

PATENT SPECIFICATION

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(54) NOVEL CATALYST COMPOSITION AND A PROCESS
 FOR THE PRODUCTION OF OLEFIN POLYMERS

(71) We, CHUBU CHEMICAL INC.,
 a Japanese Body Corporate, of No. 2, 1-
 chome, Takara-cho, Chuo-ku, Tokyo, Japan,
 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 per-
 formed, to be particularly described in and by
 the following statement:—

The present invention relates to a novel
 catalyst composition and to an improved
 process for the production of olefin polymers
 by the homopolymerization or copolymer-
 ization of olefins in the presence of the novel
 catalyst system.

It is known that catalyst systems comprising
 a transition metal compound and an organic
 metal compound can be used for the low
 pressure polymerization of olefins. Various
 proposals have heretofore been made for the
 improvement of catalysts of this type. A
 polymerization process which possesses advan-
 tages over processes using these conventional
 catalysts is described in our British Patent
 Specification No. 1,464,451. In principle, this
 process comprises polymerizing olefins in the
 presence of a catalyst system comprising

(A) a solid catalytic complex which is ob-
 tained by reacting together:

- (1) metallic magnesium;
- (2) a hydroxylated organic compound con-
 taining at least one hydroxy group
 bonded to a carbon or silicon atom;
- (3) an oxygen-containing organic compound
 of a metal (Tr) of groups IVa, Va or
 VIa of the Periodic Table being free
 from metal-halogen bonds and having
 an organic radical attached to the metal
 (Tr) via oxygen;
- (4) an aluminium halide having the formula
 AlR_xX_{3-x} wherein R is a hydrocarbon
 group containing from 1 to 20 carbon
 atoms, X is a halogen atom and x
 is any number such that $0 \leq x < 3$; and

(B) an organometallic compound of a metal
 of groups I to III of the Periodic Table.

The present inventors have now found that,
 when a halogen-containing compound of a
 metal of Group IVa, Va or VIa of the Periodic
 Table is added to the above mentioned
 starting substances in the preparation of the
 above composite catalyst component (A), the
 molecular weight distribution of the resulting
 olefin polymers can be much more easily
 controlled.

Accordingly, the present invention provides
 a catalyst composition suitable for the poly-
 merization or copolymerization of an α -olefin
 or olefins which comprises: component (A)
 which is prepared by the reaction of the
 following five substances:

- (1) a hydroxylated organic compound con-
 taining at least one hydroxy group
 bonded to a carbon or silicon atom;
- (2) metallic magnesium;
- (3) an oxygen-containing organic compound
 of a metal of Groups IVa, Va or VIa
 of the Periodic Table being free from
 metal-halogen bonds and having an
 organic radical attached to the metal
 (Tr) via oxygen;
- (4) a halogen-containing compound of a
 metal of Group IVa, Va or VIa of
 the Periodic Table, and
- (5) an aluminium halide having the formula
 AlR_xX_{3-x} wherein R is a hydrocarbon
 group containing from 1 to 20 carbon
 atoms, X is a halogen atom and z is
 any number such that $0 \leq z < 3$, pro-
 viding that substance (5) is added as
 the last ingredient, and

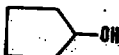
component (B) which is an organometallic
 compound of a metal of Group I, II or III
 of the Periodic Table.

The Periodic Table referred to herein is the Mendeleef Periodic Table.

The preparation of the catalyst component (A) which is used in the catalyst composition of the present invention is described below.

The preferred organic hydroxylated compounds are alcohols, organic silanols and phenols.

The alcohol may be a linear or branched chain aliphatic alcohol having from 1 to 18 carbon atoms, an alicyclic alcohol or an aromatic alcohol. Specific examples of the alcohols that may be used in the present invention are CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $n\text{-C}_3\text{H}_7\text{OH}$, $i\text{-C}_3\text{H}_7\text{OH}$, $n\text{-C}_{10}\text{H}_{21}\text{OH}$ and



or $\text{HOCH}_2\text{CH}_2\text{OH}$.

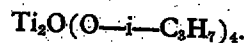
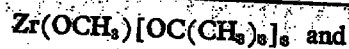
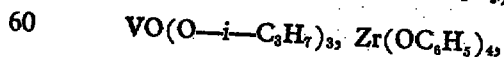
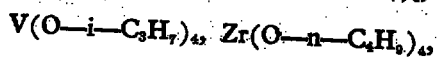
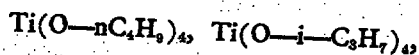
Organic silanols having at least one hydroxyl group and an organic group which is an alkyl, cycloalkyl, arylalkyl, aryl, alkylaryl or an aromatic group, each having from 1 to 12 carbon atoms, preferably 1 to 6 carbon atoms, may be used as the organic silanols. Specific examples of the organic silanols that may be used are $(\text{CH}_3)_2\text{SiOH}$, $(\text{C}_2\text{H}_5)_2\text{SiOH}$, $(\text{C}_6\text{H}_5)_2\text{SiOH}$ and $(\text{tert-C}_4\text{H}_9)_2\text{SiOH}$.

Examples of the phenols which may be used are phenol, cresol, xlenol or hydroquinone.

The metallic magnesium which is used as component (2) may be in powder, particulate, foil-like or ribbon-like form.

Preferably the oxygenated organic compound (3) is a compound of the general formula $[\text{TrO}_x(\text{OR})_y]_m$.

In the above general formula, Tr represents a metal of Group IVa, Va or VIa of the Periodic Table, the use of the metals Ti, Zr, V and Cr being particularly preferred, R represents an organic group, and x and y are numbers of $x \geq 0$ and $y > 0$ that satisfy the atomic valency of the metal Tr and m is an integer. Preferably, the oxygenated organic compound is a compound in which x is a number within the range of $0 \leq x \leq 1$, and m is an integer within the range of $1 \leq m \leq 6$. Various organic groups may be used as R. In general, however, R is an organic group having from 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms and more preferably 1 to 6 carbon atoms. Preferred organic groups are hydrocarbon groups, for example linear or branched chain alkyl groups, cycloalkyl groups, arylalkyl groups, aryl groups or alkylaryl groups. Specific examples of such oxygenated organic compounds are



The use of oxygenated organic compounds having two or more different organic groups is included within the scope of the present invention. Furthermore, the use of two or more different oxygenated organometallic compounds containing the same metal or different metals is included within the scope of the invention.

The halogen-containing metal compound (4), may be a compound of the general formula $(\text{TrO}_p\text{X}_q)_r$. In this general formula, Tr represents a metal of Group IVa, Va or VIa of the Periodic Table, and the use of Ti, Zr, V, Mo and Cr is particularly preferred. X represents a halogen atom such as F, Cl, Br and I, and p and q are numbers of $p \geq 0$ and $q > 0$ which satisfy the atomic valency of the metal Tr, and r is an integer. Preferably a halogen-containing metal compound is used in which p is within the range of $0 \leq p \leq 2$, and r is within the range of $1 \leq r \leq 6$. Specific examples of the halogen-containing metal compounds that may be used are ZrCl_4 , VCl_4 , MoCl_5 , VOCl_3 , ZrBr_4 , ZrI_4 , VBr_4 , VI_4 , TiCl_4 and VCl_3 .

The use of a halogen-containing compound containing two or more different halogen atoms is included within the scope of the present invention. Furthermore, the use of two or more different halogen-containing compounds containing the same metal or different metals is included within the scope of the invention.

The aluminum halide compound (5) is a compound represented by the general formula $\text{R}'_z\text{AlX}_3-z$. In this general formula, R' is a hydrocarbon group having from 1 to 20 carbon atoms, preferably 1 to 6 carbon atoms, X is a halogen atom, F, Cl, Br or I, and z is a number within the range of $0 \leq z < 3$. Preferably R' is a linear or branched chain alkyl group, a cycloalkyl group, arylalkyl group, aryl group or alkylaryl group. The aluminum halide may be used singly, or as a mixture of two or more thereof. Furthermore, a trialkyl aluminum compound of the general formula AlR'_3 may be used in combination with such an aluminum halide.

Specific examples of the aluminum halides, are AlCl_3 , $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$ and $\text{Al}(\text{C}_2\text{H}_5)_3\text{Cl}$. As pointed out above, a combination of an aluminum halide and a trialkyl aluminum, such as $[\text{AlCl}_3 + 1/2\text{Al}(\text{C}_2\text{H}_5)_3]$, may be used. If these compounds are combined in advance, a reaction sometimes occurs between them. The product formed by such a reaction may also be used in this invention.

Various methods may be used for the preparation of the catalyst component (A) of the catalysts of the invention, providing that

compound(s) is added as the last ingredient. Examples of such methods will now be described, but it is to be understood that the methods that can be used in the preparation of the catalysts of this invention are not limited to these methods.

A first method comprises mixing an alcohol, organic silanol or phenol (1), metallic magnesium (2) and an organic oxygenated compound (3) so that the ratio of (1) to (2) is preferably at least 2 moles per gram atom and the ratio of (2) to the metal in (3) is within the range of from 100:1 to 0.05:1, preferably from 10:1 to 0.2:1, and heating and ageing the mixture. The ageing under heating is carried out by treating the mixture in an inert gas atmosphere under reflux at atmospheric pressure or under elevated pressure at a temperature of 20 to 300° C., preferably 30 to 150° C., for 0.5 to 15 hours, preferably 1 to 6 hours. This ageing may be conducted in the presence of an inert solvent. Any of the inert solvents usually employed in this field may be used, and it is particularly preferred to use an alkane or cycloalkane having from 4 to 20 carbon atoms, such as isobutane, n-pentane, n-hexane or cyclohexane.

In this method, the ageing reaction can be promoted by the addition of one or more polar substances capable of reacting with metallic magnesium (2) or of forming an adduct with metallic magnesium (2), such as iodine, mercuric chloride, xylene, an alkyl halide, organic acid ester or an organic acid.

If low-boiling-point substances are present in the ageing reaction product, they are preferably removed by distillation after the completion of the ageing reaction.

A halogen-containing compound (4) is then added to the above reaction product. The pressure and temperature conditions adopted at this stage are not particularly critical, but it is generally preferred that the halogen-containing metal compound (4) be added at room temperature. The ageing reaction is then carried out at a temperature of 30 to 150° C. for 0.5 to 15 hours, preferably 1 to 6 hours. This reaction may be carried out in the presence of an inert solvent, such as mentioned above.

An aluminum halide (5) is then added to the resulting aged composition to obtain component (A). More specifically, the last stage of the reaction is carried out at a temperature below 200° C. (preferably 0 to 60° C.) for 1 to 8 hours (preferably 2 to 4 hours) with a magnesium:aluminum atomic ratio ranging from 10:1 to 10:1000, preferably from 10:10 to 10:200. The reaction product is composed of particles insoluble in the solvent used as a diluent. This product is usually employed in the form of suspension in an inert solvent, after the remaining unreacted

substances and by-products have been removed by filtration or decantation and the reaction product has been washed several times with an inert solvent. If the reaction product is isolated after the washing step and heated and dried in an inert gas atmosphere, the resulting powder may be stored for a long period of time as the catalyst component (A).

A second method for the preparation of the catalyst component (A) comprises reacting components (1) and (2) under reflux at atmospheric pressure or under an elevated pressure at a temperature of 30 to 150° C. for 0.5 to 15 hours, preferably 1 to 6 hours, by using components (1) and (2) in such amounts that the ratio of (1) to (2) is at least 2 moles per gram atom. This reaction may be carried out in the presence of an inert solvent. This reaction may be accelerated by the addition of one or more of polar substances capable of reacting with metallic magnesium or forming an adduct with metallic magnesium, such as iodine, mercuric chloride, xylene, an alkyl halide, organic acid ester or an organic acid. Compound (3) is then added directly to the resulting precipitate or suspension so that the atomic ratio of magnesium to the metal in compound (3) is within the range as mentioned above with respect to the first method. The ageing reaction is then carried out at a temperature of 50 to 200° C., preferably 90 to 160° C., for 5 minutes to 6 hours, preferably for 1.5 to 4 hours, while distilling off low-boiling-point substances. When the atomic ratio of magnesium to the metal in compound (3) is great, an inert solvent is generally used as a diluent in this reaction and the reaction is carried out under elevated pressure. A halogen-containing metal compound (4) is added to the so formed aged composition under the same conditions as mentioned above with respect to the first method, and the mixture is aged. The resulting composition is then treated with an aluminum halide (5) to form the catalyst component (A).

In a variation of this second method, components (1) and (2) are reacted, the resulting organic oxygenated magnesium compound is isolated and components (3) and (4) are added thereto to form a composite catalyst component. In this variation method, although the reaction rate is generally lower than in the second method in which no isolation is effected, no substantial difference in the products is encountered.

A third method for the preparation of the catalyst component (A) comprises mixing the components (1), (2), (3) and (4) to form a mixture having the composition mentioned above, ageing the mixture under heating and treating the resulting aged reaction product with component (5).

The foregoing three methods are given only

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for illustration purposes, and therefore, the preparation of catalyst component (A) is not limited to these methods.

5 In this invention, an organometallic compound of a metal of Group I, II or III of the Periodic Table is used as the catalyst component (B).

10 Metals of Groups I, II and III of the Periodic Table which are preferably used are lithium, magnesium, zinc and aluminum, the use of aluminum being particularly preferred.

15 Typical of the organic group of the component (B) is an alkyl group and linear and branched chain alkyl groups having from 1 to 20 carbon atoms are preferably employed.

20 Examples of component (B), are *n*-butyl lithium, diethyl magnesium, diethyl zinc, trimethyl aluminum, triethyl aluminum, tri-*n*-butyl aluminum, tri-*n*-butyl aluminum and tri-*n*-decyl aluminum. In general, a trialkyl aluminum having a linear or branched chain alkyl group of 1 to 10 carbon atoms is used.

25 In addition, an alkyl metal hydride containing an alkyl group of 1 to 20 carbon atoms may be used as component (B). An example of such a compound is di-isobutyl aluminum hydride.

30 Furthermore, an alkyl metal halide containing an alkyl group of 1 to 20 carbon atoms, such as ethyl aluminum sesquichloride, diethyl aluminum chloride and di-isobutyl aluminum chloride, may be used as component (B).

35 Furthermore, an organoaluminum compound obtained by the reaction between a trialkyl aluminum or dialkyl aluminum hydride containing an alkyl group of 1 to 20 carbon atoms and a diolefin having 4 to 20 carbon atoms, such as isoprenyl aluminum, may also be used.

40 The present invention also includes within its scope a process for the production of a polyolefin which comprises polymerizing an α -olefin or copolymerizing a mixture of α -olefins in the presence of a catalyst composition of the invention.

45 In accordance with this aspect of the invention, the polymerization of olefins can be conducted under the normal reaction conditions of the so-called Ziegler process. More specifically, the polymerization is preferably carried out continuously or batchwise at a temperature in the range of from 20 to 200° C., preferably at a temperature of from 50 to 90° C. in the case of slurry polymerization or at a temperature of from 120 to 150° C. in the case of solution polymerization. The polymerization pressure is not particularly critical, but the polymerization is preferably conducted at elevated pressure, generally in the range of 1.5 to 50 atmospheres. It is desirable to perform the polymerization in the presence of an inert solvent. Any of the inert solvents customarily used in this field can be employed in this invention. The use of an

alkane or cycloalkane having from 4 to 20 carbon atoms, such as isobutane, *n*-pentane, *n*-hexane or cyclohexane, is particularly preferred.

70 In carrying out this invention, the amount of catalyst component (A) used is preferably equivalent to 0.001 to 2.5 milligram atom of the metal in the component (3) per liter of the solvent or per liter of the reaction vessel. The component may be used in a larger amount depending upon the conditions.

75 The amount of the organometallic compound (component B) used is generally 0.02 to 50 millimoles, preferably 0.2 to 5 millimoles per liter of the solvent or per liter of the reaction vessel.

80 Monomers which may be polymerized according to the process of this invention, are α -olefins of the general formula $R-CH=CH_2$, wherein R represents a hydrocarbon residue, especially a linear or branched chain, substituted or unsubstituted alkyl group having 1 to 10 carbon atoms, especially 1 to 8 carbon atoms. Examples of such olefins are ethylene, propylene, butane-1, pentene-1, methylpentene-1 or octene-1.

90 A mixture of two or more of these α -olefins may be polymerized according to this invention. Preferably ethylene or a mixture of ethylene and another α -olefin are polymerized.

95 The molecular weight of the resulting polymer may be adjusted according to known methods, for example, by introducing hydrogen into the reaction system.

100 The most significant advantage of this invention is that the molecular weight distribution in the resulting polymer can easily be controlled. The ratio of the high load melt index (HLMI determined in accordance with ASTM D-1238 condition E) to the melt index (MI determined in accordance with ASTM D-1238 condition F) is used as a criterion for the molecular weight distribution. It is considered that as this HLMI/MI ratio is large, the molecular weight distribution range is broad. However, it must be noted that the HLMI/MI value has a relation to the MI value and as the MI value decreases, the HLMI/MI ratio tends to increase. In general, a polymer having a small HLMI/MI value is suitable for injection molding and a molded article having a high impact strength can be obtained from such polymer by injection molding. In contrast, a polymer having a large HLMI/MI value is preferred for blow molding and a molded article having good surface conditions can be obtained from such polymer. The HLMI/MI value can be varied to some extent by varying the atomic ratio of metallic magnesium (2) to the metal in organic oxygenated compound (3) in the preparation of catalytic component (A). For example, the HLMI/MI value can be reduced by increasing the ratio of the component (3)

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to the component (2), and conversely the value can be increased by reducing the ratio. Further, when the ratio of the component (5) to the component (2) is increased, the HLMI/MI value tends to become great. Accordingly, the MLMI/MI value can be controlled to some extent by the alteration of the ratio of these components. However, in this invention in which the catalyst composition additionally incorporates a halogen-containing metal compound (4), the HLMI/MI value can be controlled more readily and easily by changing the atomic ratio between the metal of component (4) and the metal of oxygenated organometallic compound (3), than in the prior art processes. Especially, an excellent way of increasing the HLMI/MI value can be achieved using this invention. For example, if $ZrCl_4$ is used as component (4) and the ratio of (4) to (3) is increased, it is possible to obtain a large HLMI/MI value. The prior art catalyst systems free of a halogen-containing metal compound (4) are suitable mainly for the production of polyolefins having a high impact resistance for injection molding. In contrast, using the catalyst system of this invention, any of polyolefins suitable for injection molding, blow molding and film forming can be provided by controlling the ratio of the starting materials during the catalyst preparation. It is one of great advantages of this invention that various polyolefin products applicable to various fields can be provided using one catalyst system.

Another characteristic feature of this invention is that a complicated magnesium compound requiring severe control and maintenance of preparation, handling, purchase and quality standards need not be used, but metallic magnesium which can readily be purchased, stored and controlled is used.

Furthermore, using the process of this invention, the catalytic activity, measured by the weight of the polymer obtained per unit amount of the catalyst, is very high. Accordingly, it is unnecessary to remove the catalyst from the resulting polymer, and occurrence of undesired phenomena such as degradation and discoloration at the molding step can be avoided.

Still further, the polymeric powder obtained using ethylene as the starting olefin has a high apparent specific gravity, and therefore, the process of this invention is very advantageous from the industrial viewpoint.

This invention will now be described in more detail with reference to the following examples which are intended to illustrate but not to limit the scope of this invention.

Example 1.

a) Preparation of Catalyst:

A 1000-cc capacity flask equipped with an agitator was charged with 64.1 g (0.80 mole) of butanol, and 0.5 g of iodine, 4.86 g (0.20

gram atom) of metallic magnesium powder and 17.0 g (0.05 mole) of $Ti(O-n-C_4H_9)_4$, were added thereto. Then, 11.65 g (0.05 mole) of $ZrCl_4$ was gradually added while paying attention to the temperature, and the temperature of the mixture was elevated to 80° C. and the mixture was agitated for 2 hours under nitrogen seal while discharging generated hydrogen gas. The temperature was elevated while distilling off low-boiling-point substances, to complete the aging reaction. After the aging, the reaction mixture was cooled to 60° C. and 200 ml of n-hexane was added. Then, 348 ml of a 50% solution of ethyl aluminum dichloride was added at 45° C. to the mixture over a period of 3 hours so that the inside temperature was not elevated. After completion of the gradual addition, the temperature was elevated and the mixture was agitated at 60° C. for 1 hour. N-hexane was added to the reaction product and the mixture was washed by repeating decantation, namely the steps of agitation, standing still and removal of the supernatant, until no chlorine ion was detected in the supernatant liquid. After the supernatant liquid of the suspension had been thus removed, the residue was dried under an atmosphere of dried nitrogen to obtain 36.3 g of a mud-yellow powder. Elementary analysis value of the powder were 5.33% of Ti, 10.3% of Zr, 62.0% of Cl, 11.1% of Mg and 2.8% of Al.

b) Polymerization of Ethylene:

The inside atmosphere of a 1.6-liter capacity stainless steel autoclave of the electromagnetic agitation type was sufficiently replaced by nitrogen, and 1 liter of n-hexane was charged in the autoclave and the inside temperature was adjusted to 60° C. Then, 0.20 g (1.0 millimole) of triisobutyl aluminum and 46 mg of the dried powdery catalyst component prepared in step a) above were charged into the autoclave.

The inside pressure of the autoclave was adjusted to one atmosphere. Then, hydrogen of 16 atmospheres was charged and ethylene was continuously charged for 2 hours so that the total pressure was 20 atmospheres gauge, to thereby perform polymerization. After completion of the polymerization, the reaction mixture was cooled. Unreacted gas was expelled and the resulting polyethylene was separated from the solvent by filtration and dried to give 170 g of polyethylene having a melt index of 0.30 g/10 min and an apparent density of powder of 0.34 g/cm³. Yield of the polyethylene per gram of the catalyst was 3700 g and the HLMI/MI ratio was 121.

Example 2.

a) Preparation of Catalyst:

A 1.6-liter capacity autoclave equipped with an agitator was charged with 32.16 g (0.42

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mole) of butanol, 0.5 g of iodine, 4.86 g (0.20 gram atom) of metallic magnesium powder and 17.02 g (0.05 mole) of $\text{Ti}(\text{O}-\text{n}-\text{C}_4\text{H}_9)_4$ and 200 ml of n-hexane was added thereto and the temperature was elevated to 80° C. The mixture was agitated for 1 hour under nitrogen seal while discharging generated hydrogen gas. The temperature was elevated to 120° C. and the reaction was conducted for 1 hour. Then, the temperature was lowered to 60° C., and 5.85 g (0.025 mole) of ZrCl_4 was gradually added to the reaction mixture. The temperature was elevated again to 120° C. and the aging was conducted for 1 hour. Then, 348 ml of a 50% hexane solution of ethyl aluminum dichloride was added over a period of 3 hours so that the inside temperature was not elevated, and the mixture was agitated at 50° C. for 1 hour. When the reaction product was washed with n-hexane and agitated in the same manner as described in step a) of Example 1, there was obtained 20.4 g of a mud-yellow powder. Elementary analysis values of which were 6.29% of Ti, 2.3% of Zr, 61.5% of Cl, 13.2% of Mg and 3.6% of Al.

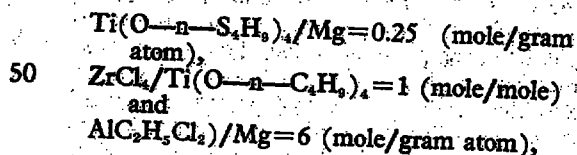
b) Polymerization of Ethylene:

In the same manner as described in step b) of Example 1, ethylene was polymerized for 2 hours in the presence of hydrogen of 11 atmospheres by using 0.30 g (1.5 millimoles) of tri-isobutyl aluminum and 23 mg of the dried powdery catalyst component prepared in step a) above while maintaining the total pressure at 20 atmospheres gauge, to give 221 g of polyethylene having a melt index of 0.32 g/10 min, an apparent density of powder of 0.32 g/cm³ and an HLMI/MI ratio of 91.0. Yield of the polyethylene per gram of the catalyst was 9610 g.

Examples 3 to 6.

Catalysts were prepared in the same manner as in step a) of Example 1 except that the mixing ratio of the starting materials were changed as indicated below.

More specifically, although the following ratios were adopted in Example 1:



in Example 3 the $\text{ZrCl}_4/\text{Ti}(\text{O}-\text{n}-\text{C}_4\text{H}_9)_4$ ratio was changed to 0.2, in Example 4 the $\text{ZrCl}_4/\text{Ti}(\text{O}-\text{n}-\text{C}_4\text{H}_9)_4$ ratio was changed to 0.50, in Example 5 the $\text{Ti}(\text{O}-\text{n}-\text{C}_4\text{H}_9)_4/\text{Mg}$ ratio was changed to 1, and in Example 6 the $\text{Ti}(\text{O}-\text{n}-\text{C}_4\text{H}_9)_4/\text{Mg}$ ratio was changed to 1 and the $\text{Al}(\text{C}_2\text{H}_5\text{Cl}_2)/\text{Mg}$ ratio was changed to 9. By using the so obtained catalysts, ethylene was polymerized in the

same manner as described in step b) of Example 1 to give the results shown in the Table below.

Example 7.

A catalyst was prepared in the same manner as described in step a) of Example 1 except for use of $\text{C}_2\text{H}_5\text{OH}$ instead of $\text{n}-\text{C}_4\text{H}_9\text{OH}$. By using the so obtained catalyst, ethylene was polymerized under the same conditions as described in step b) of Example 1 to give the results shown in the Table below.

Examples 8 to 11.

Catalysts were prepared in the same manner as described in step a) of Example 1 except that various halogen-containing compounds indicated below were used instead of ZrCl_4 .

Example 8: VCl_3

Example 9: VCl_2

Example 10: VOCl_2

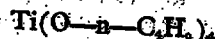
Example 11: MoCl_5

Ethylene was polymerized by using the so obtained catalysts in the same manner as described in step b) of Example 1.

Comparative Example 1.

a) Preparation of Catalyst:

In the same manner as described in step a) of Example 2, a mixture of 32.16 g (0.42 mole) of butanol, 0.5 g of iodine, 4.86 g (0.20 gram atom) of metallic magnesium powder, 17.02 g (0.05 mole) of



and 200 ml of hexane was aged and reacted at 120° C. while discharging hydrogen formed by the reaction. Without addition of ZrCl_4 , 348 ml of a 50% hexane solution of ethyl aluminum dichloride was added at 45° C. over a period of 3 hours, and the mixture was agitated at 50° C. for 1 hour. The reaction product was washed with n-hexane and dried to obtain 17.0 g of a light-brown powder. Elementary analysis values of which were 7.99% of Ti, 67.8% of Cl, 12.3% of Mg and 3.9% of Al.

b) Polymerization of Ethylene:

In the same manner as described in step b) of Example 1, ethylene was polymerized for 2 hours in the presence of hydrogen of 9.5 atmospheres by employing 0.30 g (1.5 millimoles) of tributyl aluminum and 25 mg of the dried powdery catalyst component obtained in step a) above so that the total pressure was 20 atmospheres gauge, to give 260 g of polyethylene having a melt index of 0.29 g/10 min, an apparent density of powder of 0.32 g/cm³ and an HLMI/MI ratio of 59.5. Yield of the polyethylene per gram of the catalyst was 10400 g.

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Comparative Example 2.

a) Preparation of Catalyst:

5 A catalyst was prepared in the same manner as described in step a) of Example 1 except for the absence of $\text{Ti}(\text{O}-n-\text{C}_4\text{H}_9)_4$. More specifically 66.8 g (0.90 mole) of butanol, 0.5 g of iodine and 4.86 g (0.20 gram atom) of metallic magnesium powder were charged in the flask, and 11.66 g (0.05 mole) of ZrCl_4 was added while paying attention to the temperature and hydrogen formed was removed. The aging reaction was conducted at 120°C . while removing low-boiling-point substances. Then, 348 ml of a 50% hexane solution of ethyl aluminum dichloride was added at 45°C . to the reaction product. The product was washed with n-hexane and dried to give 32.3 g of a white powder.

b) Polymerization of Ethylene:

20 In the same manner as described in step b) of Example 1, ethylene was polymerized for 2 hours in the presence of hydrogen of

18 atmospheres by using 0.30 g (1.5 millimoles) of tri-isobutyl aluminum and 422 mg of the dried powdery catalyst component obtained in step a) above so that the total pressure was 20 atmospheres gauge, to give 275 g of polyethylene having a melt index of 0.01 g/10 min, an apparent density of powder of 0.30 g/cm^3 and an HLMI/MI ratio of 66.9. Yield of the polyethylene per gram of the catalyst was 650 g.

Comparative Example 3.

5 g of the powdery catalyst component prepared in Comparative Example 1 was mixed with 2.1 g of powder of ZrCl_4 (the weight ratio of Zr to Ti was about 2). In the same manner as described in step b) of Example 1, ethylene was polymerized by using the so obtained mixed catalyst to give the results shown in the Table below.

Procedures and results of the foregoing Examples and Comparative Examples are summarized in the Table given below.

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TABLE

Example 1 Example 2 Example 3 Example 4 Example 5 Example 6

a) Preparation of Catalyst

(1) organic hydroxylated compound
(gram mole)

n-C₄H₉OH n-C₄H₉OH n-C₄H₉OH n-C₄H₉OH n-C₄H₉OH n-C₄H₉OH

0.80 0.42 0.80 0.80 0.80 0.80

(2) metallic magnesium (gram atom)

Mg Mg Mg Mg Mg Mg

0.20 0.20 0.20 0.20 0.10 0.10

(3) organic oxygenated compound
(gram mole)

← ————— Ti(O-n-C₄H₉)₄ ————— →

0.05 0.05 0.05 0.05 0.10 0.10

(4) halogen-containing metal
compound (gram mole)

ZrCl₄ ZrCl₄ ZrCl₄ ZrCl₄ ZrCl₄ ZrCl₄

0.05 0.025 0.01 0.025 0.10 0.10

(5) aluminum halide (gram mole)

← ————— AlCl₃ ————— →

1.2 1.2 1.2 1.2 0.60 0.90

Yield (g) of catalyst component (A)

36.3 20.4 34.2 34.5 45.0 62.5

TABLE (cont'd)

		Example 7	Example 8	Example 9	Example 10	Example 11
a) Preparation of Catalyst						
(1) organic hydroxylated compound (gram mole)		C_2H_5OH	$n-C_4H_9OH$	$n-C_4H_9OH$	$n-C_4H_9OH$	$n-C_4H_9OH$
		0.80	0.80	0.80	0.80	0.80
(2) metallic magnesium (gram atom)		Mg	Mg	Mg	Mg	Mg
		0.20	0.20	0.20	0.20	0.20
(3) organic oxygenated compound of metal		$\leftarrow$		$Ti(O-nC_4H_9)_4$		$\rightarrow$
		0.05	0.05	0.05	0.05	0.05
(4) halogen-containing metal compound (gram mole)		$ZrCl_4$	VCl_4	VCl_3	$VOCl_3$	$MoCl_5$
		0.05	0.025	0.05	0.08	0.05
(5) aluminum halide (gram mole)		$\leftarrow$		$AlC_2H_5Cl_2$		$\rightarrow$
		1.2	1.2	1.2	1.2	1.2
Yield (g) of catalyst component (A)		43.3	27.4	48.5	36.7	41.0

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TABLE (continued)

a) Preparation of Catalyst	Comparative Example 1	Comparative Example 2	Comparative Example 3
	n-C ₄ H ₉ OH	n-C ₄ H ₉ OH	mixed catalyst
(1) organic hydroxylated compound (gram mole)	0.42	0.9	catalyst of Comparative Example 1 + ZrCl ₄
(2) metallic magnesium (gram atom)	Mg	Mg	Zr/Ti weight ratio = 2
(3) organic oxygenated compound of metal (gram mole)	Ti(O-n-C ₄ H ₉) ₄	X	
(4) halogen-containing metal compound (gram mole)	0.05	ZrCl ₄	
(5) aluminum halide (gram mole)	AlC ₂ H ₅ Cl ₂	0.05 AlC ₂ H ₅ Cl ₂	
Yield (g) of catalyst component (A)	17.0	32.3	

TABLE (continued)

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
b) Polymerization of Ethylene						
Catalyst activity (g of polyethylene/g of catalyst component (A))	3,700	9,610	13,000	10,300	8,500	12,900
Apparent density (g/cm ³) of polyethylene powder	0.34	0.32	0.32	0.31	0.35	0.33
Melt index (g/10 min) of polyethylene	0.30	0.32	0.20	0.25	0.074	0.088
HLMI/MI Ratio	121	91.0	63.0	84.2	74.2	84.3

b) Polymerization of Ethylene

Catalyst activity (g of polyethylene/g of catalyst component (A))

Apparent density (g/cm³) of polyethylene powder

Melt index (g/10 min) of polyethylene

HLMI/MI Ratio

TABLE (continued)

	Example 7	Example 8	Example 9	Example 10	Example 11
b) Polymerization of Ethylene					
Catalyst activity (g or polyethylene/g of catalyst component (A))	1,800	18,400	13,400	25,700	7,200
Apparent density (g/cm ³) of polyethylene powder	0.29	0.30	0.33	0.34	0.37
Melt index (g/10 min) of polyethylene	0.23	0.18	1.33	2.20	0.38
HLMI/MI Ratio	152	66.8	49.9	52.6	48.2

b) Polymerization of Ethylene

Catalyst activity (g or polyethylene/g of catalyst component (A))

Apparent density (g/cm³) of polyethylene powder

Melt index (g/10 min) of polyethylene

HLMI/MI Ratio

TABLE (continued)

	Comparative Example 1	Comparative Example 2	Comparative Example 3
b) Polymerization of Ethylene			
Catalyst activity (g of polyethylene/g of catalyst component (A))	10,400	650	10,700
Apparent density (g/cm ³) of polyethylene powder	0.32	0.30	0.31
Melt index (g/10 min) of polyethylene	0.29	0.01	0.94
HLMI/MI Ratio	59.5	66.9	52.0

WHAT WE CLAIM IS:—

1. A catalyst composition suitable for the polymerization or copolymerization of an α -olefin or olefins which comprises: component A which is prepared by the reaction of the following five substances:

- (1) a hydroxylated organic compound, containing at least one hydroxy group bonded to a carbon or silicon atom;
- (2) metallic magnesium;
- (3) an oxygen-containing organic compound of a metal of Groups IVa, Va or VIa of the Periodic Table being free from metal-halogen bonds and having an organic radical attached to the metal (Tr) via oxygen;
- (4) a halogen-containing compound of a metal of Group IVa, Va or VIa of the Periodic Table, and
- (5) an aluminum halide having the formula AlR_zX_{3-z} wherein R is a hydrocarbon group containing from 1 to 20 carbon atoms, X is a halogen atom and z is any number such that $0 \leq z < 3$, providing that substance (5) is added as the last ingredient, and

component (B) which is an organometallic compound of a metal of Group I, II or III of the Periodic Table.

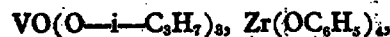
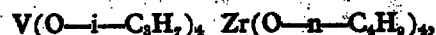
2. A catalyst composition as claimed in claim 1 wherein substance (1) is a linear or branched chain aliphatic, alicyclic or aromatic alcohol having up to 18 carbon atoms, phenol or an organic silanol containing an organic group having up to 12 carbon atoms.

3. A catalyst composition as claimed in claim 1 or claim 2 wherein substance (3) has the general formula $[TrO_x(RO)_y]_n$, wherein

Tr is titanium, zirconium, vanadium or chromium;
R is an organic group having up to 20 carbon atoms;

$x \geq 0$, $y > 0$, the sum of x and y satisfying the valency of the metal Tr; and n is an integer.

4. A catalyst composition as claimed in claim 3, wherein substance (3) is



5. A catalyst composition as claimed in any one of the preceding claims wherein substances (4) has the general formula $Tr'O_pX_q$, wherein

Tr' is titanium, zirconium, vanadium, molybdenum or chromium;

X is a halogen atom; and

$p \geq 0$, $q > 0$, the sum of p and q satisfying the valency of the metal Tr'.

6. A catalyst composition as claimed in claim 5 wherein substance (4) is $ZrCl_4$, VCl_4 , $MoCl_5$, $VOCl_3$, $ZrBr_4$, ZrI_4 , VBr_4 , VI_4 , $TiCl_4$ or VCl_3 .

7. A catalyst composition as claimed in any one of the preceding claims wherein substance (5) has the general formula R'_zAlY_{3-z} , wherein

R' is a hydrocarbon group having up to 20 carbon atoms;

X is a halogen atom; and

$0 \leq z < 3$.

8. A catalyst composition as claimed in claim 7, wherein substance (5) is $AlCl_3$, $Al(C_2H_5)_2Cl$, $Al(C_2H_5)_3$ or $Al(C_2H_5)_2Cl$.

9. A catalyst composition as claimed in any one of the preceding claims wherein component



TABLE (continued)

	Comparative Example 1	Comparative Example 2	Comparative Example 3
b) Polymerization of Ethylene			
Catalyst activity (g of polyethylene/g of catalyst component (A))	10,400	650	10,700
Apparent density (g/cm ³) of polyethylene powder	0.32	0.30	0.31
Melt index (g/10 min) of polyethylene	0.29	0.01	0.94
HLMI/MI Ratio	59.5	66.9	52.0

WHAT WE CLAIM IS:—

1. A catalyst composition suitable for the polymerization or copolymerization of an α -olefin or olefins which comprises: component A which is prepared by the reaction of the following five substances:

- (1) a hydroxylated organic compound, containing at least one hydroxy group bonded to a carbon or silicon atom;
- (2) metallic magnesium;
- (3) an oxygen-containing organic compound of a metal of Groups IVa, Va or VIa of the Periodic Table being free from metal-halogen bonds and having an organic radical attached to the metal (Tr) via oxygen;
- (4) a halogen-containing compound of a metal of Group IVa, Va or VIa of the Periodic Table, and
- (5) an aluminum halide having the formula AlR_zX_{3-z} wherein R is a hydrocarbon group containing from 1 to 20 carbon atoms, X is a halogen atom and z is any number such that $0 \leq z < 3$, providing that substance (5) is added as the last ingredient, and

component (B) which is an organometallic compound of a metal of Group I, II or III of the Periodic Table.

2. A catalyst composition as claimed in claim 1 wherein substance (1) is a linear or branched chain aliphatic, alicyclic or aromatic alcohol having up to 18 carbon atoms, phenol or an organic silanol containing an organic group having up to 12 carbon atoms.

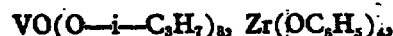
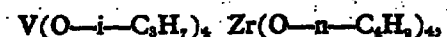
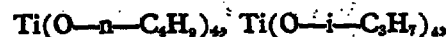
3. A catalyst composition as claimed in claim 1 or claim 2 wherein substance (3) has the general formula $[TrO_x(RO)_y]_n$, wherein

Tr is titanium, zirconium, vanadium or chromium;

R is an organic group having up to 20 carbon atoms;

$x \geq 0$, $y > 0$, the sum of x and y satisfying the valency of the metal Tr; and n is an integer.

4. A catalyst composition as claimed in claim 3, wherein substance (3) is



5. A catalyst composition as claimed in any one of the preceding claims wherein substances (4) has the general formula $Tr'O_pX_q$ wherein

Tr' is titanium, zirconium, vanadium, molybdenum or chromium;

X is a halogen atom; and

$p \geq 0$, $q > 0$, the sum of p and q satisfying the valency of the metal Tr'.

6. A catalyst composition as claimed in claim 5 wherein substance (4) is $ZrCl_4$, VCl_4 , $MoCl_5$, $VOCl_3$, $ZrBr_4$, ZrI_4 , VBr_4 , VI_4 , $TiCl_4$ or VCl_5 .

7. A catalyst composition as claimed in any one of the preceding claims wherein substance (5) has the general formula R'_zAlY_{3-z} wherein

R' is a hydrocarbon group having up to 20 carbon atoms;

X is a halogen atom; and

$0 \leq z < 3$.

8. A catalyst composition as claimed in claim 7, wherein substance (5) is $AlCl_3$, $Al(C_2H_5)_2Cl$, $Al_2(C_2H_5)_3Cl$ or $Al(C_2H_5)_3Cl$.

9. A catalyst composition as claimed in any one of the preceding claims wherein component



A is prepared by first mixing together substances (1), (2) and (3) and then adding substances (4) and (5) successively to the first mixture.

- 5 10. A catalyst composition as claimed in any one of claims 1 to 8 wherein component A is prepared by first mixing together substances (1), (2), (3) and (4) and then adding substance (5) to the reaction mixture.

- 10 11. A catalyst composition as claimed in claim 9 or claim 10 wherein substances (1), (2) and (3) are contacted in such amounts that the ratio of (1) to (2) is at least 2 moles/gram-atom and that the atomic ratio of (2) to the metal of (3) is between 10/1 and 0.2/1.

- 15 12. A catalyst composition as claimed in any one of claims 9 to 11 wherein substance (5) is added in such an amount that the magnesium/aluminum atomic ratio is between 1/1 and 1/20.

- 20 13. A catalyst composition as claimed in any one of the preceding claims wherein component B is an alkyl compound, an alkyl metal hydride or an alkyl metal halide of lithium, magnesium, zinc or aluminum.

- 25 14. A catalyst composition as claimed in claim 13 wherein component B is a trialkyl aluminum compound having alkyl groups of up to 10 carbon atoms.

- 30 15. A process for the preparation of an olefin polymer which comprises polymerizing an α -olefin or copolymerizing a mixture of α -olefins in the presence of a catalyst composition as claimed in any one of the preceding claims.

- 35 16. A process as claimed in claim 15 wherein ethylene is polymerized.

17. A process as claimed in claim 15

wherein a major amount of ethylene and a minor amount of at least one α -olefin selected from propylene, butene-1, pentene-1, 4-methyl pentene-1 and octene-1 are copolymerized.

- 40 18. A process as claimed in claim 13 wherein the polymerization or copolymerization is carried out at a temperature in the range of from 50° C. to 150° C., under a pressure in the range of from 1.5 to 50 atm.

- 45 19. A process as claimed in any one of claims 15 to 18 wherein the polymerization or copolymerization is carried out in the presence of *i*-butane, *n*-pentane, *n*-hexane or cyclohexane.

- 50 20. A process as claimed in any one of claims 15 to 19 wherein catalyst component A is used in an amount of 0.001 to 2.5 m mole per liter of internal volume of a reactor and catalyst component B in an amount of 0.02 to 50 m mole on the same basis.

- 55 21. A catalyst composition as claimed in claim 1 substantially as hereinbefore described with reference to any one of the specific Examples.

- 60 22. A process as claimed in claim 15 for the preparation of a polyolefin substantially as hereinbefore described with reference to any one of the specific Examples.

- 65 23. An olefin polymer whenever prepared by a process as claimed in any one of claims 15 to 20 or claim 22.

- 70 24. An article which is formed from an olefin polymer as claimed in claim 23.

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