

PATENT SPECIFICATION

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(54) CATALYST AND PROCESS FOR POLYMERIZATION OF
 ETHYLENE AND PROPYLENE

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 chome, Dojimahamadori, Kitaku, Osaka,
 Japan, a Japanese body corporate, 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 follow-
 ing statement:—

This invention relates to catalyst and pro-
 cess for polymerizing ethylene or propylene
 or a mixture of ethylene or propylene and
 another olefin. More particularly, it relates
 to a process for low-pressure polymerization
 of ethylene by means of a catalyst prepared
 from a novel compound of an organo- zinc-
 (or boron-) magnesium complex compound.

A process for low-pressure polymerization
 of ethylene in the presence of a catalyst con-
 sisting of an organomagnesium compound or
 organozinc compound and a transition metal
 compound has been disclosed in the specifi-
 cation of the patent issued to K. Ziegler
 (Japanese Patent Publication No. 1546/
 1957). However, since an organo-magnesium
 compound itself is insoluble in the inert
 hydrocarbon medium employed both in the
 synthesis of catalyst and in the polymeri-
 zation reaction, it cannot be effectively used,
 and it has not been possible to realize a high
 activity with this catalyst. It is also well
 known to persons skilled in the art in this
 field that organo-zinc compounds are
 soluble in inert hydrocarbon media and react
 with transition metal compounds to form
 catalysts, but the performances thereof as
 catalysts are extremely poor, and that organo-
 boron compounds do not form effective cata-
 lysts.

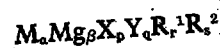
As catalysts which are capable of being
 effectively used and whose activities are

elevated by using in specialized formulations,
 there are known for example organo-
 magnesium halides, that is, a complex made
 from a Grignard reagent and an ether, and
 a system derived from an organomagnesium
 alkoxide or a system derived from dialkyl-
 magnesium and aluminum halide (West Ger-
 man Laid Open Patent Specification Nos.:
 2 024 558 and 2 116 045 and Dutch Patent
 No. 7 103 232). These catalysts have very
 high activity per unit weight of transition
 metal but have the disadvantage of leaving
 halogen deposits in the resultant polymer and
 thus a catalyst removal step cannot completely
 be omitted from the polyethylene manufactur-
 ing process.

We have found that an organo-zinc-(or
 boron-) magnesium complex, which is soluble
 in an inert hydrocarbon medium, can be pro-
 duced by reacting a specific organomagnesium
 compound and an organo-zinc- (or boron-)
 compound; and that a highly active catalyst
 can be obtained by reacting the above com-
 plex with a titanium or vanadium compound
 and then combining the resultant solid with
 an organo-aluminum compound.

According to the present invention there is
 provided a catalyst for the polymerization of
 ethylene or propylene, or the copolymerization
 thereof with another olefin, the catalyst being
 prepared by reacting (A) a hydrocarbon-
 insoluble reaction product formed by the
 reaction of

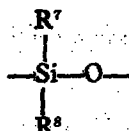
(i) an organomagnesium-containing, hydro-
 carbon-soluble complex represented by the
 general formula of



(wherein M is a zinc or boron atom, R¹ and

R^2 are a hydrogen atom or the same or different hydrocarbon radicals, each having 1—10 carbon atoms, X and Y are the same or different OR^3 or $OSiR^4R^5R^6$ groups, R^3 is a hydrocarbon radical having 1—10 carbon atoms, R^4 , R^5 and R^6 are a hydrogen atom or the same or different hydrocarbon radicals each having 1—10 carbon atoms, α and β are each greater than or equal to 1, and β/α is 1—10, p, q, r, s are each 0 or a positive number and have a relationship of $p + q + r + s = m\alpha + 2\beta$, and $0 \leq (p + q) / (\alpha + \beta) \leq 0.80$ and m is the valency of M),

or a reaction product of (i) with (ii) a linear or cyclic siloxane compound having a constitutional unit represented by the general formula

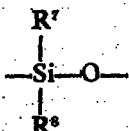


(wherein R^7 and R^8 are a hydrogen atom or different hydrocarbon radicals each having 1—10 carbon atoms), and

(iii) one or more titanium or vanadium compounds containing 1—4 halogen atoms; and

(B) an organoaluminum compound having the general formula of AlR^9Z_n (wherein R^9 is a hydrocarbon radical having 1—20 carbon atoms, Z is selected from hydrogen, halogen, alkoxy, aryloxy and siloxy radicals and n is a number in the range 2—3).

In one embodiment of the invention said organomagnesium compound has the general formula $M_2MgR^1R^2$ and is reacted with a linear or cyclic siloxane compound containing one or more constitutional units of the formula



in the dimer form or polymeric form greater than dimer.

This invention has some distinctive features. First, an extremely high catalytic efficiency can be achieved. As described later in the example, the catalyst efficiency obtained amounts to 30,000 grams of polyethylene per gram of solid component per hour per Kg/cm² of ethylene. This allows complete elimination of the catalyst removal step. As compared therewith, the catalysts according to the above patent applications (West German Laid Open Patent Specification Nos.: 2 024 558 and 2 116 045 and Dutch Patent Specification 7 103 232) provide a catalytic efficiency as

low as 10,000 g or less. This clearly proves the superiority of the catalyst according to the present invention. Secondly, polymers having higher molecular weight and higher rigidity can be obtained and easy control of molecular weight and molecular distribution can be attained through the modification of catalyst components.

These features of the present invention are realized by reacting the specified organo-zinc- (or boron-) magnesium complex and a titanium or vanadium compound and subsequently reacting the resultant hydrocarbon-insoluble solid with the specified organo-aluminum compound. In this respect, the hydrocarbon-soluble organo-zinc- (or boron-) magnesium complex is the most important component. The organo-zinc-magnesium complex is soluble in a hydrocarbon medium and forms a viscous solution, but in the synthesis of the solid component (A), it shows a performance different from that of a complex containing an organoaluminum (e.g. as disclosed in our copending patent application No. 20721/75) Serial No. 1 503 779. Since all the organo-metallic components are included in the solid product, change of catalytic properties due to after-reaction hardly occurs and hence this complex is easier to handle. Further since it is not liable to be influenced by the reaction conditions, it has a superior reproducibility of its synthesis. On the other hand the organo-boron-magnesium complex can be easily synthesized and fluctuation of performance of catalyst due to the composition of the complex is extremely small. Such stability of performance of the catalyst has extremely large benefits in the case of commercial scale production.

The above-mentioned features of this invention are more fully described by way of Examples and Comparative Examples given later. Symbols Mw and Mn used therein denote weight average molecular weight and number average molecular weight, respectively and were measured by the gel permeation chromatography (GPC). The ratio of weight average molecular weight to number average molecular weight Mw/Mn is a measure of molecular weight distribution; the lower the value of this ratio, the narrower the molecular weight distribution. As is evident from the comparison of Example 1 and Comparative Examples 1, 2 and 3, in the case where a solid reaction product is synthesized by using solely an organozinc or an organomagnesium compound or a mixture of these compounds without reaction therebetween, the resultant catalyst has an extremely inferior performance compared with the catalyst of the present invention in which a hydrocarbon-soluble organo-zinc-magnesium is used. With regard to complexes containing alkoxy, aryloxy, siloxy radical or siloxane, the solubility in a hydrocarbon medium is almost

equal to that of a complex which does not contain any of these radicals. With regard to the performance of polymerization if the content of these radicals is increased, catalytic activity increases and after passing a point of maximum value it decreases. On the other hand, molecular weight control in the polymerization becomes easier (the production of lower molecular weight polyethylene becomes easier) and the production of polyethylene having a narrower molecular weight distribution becomes possible. Thus the complex containing electro-negative groups such as alkoxy, aryloxy, siloxy radical or siloxane is preferable in the point that a polymer suitable for the production of large-size shaped articles by way of injection molding can be obtained.

Description will be given to the organo-zinc- (or boron-) magnesium complex represented by the general formula of



(wherein M, R¹, R², X, Y, α, β, p, q, r and s are as above-defined). The hydrocarbon radicals having 1—10 carbon atoms, represented by R¹ in the above-mentioned formula is preferably an alkyl radical and include, for example, methyl, ethyl, propyl, butyl, amyl, hexyl, octyl, decyl as preferred radicals. The hydrocarbon radical having 1—10 carbon atoms, represented by R² in the above-mentioned formula may be alkyl or aryl and includes for example, methyl, ethyl, propyl, butyl, amyl, hexyl, octyl, phenyl as preferred radicals. R¹ and R² can also be hydrogen atoms.

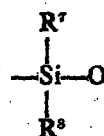
In the radicals OR³ and OSiR⁴R⁵R⁶ represented by X, it is preferable if the hydrocarbon radical R³ having 1—10 carbon atoms is an alkyl, cycloalkyl or aryl radical for example, methyl, ethyl, propyl, butyl, amyl, hexyl, octyl, decyl, cyclohexyl, or phenyl radicals. Further R⁴, R⁵ and R⁶ are a hydrogen atom or the same or different hydrocarbon radicals having 1—10 carbon atoms. Among such hydrocarbons, for example, alkyl radicals such as methyl, ethyl, propyl, butyl hexyl, and octyl; cycloalkyl radicals such as cyclohexyl and methylcyclohexyl; and aryl radicals such as phenyl and naphthyl are preferable. As examples of the siloxy radical, there can be mentioned methyldihydrosiloxy, dimethyldihydrosiloxy, trimethylsiloxy, methyl-ethylhydrosiloxy, methyldiethylsiloxy, triethylsiloxy, methylbutylhydrosiloxy, dimethylbutylsiloxy, methylphenylhydrosiloxy, ethylphenylhydrosiloxy, methylethylphenylsiloxy, triphenylsiloxy, and α-naphthylphenylmethylsiloxy.

The ratio of magnesium to zinc or boron β/α is particularly important to obtain the active solid component of the present invention. In order to synthesize the solid

component of suitable activity, it is necessary that the complex used in the synthesis participates in the reaction effectively under the reaction condition. For that purpose, the existence of the zinc or boron component in an amount suitable to stabilize the dissolved state is important. Both too high values or too low values of β/α, lower the stability of the complex and in turn, lower its solubility. If the value of β/α in the zinc-magnesium complex, is lower, the participation of the zinc component becomes greater, resulting in a reduction of catalytic activity. As evident from examples 1, 16—19 and comparative example 4, hereinafter described, the effective range is 1—10 and preferably 2—6.

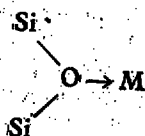
Further the ratio of (p+q)/(α+β) relative to the content of radicals X and Y is also important in attaining an effective catalyst of the present invention. As is evident from example 20 and 21 and comparative example 5 hereinafter described, with higher values of (p+q)/(α+β), activity is reduced. Accordingly, the effective range of (p+q)/(α+β) is ≤ 0.8. In order to attain a polymer having a narrow molecular weight distribution, (p+q)/(α+β) is preferably in the range of 0.30—0.80. A complex containing no alkoxy, aryloxy or siloxy group, can be prepared by reacting the organozinc (or boron) compound represented by the general formula ZnR¹₂, BR¹₃ or BR¹₂H (R¹ is a hydrocarbon) and organomagnesium compound, represented by the general formula of MgR²₂ or MgR²₂Q wherein R² is a hydrocarbon radical and Q is a halogen. The reaction is performed at a temperature ranging from room temperature to 150°C in the inert hydrocarbon medium such as hexane, heptane, cyclohexane, benzene or toluene. Among alkyl radicals bonded with the boron atom, methyl, ethyl and propyl radicals are particularly preferred because of the ease of forming their complexes. Introducing alkoxy, aryloxy or siloxy groups into the above-mentioned complex is accomplished by reacting the complex and oxygen, an alcohol, silanol, aldehyde, ketone or ester of carboxylic acid at room temperature, or otherwise by the reaction of ZnR¹₂ or BR¹₃ and MgX₂ or R³MgX or by the reaction of MgR²₂ and ZnX₂, R¹ZnX, R¹ BX, R¹ BX₂ or BX₃ wherein X has the same meaning specified above (which does not include halogen).

Description of the siloxane compound represented by the general formula of



will now be given. The substituents R⁷ and

4
 R^a are hydrogen atoms or the same or different hydrocarbon radicals having 1 to 10 carbon atoms. Among hydrocarbon radicals, for example such radicals as methyl, ethyl, propyl, butyl, hexyl, octyl, cyclohexyl, or phenyl are recommended. These compounds can be used in the form of linear or cyclic dimers or a polymer greater than dimer consisting of one or more of the defined constituting units. Illustrative compounds include sym. dihydrotetramethyldisiloxane, hexamethyldisiloxane, pentamethyltrihydrotrisiloxane, cyclic methylhydrotetrasiloxane, polymethylhydrosiloxane whose terminal groups are blocked with methyl group, polydimethylsiloxane, polyphenylhydrosiloxane whose terminal groups are blocked with methyl groups, and polymethylphenylsiloxane. The reaction of the organo-zinc- (or born-) magnesium complex and siloxane is carried out in an inert reaction medium (e.g. hexane, heptane, benzene and toluene) at a temperature of -20 to 150°C. The reaction ratio as expressed by Si-O/[Mg+Zn(orB)] is in the range of 0.3-5, preferably 0.5-2. In this reaction the forming of the Si-O-M linkage and the complex linkage of

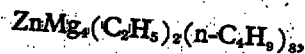


30 (wherein M is Zn, B or Mg) can be confirmed by infrared spectrum analysis and nuclear magnetic resonance spectroscopy. It is preferable that the mole ratio of Si-O-M/[Zn(or B)+Mg] in the complex is 0.8 or lower than 0.8 from the point of catalyst activity. The above-mentioned complex linkage is preferable because it hardly influences catalyst activity but narrows the molecular weight distribution and lowers the chlorine content of solid component (A). The structure of the complex is not known, but it is presumed that there results a single or compound complex consisting of zinc (or boron) and magnesium components. This assumption is based on the fact that R₂Mg is insoluble in inert hydrocarbon solvents whereas the said complex is soluble in those media. It is also assumed that there occurs an exchange reaction between the groups attached to the zinc (or boron) and magnesium atoms, respectively.

50 The titanium or vanadium compound containing at least one halogen atom (catalyst component (iii)) includes titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, ethoxytitaniumtrichloride, propoxytitanium trichloride, butoxytitanium trichloride, dibutoxytitanium dichloride, tributoxytitanium monochloride, vanadium tetrachloride, vanadyl trichloride, mono-

butoxyvanadyl dichloride, dibutoxyvanadyl monochloride; titanium and vanadium halides; hydroxyhalides, alkoxy halides; or combinations thereof. Particularly those having 3-4 halogen atoms are preferable.

The reaction method between the organo-zinc (or boron) magnesium complex and the titanium or vanadium compound is important in obtaining an effective catalyst of the present invention. The reaction takes place at a temperature up to 100°C, preferably below 20°C in an inert reaction medium, e.g. an aliphatic hydrocarbon such as hexane or heptane; an aromatic hydrocarbon such as benzene, toluene or xylene; or an alicyclic hydrocarbon such as cyclohexane or methylcyclohexane. To ensure high activity, it is recommended that the reaction ratio of the two different components of catalysts is 0.05-50 mols, especially 0.2-5 mols of the organo-zinc- (or boron-) magnesium complex per mol of the titanium or vanadium compound. For the number of moles of the organo-zinc- (or boron-) magnesium complex the molar sum of zinc (or boron) and magnesium atoms is used. Taking as an example the complex



677.7 grams (corresponding to the gram-molecular weight based on this structural formula is equivalent to 5 mols. In order to obtain a higher catalyst activity, it is preferable to use a method in which the reaction is carried out while the two catalyst components (A) and (B) are simultaneously added to a reaction zone (i.e. simultaneous addition method). The hydrocarbon-insoluble reaction product may be used directly, provided the reaction is complete but is desirably separated from the reaction mixture to enhance the reproducibility of polymerization. A catalyst capable of producing polymers having more uniform particle sizes and higher bulk densities can be prepared by reacting the reaction products thus obtained with halides of aluminum, silicon, tin, titanium, and vanadium.

As the organoaluminum compound (catalyst component B) which is another component of the catalyst of the present invention, a single compound, or a mixture thereof, represented by the general formula of $\text{AlR}^a_n\text{Z}_{3-n}$ is used. The hydrocarbon radical R^a having 1-20 carbon atoms may be an aliphatic, aromatic or alicyclic hydrocarbon. The group Z is a hydrogen atom, a halogen atom, an alkoxy group, aryloxy group or siloxy group; n is a number in the range of 2-3. Recommended compounds include, for example, triethylaluminum, tri-n-propylaluminum, tri-isopropylaluminum, tri-n-butylaluminum, tri-isobutylaluminum, trihexylaluminum, trioctylaluminum, tridecyl-

aluminum, tridoecylaluminum, trihexadecylaluminum, diethylaluminum halide, di-isobutylaluminum halide, diethylaluminum ethoxide, di-isobutylaluminum ethoxide, di-isobutylaluminum butoxide, di-isobutylaluminum octyloxyde, diethylaluminum chloride, di-isobutylaluminum chloride, dimethyl, ethylmethylhydrosiloxyaluminum diethyl, ethyldimethylsiloxyaluminum diethyl and combinations thereof.

When combined with the hydrocarbon-insoluble solid, said alkylaluminum compound offers higher catalyst activity. To achieve a maximum catalytic activity, it is preferable to use specifically trialkylaluminum or dialkylaluminum hydride. When incorporating a group X (as previously defined) which is electronegative, with trialkylaluminum or dialkylaluminum hydride, the resultant catalyst tends to decrease in activity but has characteristic polymerization behaviour. Thus it is possible to produce various polymers of practical use under high-activity conditions. As an example, introducing alkoxy group renders easier control of molecular weight.

The reaction between components (A) and (B) according to this invention may be conducted by adding both catalytic components to the polymerization system under the polymerization conditions, or otherwise in advance of polymerization. The reaction ratio of the components is preferably 1—3,000 m mols of component (B) per gram of component (A).

Polymers having a broad distribution of molecular weight suitable for blow molding, film or sheet molding, can be produced by using a catalyst of the present invention which is obtained by reacting components (A) and (B) with a halogenated hydrocarbon. Preferably, such halogenated hydrocarbons have an atomic ratio of halogen/carbon of 2 or less, and 2 or more carbon atoms. Examples of halogenated hydrocarbons suitable for use in the present invention are 1,2 - dichloroethane, 1,2 - dichloro - propane, 2,3 - dichloro - butane, 1,1,2 - trichloro - ethane, 1,2 - dibromo - ethane, 1,2 - dichloro - hexane, and 1,1,2,2 - tetrachloro - ethane.

Such effects as extremely high catalyst activity and yet a broad distribution of molecular weight in the resultant polymer are observed only when the hydrocarbon-insoluble solids of the present invention are employed in the polymerization reaction, and are not achieved by the aforementioned prior art methods. The amount of halogenated hydrocarbon to be used is 0.05 to 10 moles, preferably 0.1 to 1 mole, per mole of the component B.

As the polymerization method there may be used conventional suspension-, solution-, or gas phase-polymerization. In the cases of suspension and solution polymerization pro-

cesses, the catalyst is let into the reactor with a polymerization medium, e.g. aliphatic hydrocarbon such as hexane or heptane; aromatic hydrocarbon such as benzene, toluene or xylene; or alicyclic hydrocarbon such as cyclohexane or methylcyclohexane. Then, ethylene is added up to 1—50 Kg/cm². On the other hand, the gas phase polymerization is possible by carrying out the polymerization using a procedure such as fluidized bed, moving bed, mixing with a stirrer, so as to give better contact of ethylene with the catalyst and with an ethylene pressure of 1—50 Kg/cm² and a temperature of from room temperature to 150°C. In order to control the molecular weight of the polymer, there may be added hydrogen, or an organometallic compound which is liable to effect chain transfer.

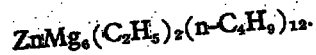
The present invention also encompasses using the catalysts of the present invention for polymerizing ethylene or propylene or copolymerizing them with other monoolefins such as propylene, butene-1, and hexene-1.

The following Examples illustrate but do not limit this invention. Symbols Mw, Mn and Mw/Mn therein have the meanings given above. The units of the catalyst efficiencies quoted in the Examples are gram(s) of polymer per gram of solid component per hour per Kg/cm² of ethylene pressure.

Example 1.

(1) Synthesis of the organo - zinc - magnesium complex

In a 500-ml flask were placed 13.80 g of di-n-butylmagnesium and 2.06 g of diethylzinc with 200 ml of n-heptane. The mixture was reacted, with stirring, at 80°C for 2 hours. There was obtained a complex having the composition



(2) Synthesis of the hydrocarbon-insoluble solid component

A 500 ml flask equipped with two dropping funnels was evacuated to remove oxygen and moisture, and then purged with dry nitrogen, 160 ml of n-heptane was introduced into this flask and cooled. Then 80 ml of n-heptane solution containing 40 m mols of the above-mentioned complex and 80 ml of a n-heptane solution containing 40 m mols of titanium tetrachloride were placed in separate dropping funnels. Both the components were simultaneously added with stirring at -10°C for 2 hours and reaction was continued for 3 hours at this temperature. The resultant hydrocarbon-insoluble solid was isolated, washed with n-heptane and dried to give 10.3 g of solid.

(3) Polymerization reaction

- In a 5-liter autoclave which had been evacuated and purged with nitrogen, were placed 5 mg of the above hydrocarbon-insoluble solid and 1.5 m mol of tri-isobutylaluminum plus 3 liters of n-heptane previously dehydrated and degassed. While the temperature of the autoclave was kept at 85°C, there were added hydrogen up to 2.0 Kg/cm² gauge pressure and then ethylene up to 6.0 Kg. total gauge pressure. The polymerization was performed for one hour while additional ethylene is fed to maintain this total gauge pressure. 605 g of polymer was obtained; Mw, 85,000 and Mw/Mn, 8.5. The catalyst efficiency was 30,300.

Comparative Example 1.

- The synthesis of catalyst and the polymerization were carried out as in Example 1 except that di-n-butyl-magnesium was used instead of the organo-zinc-magnesium complex and this material was turned into slurry and a TiCl₄ solution was added from a dropping funnel. 90 g of polymer was obtained. The catalyst efficiency was 4,500.

Comparative Example 2.

- The synthesis of catalyst and the polymerization were conducted as in Example 1 except that diethylzinc was used instead of the organo-zinc-magnesium complex. 15 g of polymer was obtained. The catalyst efficiency was 750.

Comparative Example 3.

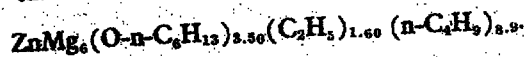
- The polymerization was carried out as in Example 1 except that 5.7 m mols of diethylzinc and 34.3 m mols of di-n-butylmagnesium were used instead of the organo-zinc-magnesium complex and the mixture was slurried and a TiCl₄ solution was added from a dropping funnel. 64 g of polymer was obtained. The catalyst efficiency was 3,200.

Example 2.

In a 200-ml flask was placed a solution containing 50 m mols organo-zinc-magnesium complex having the composition



prepared in Example 1, in 60 ml of heptane. Then, 25 m mols of n-hexylalcohol in heptane was added, with stirring, dropwise at 10°C for 30 minutes. A portion of this solution was sampled and oxidized by dry air, then hydrolized to convert alkyl and alkoxy groups into their alcohols. The final product was analyzed by gas chromatography. From the analytical values based on ethanol, n-butanol n-hexylalcohol, the composition turned out to be



In the same manner as in Example 1, 40 m mols of the complex and 40 m mols of titanium tetrachloride were reacted, at -10°C for 4 hours. Using 5 mg. of the resultant hydrocarbon-insoluble solid and 1.5 m mol of tri-isobutylaluminum, the polymerization was performed under the same condition as in Example 1. 590 g of polymer was obtained, Mw 51,000 and Mw/Mn, 4.6. The catalyst efficiency was 29,500.

Examples 3 to 9.

Using, in combination, the hydrocarbon-insoluble solid prepared by the same method as in Example 1 with the synthesis condition shown in Table 1, and the organo-aluminum component (Table 1), the polymerization was performed under the same condition as in Example 1. The results are shown in Table 1. The organo-zinc-magnesium complex used was prepared as in Examples 1 and 2, using diethylzinc, di-n-butylmagnesium, and alcohols or silanol.

TABLE I

Example	Catalyst						Results of polymerization			
	Hydrocarbon-insoluble solid						Yield g	Mw	$\frac{Mw}{Mn}$	Catalyst efficiency g/g solid hr. Kg/cm ² ethylene pressure
	Zn-Mg complex	Ti compound	Molar ratio Zn+Mg/ Ti	Temperature (°C) × Time (hr)	Amount of addition, mg.	Organo- aluminum (addition, m mol)				
3	ZnMg ₂ (C ₂ H ₅) ₂ (n-C ₄ H ₉) ₆	Ti Cl ₄	1/1	-10×4	5	Al(C ₂ H ₅) ₃ (3.0)	575	78000	9.2	28800
4	ZnMg ₂ (C ₂ H ₅) ₂ (n-C ₄ H ₉) ₆	Same as above	1/1	-10×4	5	Same as above	560	74000	9.5	28000
5	ZnMg ₂ (O-nC ₄ H ₉) _{3.25} (C ₂ H ₅) _{1.40} (n-C ₄ H ₉) _{5.35}	Same as above	2/1	0×4	5	Al(C ₂ H ₅) ₃ (3.0)	720	47000	4.1	36000
6	ZnMg (O-C ₄ H ₉) _{0.90} (C ₂ H ₅) _{1.60} (n-C ₄ H ₉) _{1.50}	Same as above	0.8/1	0×4	5	Same as above	540	56000	5.3	27000
7	ZnMg ₂ [OSi(CH ₃) ₂] _{4.90} (C ₂ H ₅) _{0.90} (n-C ₄ H ₉) _{6.20}	Same as above	1.5/1	-20×4	5	Al(i-C ₄ H ₉) ₃ (1.5)	512	49000	3.8	25600
8	ZnMg ₂ [OSi·C ₂ H ₅ (CH ₃) ₂] _{2.50} (C ₂ H ₅) _{1.30} (n-C ₄ H ₉) _{6.20}	a 2:1 mol ratio mixture of TiCl ₄ and VCl ₄	1/1	-10×4	5	Al(i-C ₄ H ₉) ₂ H (1.5)	484	56000	4.5	29200
9	ZnMg ₂ (OSi·H·CH ₃ ·C ₂ H ₅) (C ₂ H ₅) (n-C ₄ H ₉) ₆	a 2:1 mol ratio mixture of TiCl ₄ and TiCl ₃ (O-n-C ₄ H ₉)	1/1	0×4	5	Al(n-C ₄ H ₉) ₃ (1.5)	450	62000	4.2	22500

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Example 10.

As in Example 1 organo - zinc - magnesium complex of the composition



- 5 was synthesized from di - n - propyl zinc and di - n - hexyl magnesium. In the same way as in Example 1, 40 m mols of a 1:1 by mole mixture of titanium tetrachloride/monobutoxytitanium trichloride and 40 m mol of the above complex were reacted at 10°C for 4 hours. Using as catalyst 5 mg of the resultant hydrocarbon - insoluble solid plus 3.0 m mols of tridodecylaluminum, the polymerization was carried out as in Example 1. 15 370 g of polymer was obtained; Mw, 66,000 and Mw/Mn, 8.1. The catalyst efficiency was 18,500.

Example 11.

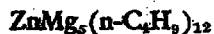
- 20 As in Example 2, organo - zinc - magnesium complex of the composition



- 25 was made from the organo - zinc - magnesium complex prepared in Example 10 and isobutanol. In the same way as in Example 1, 40 m mols of vanadium tetrachloride and 40 m mols of this complex were reacted at 0°C for 4 hours. Using as catalyst 5 mg of the resulting hydrocarbon-insoluble solid plus 3.0 m mol of tridodecylaluminum, the polymerization was carried out as in Example 1. 30 495 g of polymer was obtained; Mw, 72,000 and Mw/Mn, 4.5. The catalyst efficiency was 24,800.

Example 12.

- 35 As in Example 1, organo - zinc - magnesium complex of the composition of

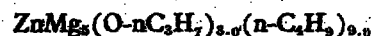


- 40 was made from di - n - butylzinc and di - n - butylmagnesium. In the same manner as in Example 1, 40 m mols of this complex and 40 m mols of vanadyl trichloride were reacted at 0°C for 4 hours. Using as catalyst 5 mg of the resulting hydrocarbon - insoluble solid plus organoaluminum compound of the composition 45 $\text{Al}(\text{i-C}_4\text{H}_9)_{2.5}(\text{OC}_2\text{H}_5)_{0.5}$, the polymerization was conducted as in Example 1. 560 g of polymer was obtained; Mw, 95,000

and Mw/Mn, 9.6. The catalyst efficiency was 28,000.

Example 13.

As in Example 2, organo - zinc - magnesium complex of the composition



was made from the organo - zinc - magnesium complex prepared in Example 12 and n-propanol. In the same manner as in Example 1, 40 m mols of a 1:1 by mole mixture of titanium tetrachloride / vanadium tetrachloride and 40 m mols of this complex were reacted at -20°C for 4 hours. Using as catalyst 5 mg of the resulting hydrocarbon insoluble solid plus organoaluminum compound of the composition



the polymerization was performed as in Example 1. 630 g of polymer was obtained; Mw, 49,000 and Mw/Mn, 5.3. The catalyst efficiency was 31,500.

Example 14.

Using the same catalyst and polymerization condition as in Example 1 except an ethylene-propylene mixture gas containing 3 percent propylene was employed instead of ethylene, the polymerization was conducted. 720 g of polymer was obtained; Mw, 41,000 and Mw/Mn, 4.6. The catalyst efficiency was 36,000.

Example 15.

Using the same catalyst and polymerization condition as in Example 1 except that an ethylene - butene - 1 mixture gas containing 4 percent butene - 1 was employed instead of ethylene, the polymerization was conducted. 740 g of polymer was obtained; Mw, 35,000 and Mw/Mn 4.2. The catalyst efficiency was 38,000.

Examples 16-22 and Comparative

Examples 4-5.

Solid components were prepared using the same catalyst components and synthetic conditions as in Example 1, except that organo-zinc-magnesium complexes given in Table 2 were used. These solid components were then used in polymerization to give the results shown in Table 2.

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TABLE 2

Examples	Organo-magnesium complexes	Results of polymerization			
		Yield g	Mw ($\times 10^4$)	Mw/Mn	Catalyst efficiency
16	$\text{ZnMg}_9(\text{C}_2\text{H}_5)_2(\text{n-C}_4\text{H}_9)_{18}$	370	9.2	8.7	18500
17	$\text{ZnMg}_4(\text{C}_2\text{H}_5)_2(\text{n-C}_4\text{H}_9)_8$	644	9.1	7.6	32200
18	$\text{ZnMg}_2(\text{C}_2\text{H}_5)_2(\text{n-C}_4\text{H}_9)_4$	590	8.7	8.8	29500
19	$\text{ZnMg}(\text{C}_2\text{H}_5)_2(\text{n-C}_4\text{H}_9)_2$	436	9.3	9.1	21800
20	$\text{ZnMg}_4(\text{O-nC}_4\text{H}_9)_{0.75}(\text{C}_2\text{H}_5)_{1.75}(\text{n-C}_4\text{H}_9)_{7.50}$	694	5.8	6.7	34700
21	$\text{ZnMg}_4(\text{O-nC}_4\text{H}_9)_{1.00}(\text{C}_2\text{H}_5)_{1.00}(\text{n-C}_4\text{H}_9)_{4.95}$	390	5.3	3.7	19500
22	$\text{ZnMg}_4(\text{C}_2\text{H}_5)_2(\text{C}_{10}\text{H}_{21})_8$	374	8.7	9.2	18700
Comparative Example 4	$\text{Zn}_2\text{Mg}(\text{C}_2\text{H}_5)_4(\text{n-C}_4\text{H}_9)_2$	104	9.7	9.5	5200
Comparative Example 5	$\text{ZnMg}_4(\text{O-nC}_4\text{H}_9)_{5.0}(\text{C}_2\text{H}_5)_{0.00}(\text{n-C}_4\text{H}_9)_{4.20}$	170	4.9	4.2	8500

Examples 23—26.

(i) Reactions of organozinc-magnesium complexes with siloxane

5 A 50 ml solution of heptane containing 1.0 mole/l of an organozinc-magnesium complex prepared as in Example 1 was reacted in a 200-ml flask with a 50 ml solution of heptane containing 0.5 to 2.0 moles/l, based on the

10 Si—O bond, of a siloxane compound.

Those organozinc-magnesium complexes, siloxane compounds, and reaction conditions shown in Table 3 were used in the reaction.

15 The Si—O—M bond (wherein M is zinc or magnesium) was determined by concentrating the above reaction mixture, and measuring quantitatively the gas emitting when the concentrated mixture was hydrolyzed.

20 (ii) Synthesis of hydrocarbon-insoluble solids

These solids were prepared as in Example 1 under the conditions given in Table 3.

(iii) Polymerization

25 A hydrocarbon-insoluble solid (5 mg) prepared in (ii), above, an aluminum component shown in Table 3, and 800 ml of vacuum-deaerated hexane were charged into a 1.5-litre autoclave which has been vacuum-deaerated and in which air has been substituted with dry nitrogen. The temperature within the autoclave was maintained at 85°C. Hydrogen and ethylene were forced into the autoclave at pressures of 1.0 Kg/cm² and 3.0 Kg/cm², respectively, so that the pressures, together with a vapour pressure of hexane, would give a total pressure of 4.7 Kg/cm² gauge. Polymerization was conducted for an hour while maintaining a total pressure of 4.7 Kg/cm² gauge by supplying ethylene, 40 to give the results given in Table 3.

TABLE 3

Catalyst															Results of polymerization			
Hydrocarbon-insoluble solids																		
Reaction of organozinc-magnesium complexes with siloxane compounds																		
Examples	Organozinc-magnesium complexes		Si-O- (Mg+Zn) moles ratio		Temp. (°C) × Time (hr)		Si-O-M/ Mg+Zn moles ratio		Ti compounds	Ti/Mg+Zn moles ratio	Temp. (°C) × Time (hr)	Composition wt%		Organoaluminum compounds (in mol)	Yield g	Catalyst efficiency	Mw (×10 ³)	Mw/Mn
	Siloxane	Organozinc-magnesium complexes	Si-O- (Mg+Zn) moles ratio	Temp. (°C) × Time (hr)	Si-O-M/ Mg+Zn moles ratio	Ti	Cl											
23	ZnMg ₂ (C ₂ H ₅) ₂ (n-C ₄ H ₉) ₁₂	Hexamethyl- disiloxane	1/1	100×5	0.12		TiCl ₄	1/1	-5×4	14.2	42.6	Al(n-C ₄ H ₉) ₃ (2.0)	317	21100	5.5	4.5		
24	ZnMg ₂ (C ₂ H ₅) ₂ (C ₆ H ₁₃) ₄	Phenylhydro- polysiloxane 30 centistokes, 30°C	1/1	80×5	0.54		TiCl ₄	2/1	5×4	11.6	42.1	Al(i-C ₄ H ₉) ₃ (0.5)	243	16200	5.4	3.8		
25	ZnMg ₂ (n-C ₄ H ₉) ₁₀	Symmetrical tetramethyl- dihydrodi- siloxane	2/1	20×1	0.78		TiCl ₄	1/1	20×4	10.5	35.6	Al(C ₂ H ₅) ₃ (0.5)	298	19900	5.8	3.2		
26	ZnMg ₂ (C ₂ H ₅) ₂ (n-C ₄ H ₉) ₆	Cyclic methyl- hydrotetra- siloxane	1/2	10×1	0.25		Mixture of TiCl ₄ and Ti(O-n-C ₄ H ₉) ₂ (2:1)	1/1	-20×4	14.6	44.6	Al(C ₂ H ₅) ₃ (1.0)	335	22300	6.2	5.8		

Example 27.

(i) Synthesis of an organoboron-magnesium complex

Di-n-butyl magnesium (13.8 g), 1.63 g of triethylboron, and 200 ml of n-heptane were placed in a 500-ml flask and stirred at 50°C for 2 hours to form a complex of $\text{BMg}_2(\text{C}_2\text{H}_5)_2(n\text{-C}_4\text{H}_9)_{12}$.

(ii) Synthesis of a hydrocarbon-insoluble solid component

Oxygen and moisture were removed by evacuation from a 500-ml flask equipped with two dropping funnels, and the flask was purged with dry nitrogen. After 160 ml of n-heptane was added, the flask was cooled to

-10°C. A solution of 40 m mol, based on magnesium atom, of the complex in 80 ml of n-heptane was placed in one dropping funnel, and a solution of 40 m mols of titanium tetrachloride in 80 ml of n-heptane placed in the other funnel. Both solutions were added dropwise simultaneously over a period of 1 hour, while stirring the mixture at a temperature of -10°C. The mixture was further stirred at this temperature for additional 3 hours. The hydrocarbon-insoluble solid thus formed was isolated, washed with n-heptane and dried to give 9.6 g of the solid.

(iii) Polymerization reaction

A hydrocarbon-insoluble solid (5 mg) pre-

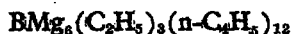
pared in (ii), above, 0.4 mmol of triisobutyl aluminum, and 0.8 litre of dehydrated and deaerated n-heptane were charged into a 1.5-litre autoclave which had been vacuum-deaerated and in which air had been purged with dry nitrogen. The temperature within the autoclave was maintained at 85°C. Hydrogen was forced into the autoclave at a gauge pressure of 1.6 Kg/cm², and then ethylene was charged so that the total gauge pressure of 4.0 Kg/cm² was reached. Polymerization was conducted for an hour while maintaining a total gauge pressure of 4.0 Kg/cm² by supplying ethylene, thereby obtaining 312 g of a polymer. The polymer had a Mw of 78,000 and a Mw/Mn ratio of 9.2. The catalyst efficiency was 26,000.

Example 28.

Catalyst synthesis and polymerization were conducted in a similar manner as in Example 27, except that a complex having composition of $\text{BMg}_6(\text{C}_2\text{H}_5)_3(\text{n-C}_4\text{H}_9)_4$ prepared as in Example 27 was used. This resulted in the formation of 293 g of a polymer, which had a Mw of 75,000 and a Mw/Mn ratio of 9.5. The catalyst efficiency was 24,500.

Example 29.

A solution of 50 m mols, based on the sum of boron and magnesium atoms, of a complex having composition of



prepared in Example 27 in 60 ml of heptane was placed in a 200-ml flask. To this was

added dropwise a solution of 25 m mols of octyl alcohol in 40 ml of heptane with stirring at 10°C over a period of 30 minutes. A part of this solution was taken, oxidized with dry air, then hydrolyzed to convert all the alkyl and alkoxy radicals to alcohol, and analyzed by gas chromatography. The analytical values of ethanol, n-butanol, and n-octanol indicated that the complex had composition of



The above complex (40 m mols based on magnesium atom) was reacted with 40 m mols of titanium tetrachloride, as in Example 1; to give a hydrocarbon-insoluble solid. Using 5 mg of the solid and 0.2 m mol of triisobutylaluminum, polymerization reaction was conducted under the same conditions as in Example 27, to give 258 g of a polymer. The polymer had a Mw of 47,000 and a Mw/Mn ratio of 3.4. The catalyst efficiency was 21,500.

Examples 30—34.

The hydrocarbon-insoluble solids were prepared as in Example 27 under those synthetic conditions described in Table 4. Using as catalysts said hydrocarbon-insoluble solids and the organoaluminum components given in Table 4, polymerization reaction was conducted under the same conditions as in Example 27 to give the results shown in Table 4. Those organoboron-magnesium complexes used in the polymerization were prepared as in Examples 27 and 29.

TABLE 4

Examples	Catalyst					Results of polymerization				
	Hydrocarbon-insoluble solids			Temp. (°C) × Time (hr)	organo- aluminum compounds (amount used m mol)	Yield g	Mw	Mw — Mn	Catalyst efficiency	
	B-Mg complexes	Ti, V compounds (molar ratio)	Mol ratio of Ti+V/ Mg							
30	$\text{BMg}_2(\text{C}_2\text{H}_5)_3$ (C_6H_{13}) _{1.6}	VCl_4	1/1	-10×4	$\text{Al}(\text{C}_6\text{H}_{17})_3$ (1.6)	336	95000	8.7	28000	
31	$\text{BMg}(\text{n-C}_4\text{H}_9)_3$ ($\text{n-C}_4\text{H}_9$) ₂	TiCl_4 / $\text{Ti}(\text{OnBu})\text{Cl}_3$ ≈2/1	1/1	-20×4	$\text{Al}(\text{C}_6\text{H}_{13})_3$ (1.6)	282	68000	6.5	23500	
32	$\text{BMg}_2(\text{C}_2\text{H}_5)_3$ ($\text{n-C}_3\text{H}_7$) _{4.5} (OC_2H_5) _{2.5}	TiCl_4 / VOCl_3 ≈2/1	1/1	0×4	$\text{Al}(\text{i-C}_4\text{H}_9)_2\text{H}$ (0.4)	290	54000	3.8	24200	
33	$\text{BMg}_2(\text{C}_2\text{H}_5)_3$ ($\text{n-C}_4\text{H}_9$) _{3.0} ($\text{OSi}(\text{CH}_3)_2$) _{1.0}	TiCl_4	1/2	-5×4	$\text{Al}(\text{i-C}_4\text{H}_9)_2.5$ (OC_2H_5) _{0.5} (0.4)	228	57000	4.1	19000	
34	$\text{BMg}_2(\text{C}_2\text{H}_5)_3$ ($\text{n-C}_4\text{H}_9$) _{2.5} (OSi.H.CH_3 , C_4H_9) _{1.5}	TiCl_4	2/1	20×4	$\text{Al}(\text{i-C}_4\text{H}_9)_2.5$ $\text{Cl}_{0.5}$ (0.4)	216	51000	3.6	18000	

Examples 35—38.

Organomagnesium complexes prepared as in Example 27 were reacted with siloxane compounds under those conditions given in Table 5. The reaction products were then reacted with titanium tetrachloride as in Example 27 at a molar ratio of Mg/Ti of 1:1 at 10°C for 4 hours, to give hydrocarbon-insoluble solids. Using 5 mg of these solids

and organoaluminum components given in Table 5, polymerization reaction was conducted as in Example 27, except that a hydrogen partial pressure of 1.0 Kg/cm² and an ethylene partial pressure of 3.0 Kg/cm² were used for polymerization, and the results given in the table were obtained. Amounts of Si—O—Mg were determined by quantitative analysis of the gas emitting when the reaction products were hydrolysed.

TABLE 5

Examples	Catalysts					Results of polymerization			
	Reaction products of organomagnesium complex and siloxane					Yield g	Mw	Mw — Mn	Catalyst efficiency
	Organo- magnesium complex	Siloxane	Si-O/ Mg molar ratio	Temp. (°C) × Time (hr)	Si-O-Mg/ Mg molar ratio				
35	$\text{BMg}_2(\text{C}_2\text{H}_5)_3$ $(\text{n-C}_4\text{H}_9)_{12}$	Symmetrical dihydro- tetramethyl disiloxane	1/1	0×1	0.15	338	61000	3.4	22500
36	$\text{BMg}_2(\text{C}_2\text{H}_5)_3$ $(\text{n-C}_4\text{H}_9)_{16}$	Methyl hydro- siloxane (Visco- sity of 30 centistokes at 30°C)	1/2	50×3	0.35	264	52000	4.2	17600
37	$\text{BMg}_2(\text{C}_2\text{H}_5)_3$ $(\text{n-C}_4\text{H}_9)_6$	Cyclic tetramer of methyl hydrosiloxane	2/1	30×2	0.60	318	58000	3.9	21200
38	$\text{BMg}_2(\text{C}_2\text{H}_5)_3$ $(\text{n-C}_4\text{H}_9)_6$	Hexamethyl disiloxane	1/1	100×5	0.25	278	52000	4.0	18500

Example 39.

Ethyl-diethoxy-boron was reacted with di-
n-butylmagnesium, as in Example 27,
thereby forming a complex having compo-
sition of



This complex was then reacted with titanium
tetrachloride under the same conditions as in
Example 27 to give a hydrocarbon-insoluble
solid. Using said solid and tri-isobutyl alumi-
num, a polymerization reaction was conducted
under the same conditions as in Example 27
to give 252 g of a polymer. The polymer had

a Mw of 53,000 and a Mw/Mn ratio of 4.7. 15
The catalyst efficiency was 21,000.

Example 40.

The solid component (2 g) prepared in
Example 1 and 30 ml of n-heptane were
placed in a 100-ml flask, and 20 ml of 20
titanium tetrachloride was added. The mix-
ture was reacted at 100°C for an hour. The
solid component was isolated and washed with
heptane.

Polymerization was conducted as in Ex- 25
ample 1, except that 5 mg of said solid was
used, thereby obtaining 558 g of a polymer.
The polymer had a Mw of 92,000 and a Mw/

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Mn ratio of 10.8. The catalyst efficiency was 27,900.

Example 41.

Polymerization was conducted using the same catalyst components and polymerization conditions as in Example 27, except that 0.2 m mol of 1,1 - dichloro - ethane was used as a catalyst component, thereby obtaining 266 g of a polymer. The polymer had a Mw of 106,000 and a Mw/Mn ratio of 17.8. The catalyst efficiency was 22,200.

WHAT WE CLAIM IS:—

1. A catalyst for the polymerization of ethylene or propylene, or the copolymerization thereof with another olefin, the catalyst being prepared by reacting (A) a hydrocarbon-insoluble reaction product formed by the reaction of

(i) an organomagnesium-containing, hydrocarbon-soluble complex represented by the general formula of



(wherein M is a zinc or boron atom, R¹ and R² are a hydrogen atom or the same or different hydrocarbon radicals, each having 1—10 carbon atoms, X and Y are the same or different OR³ or OSiR⁴R⁵R⁶ groups, R³ is a hydrocarbon radical having 1—10 carbon atoms, R⁴, R⁵ and R⁶ are a hydrogen atom or the same or different hydrocarbon radicals each having 1—10 carbon atoms, α and β are each greater than or equal to 1, and β/α is 1—10, p, q, r, s are each 0 or a positive number and have a relationship of p + q + r + s = mα + 2β, and 0 ≤ (p + q) / (α + β) ≤ 0.80 and m is the valency of M),

or a reaction product of (i) with (ii) a linear or cyclic siloxane compound having a constitutional unit represented by the general formula

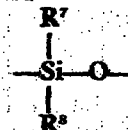


(wherein R⁷ and R⁸ are a hydrogen atom or the same or different hydrocarbon radicals each having 1—10 carbon atoms), and

(iii) one or more titanium or vanadium compounds containing 1—4 halogen atoms; and

(B) an organoaluminum compound having the general formula of AlR⁹_{3-n}Z_n (wherein R⁹ is a hydrocarbon radical having 1—20 carbon atoms, Z is selected from hydrogen, halogen, alkoxy, aryloxy and siloxy radicals and n is a number in the range 2—3).

2. A catalyst according to claim 1 wherein said organomagnesium-containing compound has the general formula M.Mg_xR¹_yR² and is reacted with a linear or cyclic siloxane compound containing one or more constitutional units of the formula



in the dimer form or polymeric form greater than dimer.

3. A catalyst according to claim 1 or 2 wherein the ratio of β/α is in the range of 2—6.

4. A catalyst according to claim 1, 2 or 3 wherein the ratio of (p + q) / (α + β) is in the range of 0.30—0.80.

5. A catalyst according to any one of claims 1 to 4 wherein said titanium or vanadium compound is titanium tetrachloride, butoxy-titanium trichloride, monopropoxytitanium trichloride, monoethoxytitanium trichloride, vanadium tetrachloride, or vanadyl trichloride or a mixture thereof.

6. A catalyst according to any one of claims 1 to 5 wherein the reaction of said organomagnesium-containing complex, a siloxane compound and a titanium or vanadium compound is carried out at a temperature lower than 20°C.

7. A catalyst according to any one of claims 1 to 6 wherein said organomagnesium-containing complex component and the titanium or vanadium compound component are simultaneously added to a reaction zone in the preparation of hydrocarbon insoluble reaction product (A).

8. A catalyst according to any one of claims 1 to 7 wherein 0.2—5 mols of said organomagnesium-containing complex is reacted with one mol of titanium or vanadium compound.

9. A catalyst according to any one of claims 1 to 8 wherein said organoaluminum compound represented by the general formula AlR⁹_{3-n}Z_n is trialkylaluminum or dialkylaluminum hydride.

10. A catalyst according to any one of claims 1 to 9 wherein 1—3000 m mols of the (B) component is reacted with 1 g of the (A) component.

11. A catalyst according to any one of claims 1 to 10, further comprising adding a halogenated hydrocarbon to the reactant mixture of (A) and (B).

12. A catalyst according to any one of claims 1 to 11 wherein reaction product (A) is further reacted with an aluminum, silicon, tin, titanium or vanadium halogen compound before reaction with (B).

13. A catalyst according to claim 1 substantially as described in any one of the Examples.

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Mn ratio of 10.8. The catalyst efficiency was 27,900.

Example 41.

- 5 Polymerization was conducted using the same catalyst components and polymerization conditions as in Example 27, except that 0.2 m mol of 1,1 - dichloro - ethane was used as a catalyst component, thereby obtaining 266 g of a polymer. The polymer had a Mw of 106,000 and a Mw/Mn ratio of 17.8. The catalyst efficiency was 22,200.

WHAT WE CLAIM IS:—

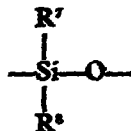
1. A catalyst for the polymerization of ethylene or propylene, or the copolymerization thereof with another olefin, the catalyst being prepared by reacting (A) a hydrocarbon-insoluble reaction product formed by the reaction of

- (i) an organomagnesium-containing, hydrocarbon-soluble complex represented by the general formula of



- (wherein M is a zinc or boron atom, R¹ and R² are a hydrogen atom or the same or different hydrocarbon radicals, each having 1—10 carbon atoms, X and Y are the same or different OR³ or OSiR⁴R⁵R⁶ groups, R³ is a hydrocarbon radical having 1—10 carbon atoms, R⁴, R⁵ and R⁶ are a hydrogen atom or the same or different hydrocarbon radicals each having 1—10 carbon atoms, α and β are each greater than or equal to 1, and β/α is 1—10, p, q, r, s are each 0 or a positive number and have a relationship of p + q + r + s = mα + 2β, and 0 ≤ (p + q)/(α + β) ≤ 0.80 and m is the valency of M),

- or a reaction product of (i) with (ii) a linear or cyclic siloxane compound having a constitutional unit represented by the general formula

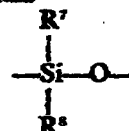


- (wherein R⁷ and R⁸ are a hydrogen atom or the same or different hydrocarbon radicals each having 1—10 carbon atoms), and

- (iii) one or more titanium or vanadium compounds containing 1—4 halogen atoms; and

- (B) an organoaluminum compound having the general formula of AlR⁹_nZ_{3-n} (wherein R⁹ is a hydrocarbon radical having 1—20 carbon atoms, Z is selected from hydrogen, halogen, alkoxy, aryloxy and siloxy radicals and n is a number in the range 2—3).

2. A catalyst according to claim 1 wherein said organomagnesium-containing compound has the general formula M_nMg_xR¹_pR²_q and is reacted with a linear or cyclic siloxane compound containing one or more constitutional units of the formula



in the dimer form or polymeric form greater than dimer.

3. A catalyst according to claim 1 or 2 wherein the ratio of β/α is in the range of 2—6.

4. A catalyst according to claim 1, 2 or 3 wherein the ratio of (p + q)/(α + β) is in the range of 0.30—0.80.

5. A catalyst according to any one of claims 1 to 4 wherein said titanium or vanadium compound is titanium tetrachloride, butoxytitanium trichloride, monopropoxytitanium trichloride, monoethoxytitanium trichloride, vanadium tetrachloride, or vanadyl trichloride or a mixture thereof.

6. A catalyst according to any one of claims 1 to 5 wherein the reaction of said organomagnesium-containing complex, a siloxane compound and a titanium or vanadium compound is carried out at a temperature lower than 20°C.

7. A catalyst according to any one of claims 1 to 6 wherein said organomagnesium-containing complex component and the titanium or vanadium compound component are simultaneously added to a reaction zone in the preparation of hydrocarbon insoluble reaction product (A).

8. A catalyst according to any one of claims 1 to 7 wherein 0.2—5 mols of said organomagnesium-containing complex is reacted with one mol of titanium or vanadium compound.

9. A catalyst according to any one of claims 1 to 8 wherein said organoaluminum compound represented by the general formula AlR⁹_nZ_{3-n} is trialkylaluminum or dialkylaluminum hydride.

10. A catalyst according to any one of claims 1 to 9 wherein 1—3000 m mols of the (B) component is reacted with 1 g of the (A) component.

11. A catalyst according to any one of claims 1 to 10, further comprising adding a halogenated hydrocarbon to the reactant mixture of (A) and (B).

12. A catalyst according to any one of claims 1 to 11 wherein reaction product (A) is further reacted with an aluminum, silicon, tin, titanium or vanadium halogen compound before reaction with (B).

13. A catalyst according to claim 1 substantially as described in any one of the Examples.

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14. A process for the polymerization of ethylene or propylene or the copolymerization thereof with another olefin in the presence of a catalyst, wherein the catalyst is a catalyst according to any one of claims 1 to 13.

15. A process according to claim 14 substantially as described in any one of the Examples.

16. A polymer or copolymer obtained by a process according to claim 14 or 15.

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