are present.

6. A catalyst component according to claim 5, in which the said content of extractable titanium compound is less than 20% by weight of the said compound.

7. A catalyst component according to claim 1, substantially as described in any one of Examples 1 to 10 and 12 to 16.

8. A catalyst component according to claim 1, prepared by reacting a tetravalent titanium compound having at least one Ti-halogen bond with one or more magnesium compounds of the formula:



in which: $0 < n \leq 2$, R is an alkyl, aryl or cycloalkyl radical of 1 to 20 carbon atoms, X is a halogen atom or a group OR' in which R', which may be the same or different

Ti=2.65% Cl=59.8%; Si=0.1%; ethyl benzoate=9%.

b) Polymerization of propylene

The polymerization was conducted under the same conditions of example 12b) and 321 g of polymer were obtained, the yield being of 222,100 g of polymer/g of Ti.

EXAMPLE 15

a) Preparation of the catalyst component

16.8 g of the solid product prepared according to example 9a) and containing Mg=14.5%, Cl=40.83%, Si=0.16%, were reacted with 3 g of ethyl benzoate in 60 cc of n-octane for 1 hour at 60°C. The suspension was added to 200 ml of TiCl₄ and reacted at 120°C for 2 hours; after filtration, an analogous treatment was carried out. After repeated washings with heptane at 80°C, a part of the product was suspended in heptane, while the other part was dried under vacuum at 40°C. From an analysis of the dry product the following results were obtained:

Ti=2.2%; Cl=55.1%; Si=0.2%; ethyl benzoate=8%.

b) Polymerization of propylene

This test was conducted under the same conditions of example 12b). There were obtained 287 g of polymer, corresponding to a yield of 201,000 g of polymer/g of Ti.

EXAMPLE 16

a) Preparation of the catalyst component

37.7 g of the product prepared according to example 7a) and containing Mg=11%, Cl=37.65%, Si=0.1%, were reacted with 3 g of ethyl benzoate in 60 cc of n-octane for 1 hour at 60°C. The resulting suspension was reacted with TiCl₄ under the same conditions of example 12. On analysis, the dry product gave the following results;

Ti=1.8%; Cl=68.9%.

b) Polymerization of propylene

This test was carried out under the same conditions of example 12b). 350 g of polymer were obtained, corresponding to a yield of 296,000 g of polymer/g of Ti. The residue after extraction with boiling n-heptane was equal to 91.5%.

WHAT WE CLAIM IS:—

1. A component of a catalyst for the polymerization of olefins, in the form of spheroidal particles at least 80% of which have a size from 5 to 25 microns, a surface area between 90 and 700 m²/g and a porosity between 0.1 and 0.3 cc/g, the said particles consisting of a magnesium dihalide carrier on which a titanium compound is chemically bound.

2. A catalyst component according to claim 1, in which an electron donor compound is also chemically bound to the carrier, and the electron donor compound/titanium compound molar ratio is between 0.2 and 2.

3. A catalyst component according to claim 2, in which the electron donor compound is an alkyl benzoate, toluate, or anisate.

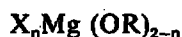
4. A catalyst component according to claim 1, 2 or 3, in which the titanium compound is a tetravalent titanium compound having at least one Ti-halogen bond.

5. A catalyst component according to claim 4, in which the content of tetravalent titanium compound extractable with TiCl₄ at 80°C is lower than 50% by weight of the tetravalent titanium compounds that are present.

6. A catalyst component according to claim 5, in which the said content of extractable titanium compound is less than 20% by weight of the said compound.

7. A catalyst component according to claim 1, substantially as described in any one of Examples 1 to 10 and 12 to 16.

8. A catalyst component according to claim 1, prepared by reacting a tetravalent titanium compound having at least one Ti-halogen bond with one or more magnesium compounds of the formula:



in which: $0 \leq n \leq 2$, R is an alkyl, aryl or cycloalkyl radical of 1 to 20 carbon atoms, X is a halogen atom or a group OR' in which R', which may be the same or different



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5 from R, is an alkyl, aryl or cycloalkyl radical of 1 to 20 carbon atoms, the said magnesium compound or compounds being in the form of particles having a surface area between 90 and 700 m²/g and a porosity between 0.1 and 0.2 cc/g. and being one obtained either by reaction of a metallorganic magnesium compound with an ester of orthosilicic acid or by reacting with one another magnesium metal, an ester of orthosilicic acid, and an organic halide of formula RX where X is Cl or Br and R is an alkyl, cycloalkyl or aryl radical having 1 to 20 carbon atom.

9. A catalyst component according to claim 8, prepared by reacting with one another:

- 10 a) a tetravalent titanium compound having at least one Ti-halogen bond; 10
- b) one or more magnesium compounds as defined in claim 8;
- c) an electron donor compound capable of forming adducts with the titanium compound.

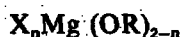
15 10. A catalyst component according to claim 9, in which compound b) having a Mg-OR bond, is reacted, prior to the reaction with the titanium compound, with a halogenating agent capable of exchanging a halogen atom for each OR group present in the magnesium compound. 15

11. A catalyst component according to claim 10 in which the reaction with the halogenating agent is conducted in the presence of the electron-donor compound.

20 12. A catalyst component according to claim 11, in which the electron donor compound is reacted with the product of the reaction between compound b) and the halogenating agent. 20

13. A catalyst component according to any of claims 10 to 12, in which the halogenating agent is anhydrous hydrogen chloride.

25 14. A catalyst component according to any of claims 8 to 13, in which compounds of formula: 25

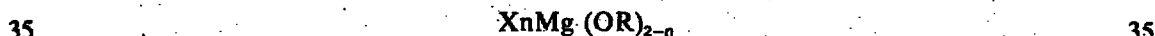


in which n is lower than 2, are prepared by reacting a magnesium metallorganic compound of formula:



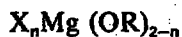
where $0 \leq n < 2$, R is an alkyl, aryl or cycloalkyl radical having 1 to 20 carbon atoms, and X is Cl or Br with an ester of orthosilicic acid.

15. A catalyst component according to any of claims 8 to 13, in which compounds of formula:



in which n is lower than 2, are prepared by reacting with one another magnesium metal, an ester of orthosilicic acid, and an organic halide of formula RX, in which X is Cl or Br and R is alkyl, aryl or cycloalkyl radical containing 1 to 20 carbon atoms.

40 16. A catalyst component according to Claim 8 in which compounds of formula: 40



45 in which n is about 2, X is halogen and R is as defined in Claim 8, are prepared by reacting with one another magnesium metal, an ester of orthosilicic acid, an organic halide of formula RX and a halogenating agent. 45

17. A catalyst component according to Claim 2, consisting of the product of the reaction of at least the following components:

- (a) a tetravalent titanium compound soluble in hydrocarbons;
- 50 (b) an adduct of a magnesium dihalide with an aliphatic or cycloaliphatic alcohol or a phenol, prepared from a compound of the formula $X_nMg(OR)_{2-n}$ (in which X is halogen, R is alkyl, aryl or cycloalkyl having 1 to 20 carbon atoms, and $0 \leq n < 2$), and 50
- (c) an electron-donor compound not containing active hydrogen atoms; c)

55 being simultaneously reacted with a) and b) or present in a combined form in b); the amount of electron-donor as defined in c), which after extraction of the catalyst component with $TiCl_4$ at 80°C for 2 hours remains bound thereto, being 0.5 to 3 moles/gram atom of titanium, and the titanium compounds extractable with $TiCl_4$ at 80°C being less than 50%. 55



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18. A catalyst component according to claim 17, in which adduct b) is obtained by reacting an anhydrous hydrogen halide or mixture thereof with an aliphatic or cycloaliphatic alcohol or a phenol, with a compound of formula $X_nMg(OR)_{2-n}$ as defined in claim 17.

19. A catalyst component according to claim 17 or 18, in which electron-donor compound c) is an aliphatic, aromatic or cycloaliphatic ester of an aromatic acid.

20. A catalyst component according to claim 19 in which the aromatic acid is benzoic acid.

21. A catalyst component according to any of claims 17 to 20, in which the titanium compound a) is $TiCl_4$ or $TiBr_4$.

22. A catalyst for the polymerization of alpha-olefins, comprising the product of the reaction of

(a) a metallorganic aluminium compound, with

(b) a catalyst component as defined in any of claims 1 to 21.

23. A catalyst according to claim 22 in which the component A is an aluminium trialkyl.

24. A catalyst according to claim 22 or 23, in which component A) is at least 10% complexed with an electron-donor compound.

25. A catalyst according to claim 22, substantially as described in any one of the foregoing Examples.

26. A process for the polymerization of an alpha-olefin, which comprises contacting the said alpha-olefin with a catalyst as claimed in any of claims 22 to 25.

27. A process according to claim 26, in which the said alpha-olefin is propylene.

28. Poly-alpha-olefins when produced by the process of claims 26 or 27.

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