



(22) Date de dépôt/Filing Date: 1992/02/27

(41) Mise à la disp. pub./Open to Public Insp.: 1992/08/28

(45) Date de délivrance/Issue Date: 2003/04/08

(30) Priorité/Priority: 1991/02/27 (33107/1991) JP

(51) Cl.Int.⁵/Int.Cl.⁵ C08F 10/00

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(54) Titre : PREPARATION DE POLYMERES OLEFINIQUES

(54) Title: PRODUCTION OF OLEFIN POLYMERS

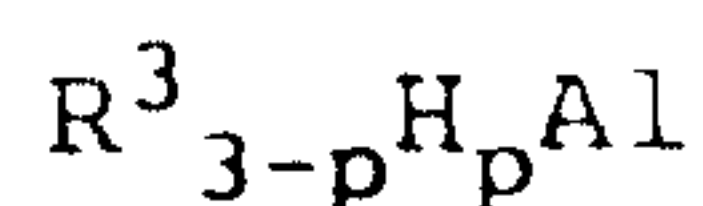
(57) **Abrégé/Abstract:**

Ziegler polymerization of C_3 or higher α -olefins is disclosed which is characterized by a solid catalyst component and an organoaluminum component used in the Ziegler catalyst, and also by the temperature used which is 150 to 300°C. The solid catalyst component, Component (A), comprises Sub-component (i) which is a solid catalyst component for Ziegler catalysts comprising Ti, Mg and a halogen; Sub-component (ii) which is a silicon compound represented by a formula: $R^1_m X_n Si(OR^2)_{4-n-m}$ wherein R^1 indicates a hydrocarbyl group, R^2 which may be the same as or different from R^1 indicates a hydrocarbyl group, X is a halogen atom, and m and n are each a number satisfying equations $0 \leq m \leq 3$, $0 \leq n \leq 3$ and $0 \leq m+n \leq 3$; and Sub-component (iii) which is an organometal compound of a metal of Groups I to IV of the Periodic Table. The organoaluminum component (B) is an organoaluminum compound represented by a formula $R^3_{3-p} H_p Al$ wherein R^3 indicates a hydrocarbyl group of up to 5 carbon atoms and p is a number satisfying an equation $0 \leq p \leq 1$; wherein the mole ratio of the Al in Component (B) to the Ti in Component (A) is equal to or less than 1. The poly α -olefins produced have a broader molecular weight distribution than those produced at a lower polymerization temperature.



ABSTRACT OF THE DISCLOSURE

Ziegler polymerization of C_3 or higher α -olefins is disclosed which is characterized by a solid catalyst component and an organoaluminum component used in the Ziegler catalyst, and also by the temperature used which is 150 to 300°C. The solid catalyst component, Component (A), comprises Sub-component (i) which is a solid catalyst component for Ziegler catalysts comprising Ti, Mg and a halogen; Sub-component (ii) which is a silicon compound represented by a formula: $R^1_m X_n Si(OR^2)_{4-n-m}$ wherein R^1 indicates a hydrocarbyl group, R^2 which may be the same as or different from R^1 indicates a hydrocarbyl group, X is a halogen atom, and m and n are each a number satisfying equations $0 \leq m \leq 3$, $0 \leq n \leq 3$ and $0 \leq m+n \leq 3$; and Sub-component (iii) which is an organometal compound of a metal of Groups I to IV of the Periodic Table. The organoaluminum component (B) is an organoaluminum compound represented by a formula



wherein R^3 indicates a hydrocarbyl group of up to 5 carbon atoms and p is a number satisfying an equation $0 \leq p \leq 1$;

wherein the mole ratio of the Al in Component (B) to the Ti in Component (A) is equal to or less than 1. The poly α -olefins produced have a broader molecular weight distribution than those produced at a lower polymerization temperature.

PRODUCTION OF OLEFIN POLYMERS

BACKGROUND OF THE INVENTIONField of the Art

5 The present invention relates to Ziegler polymerization of olefins. More particularly, the present invention is concerned with Ziegler polymerization of olefins, typically α -olefins of at least 3 carbon atoms, characterized by, among others, the
10 solid catalyst components comprising a transition metal in Ziegler catalysts and the polymerization temperature used which is no lower than 150°C.

Use of the solid catalyst component in accordance with the present invention in Ziegler catalysts as the
15 transition metal component at the temperature will make it possible to produce polymers endowed with improved stereoregularity and broadened molecular weight distribution.

Background of the Invention

20 The catalysts heretofore proposed for the polymerization of olefins comprising a solid catalyst component containing titanium, magnesium and a halogen as the essential components and an organoaluminum compound (and an electron donor, if desired) have produced highly
25 stereoregular polymers.

Such prior art catalysts are such that their catalyst activity may often be found at a polymerization temperature of 90°C or lower, preferably 80°C or lower.

It has been known in the art that ethylene
30 polymerizes at such a higher temperature as 150 to 250°C similarly at a temperature of 70 to 90°C and that polymerization of ethylene at such a higher temperature is known to have such preferable characteristics that the polyethylenes produced have a narrower molecular weight
35 distribution or copolymerizability of ethylene with another monomer is improved.

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It has also been known in the art that propylene will not produce polymers endowed with acceptably high stereoregularity when it is polymerized at such a high temperature as 150°C or higher. One possible reason therefor may be such that the solid structure comprising the titanium component capable of polymerizing propylene into polymers of high stereoregularity is destroyed at a temperature no lower than 150°C, the titanium component is agglomerated or excessively reduced by the organoaluminum component as a co-catalyst, or, when an electron donor is used during polymerization as what is called "outside electron donor", it reacts so strongly with the titanium component or with the organoaluminum component at such a higher temperature that the catalyst activity is thus lowered.

Catalysts which are capable of producing highly stereoregular polymers at such a high temperature as no lower than 150°C have, to the best of the present inventors, not been proposed.

It has also been known to use as an organoaluminum component in the Ziegler catalysts organoaluminum compounds which contain a halogen atom. The halogen atom may have such a problem due to its inherent corrosive nature that polyolefins produced therewith can corrode or rust processing machines for the polymers. An organoaluminum component in Ziegler catalysts which is free from a halogen contained therein has heretofore been desired.

SUMMARY OF THE INVENTION

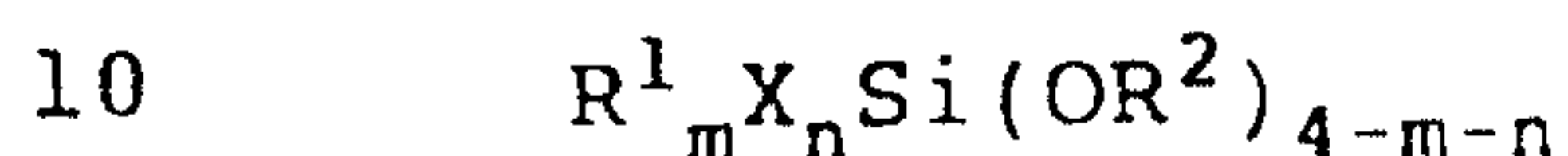
The present invention is based on the discovery that the above problems can be solved by use of a specified solid catalyst component in Ziegler catalysts.

More particularly, the present invention presents a process for producing α -olefin polymers which comprises contacting at a temperature of 150°C to 300°C an olefin with a catalyst thereby to polymerize the olefin, the catalyst comprising:

Component (A) which is a solid catalyst component for Ziegler catalysts, which solid catalyst component is obtained by contacting the following Sub-components (i) to (iii):

5 Sub-component (i) which is a solid catalyst component for Ziegler catalysts comprising titanium, magnesium and a halogen as the essential components;

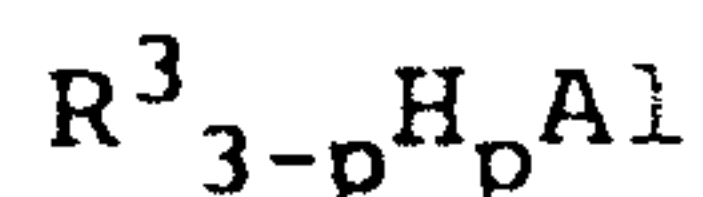
Sub-component (ii) which is a silicon compound represented by a formula



wherein R^1 indicates a hydrocarbyl group of 1 to 20 carbon atoms, R^2 which may be the same as or different from R^1 indicates a hydrocarbyl group of 1 to 20 carbon atoms, X indicates a halogen atom, and
15 m and n are each numbers satisfying equations $0 \leq m \leq 3$, $0 \leq n \leq 3$ and $0 \leq (m+n) \leq 3$; and

Sub-component (iii) which is an organometal compound of a metal of the Groups I to III of the Periodic Table; and

20 Component (B) which is an organoaluminum compound represented by a formula



wherein R^3 indicates a hydrocarbyl group of up to 5 carbon atoms and p is a number satisfying an
25 equation $0 \leq p \leq 1$;

wherein the mole ratio of the Al in Component (B) to the Ti in Component (A) is equal to or less than 1.

It has now been possible in accordance with the present invention that highly stereoregular olefin
30 polymers are produced at a temperature of 150°C or higher where it would have not been possible to prepare such polymers in yield of a level comparable to that obtained by polymerization at a lower temperature of 80°C or lower using known Ziegler catalysts.

35 The polymer produced by the present invention is characterized by the fact that they have broader

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molecular weight distribution than those produced at a lower polymerization temperature of 80°C or lower.

DETAILED DESCRIPTION OF THE INVENTION

[I] Catalyst

5 The catalyst of the present invention comprises a combination of specific components (A) and (B). Here, the wording "comprises" means that the components are not limited only to those mentioned (namely, A and B), and includes co-presence of other components compatible with
10 or suited for the purpose, such as an outside electron donor which is not essential but can be used if desired.

Component (A)

 The Component (A) of the catalyst of the present invention is a solid catalyst component for Ziegler
15 catalysts obtained by contacting the Sub-components (i) to (iii) shown below. The contact product of the Sub-components (i) to (iii) is washed amply with an inert hydrocarbon solvent to form the Component (A). Here, the wording "obtained by contacting" means that the
20 components are not limited only to those mentioned, namely (i) to (iii), and includes co-presence of other components suited for the purpose.

Sub-component (i)

 Sub-component (i) is a solid component comprising
25 titanium, magnesium and a halogen as the essential components. Here, the wording "comprising as the essential components" indicates that it can also contain other elements suited for the purpose than the three components mentioned, that these elements can exist in
30 any desired compound suited for the purpose respectively, and also that these elements can also exist in the form mutually bonded together. Solid components containing titanium, magnesium and a halogen are known *per se*. For example, those as disclosed in Japanese Laid-open Patent
35 Publications Nos. 45688/1978, 3894/1979, 31092/1979, 39483/1979, 94591/1979, 118484/1979, 131589/1979, 75411/1980, 90510/1980, 90511/1980, 127405/1980,

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147507/1980, 155003/1980, 18609/1981, 70005/1981,
 72001/1981, 86905/1981, 90807/1981, 155206/1981,
 3803/1982, 34103/1982, 92007/1982, 121003/1982,
 5309/1983, 5310/1983, 5311/1983, 8706/1983, 27732/1983,
 5 32604/1983, 32605/1983, 67703/1983, 117206/1983,
 127708/1983, 183708/1983, 183709/1983, 149905/1984 and
 149906/1984 may be employed.

As the magnesium compound which is the magnesium
 source to be used in the present invention, magnesium
 10 dihalides, dialkoxymagnesiums, alkoxymagnesium halides,
 magnesium oxyhalides, dialkylmagnesiums, magnesium oxide,
 magnesium hydroxide, carboxylates of magnesium, etc. are
 exemplified. Among these magnesium compounds, magnesium
 dihalides, dialkoxymagnesiums and alkoxymagnesium
 15 halides, particularly $MgCl_2$, are preferred.

As the titanium compound which is the titanium
 source, compounds represented by the formula $Ti(OR^4)_{4-q}X_q$
 (wherein R^4 is a hydrocarbyl group, preferably having
 about 1 to 10 carbon atoms, X represents a halogen atom
 20 and q is an integer of $0 \leq q \leq 4$) and polymers of a
 titanium tetraalkoxide.

Specific examples may include:

titanium tetrahalides such as $TiCl_4$, $TiBr_4$ and the
 like;

25 alkoxytitanium halides such as

$Ti(OC_2H_5)Cl_3$,
 $Ti(OC_2H_5)_2Cl_2$,
 $Ti(OC_2H_5)_3Cl$,
 $Ti(O-iC_3H_7)Cl_3$,
 30 $Ti(O-nC_4H_9)Cl_3$,
 $Ti(O-nC_4H_9)_2Cl_2$,
 $Ti(OC_2H_5)Br_3$,
 $Ti(OC_2H_5)(OC_4H_9)_2Cl$,
 $Ti(O-nC_4H_9)_3Cl$,
 35 $Ti(O-C_6H_5)Cl_3$,
 $Ti(O-iC_4H_9)_2Cl_2$,

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Ti(OC₅H₁₁)Cl₃,

Ti(OC₆H₁₃)Cl₃, and the like;

and titanium tetraalkoxides such as

Ti(OC₂H₅)₄,

5 Ti(O-iC₃H₇)₄,

Ti(O-nC₃H₇)₄,

Ti(O-nC₄H₉)₄,

Ti(O-iC₄H₉)₄,

Ti(O-nC₅H₁₁)₄,

10 Ti(O-nC₆H₁₃)₄,

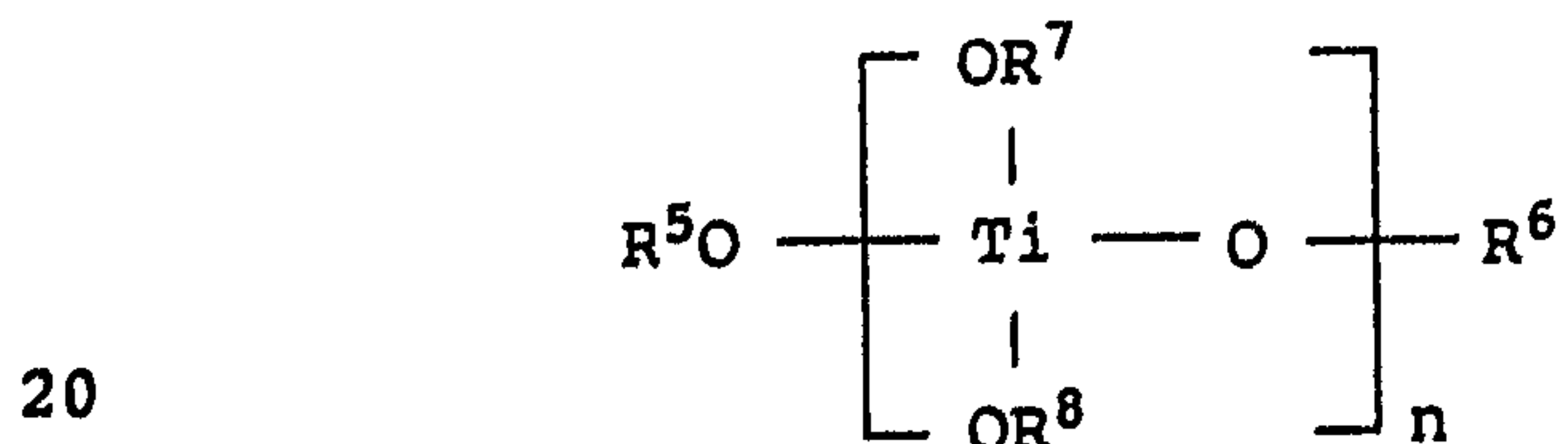
Ti(O-nC₇H₁₅)₄,

Ti(O-nC₈H₁₇)₄,

Ti[OCH₂CH(CH₃)₂]₄,

Ti[OCH₂CH(C₂H₅)C₄H₉]₄, and the like.

15 Polymers of a titanium tetraalkoxide may include those represented by the following formula:



wherein, R⁵ - R⁸ represent the same or different hydrocarbyl groups, preferably aliphatic hydrocarbyl group having 1 to 10 carbon atoms or aromatic hydrocarbyl groups, particularly aliphatic hydrocarbyl groups having 2 to 6 carbon atoms. n represents a number of 2 or more, particularly a number up to 20. The value of n should be desirably selected so that the polytitanate itself or as a solution can be provided in a liquid state for the contact step with other components. A suitable n selected in view of ease of handling may be about 2 to 14, preferably 2 to 10. Specific examples of such polytitanates may include n-butylpolytitanate (n = 2 to 10), hexylpolytitanate (n = 2 to 10), n-octylpolytitanate (n = 2 to 10), and the like. Among them, n-butylpolytitanate is preferred.

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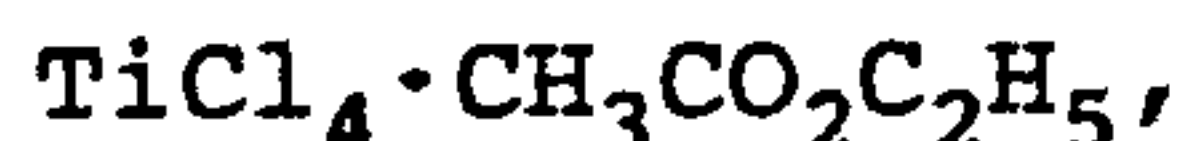
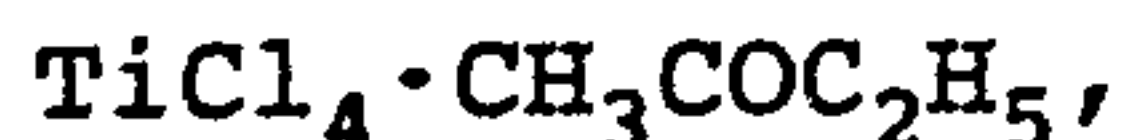
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It is also possible to use, as the titanium compound for the titanium source, a molecular compound obtained by reacting an electron donor as described below with a compound TiX'_4 (where X' represents a halogen). Specific

5 examples may include:

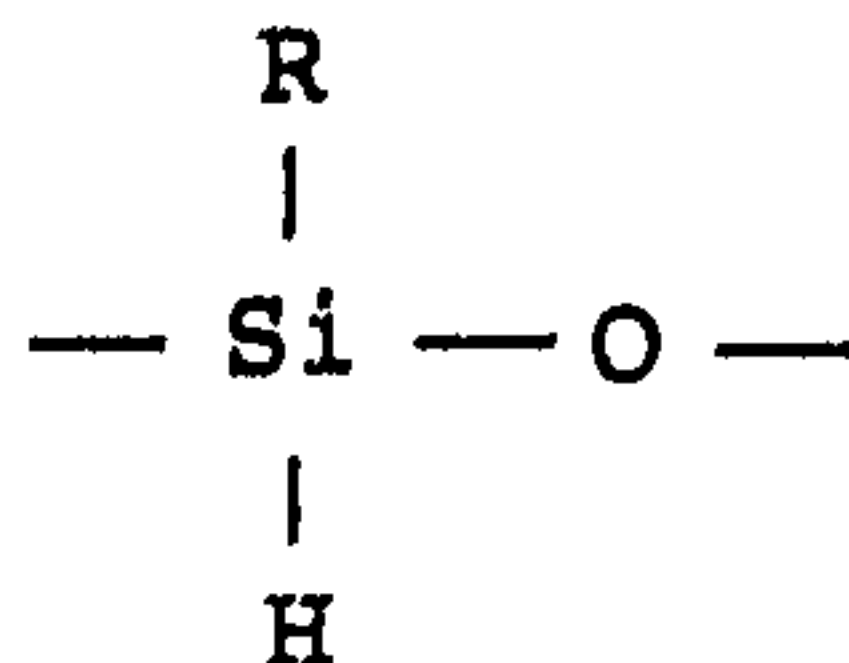


Among these titanium compounds, $TiCl_4$, $Ti(OC_2H_5)_4$,
 15 $Ti(O-nC_4H_9)_4$, and $Ti(O-nC_4H_9)Cl_3$ are preferred. Particularly, $TiCl_4$ and $Ti(O-nC_4H_9)_4$ are preferred.

As to the halogen source, it is a common practice to supply the halogen from the halide compounds of magnesium and/or titanium as described above, but it can be also
 20 supplied from known halogenating agents such as halogen compounds of aluminum, halogen compounds of silicon, halogen compounds of phosphorus, and the like.

The halogen contained in the catalyst components may be fluorine, chlorine, bromine, iodine or a mixture of
 25 these, particularly preferably chlorine.

The solid component to be used in the present invention can also include, in addition to the above essential components: a silicon compound such as $SiCl_4$, CH_3SiCl_3 , and the like; a polymeric silicon compound
 30 having the structure represented by the following formula:



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(wherein R is a hydrocarbyl group having about 1 to 10, preferably about 1 to 6 carbon atoms) and having a viscosity of about 1 centistoke to 100 centistokes, such as methylhydrogenpolysiloxane, ethylhydrogenpolysiloxane, 5 phenylhydrogenpolysiloxane, cyclohexylhydrogenpolysiloxane, 1,1,3,3-tetramethyldisiloxane, 1,3,5,7-tetramethylcyclotetrasiloxane, 1,3,5,7,9-pentamethylcyclopentasiloxane and the like; an aluminum compound such as $\text{Al}(\text{O}i\text{C}_3\text{H}_7)_3$, AlCl_3 , AlBr_3 , $\text{Al}(\text{OC}_2\text{H}_5)_3$, 10 $\text{Al}(\text{OCH}_3)_2\text{Cl}$; a boron compound such as $\text{B}(\text{OCH}_3)_3$, $\text{B}(\text{OC}_2\text{H}_5)_3$, $\text{B}(\text{OC}_6\text{H}_5)_3$; WCl_6 and MoCl_5 . These optional compounds may remain in the solid component as the components of silicon, aluminum and boron.

Further, in preparing the solid component, use can 15 also be made of an electron donor as what is called "an inside donor".

Examples of the electron donor or the inside donor which can be used for preparation of the solid component may include oxygen-containing electron donors such as 20 alcohols, phenols, ketones, aldehydes, carboxylic acids, esters of an organic acid or an inorganic acid, ethers, acid amides, acid anhydrides, and the like; and nitrogen-containing electron donors such as ammonia, amines, nitriles, isocyanates, and the like.

25 More specifically, there may be included: (a) alcohols having 1 to 18 carbon atoms, such as methanol, ethanol, propanol, pentanol, hexanol, octanol, dodecanol, octadecyl alcohol, benzyl alcohol, phenylethyl alcohol, isopropylbenzyl alcohol and the like; (b) phenols having 30 6 to 25 carbon atoms which may or may not have an alkyl group, such as phenol, cresol, xylenol, ethylphenol, propylphenol, isopropylphenol, nonylphenol, naphthol and the like; (c) ketones having 3 to 15 carbon atoms, such as acetone, methyl ethyl ketone, methyl isobutyl ketone, 35 acetophenone, benzophenone and the like; (d) aldehydes having 2 to 15 carbon atoms, such as acetaldehyde, propionaldehyde, octylaldehyde, benzaldehyde,

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tolualdehyde, naphthaldehyde and the like; (e) organic acid esters having 2 to 20 carbon atoms, such as methyl formate, methyl acetate, ethyl acetate, vinyl acetate, propyl acetate, octyl acetate, cyclohexyl acetate, 5 cellosolve acetate, ethyl propionate, methyl butyrate, ethyl valerate, ethyl stearate, methyl chloroacetate, ethyl dichloroacetate, methyl methacrylate, ethyl crotonate, ethyl cyclohexanecarboxylate, methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, octyl 10 benzoate, cyclohexyl benzoate, phenyl benzoate, benzyl benzoate, methyl toluylate, ethyl toluylate, amyl toluylate, ethyl ethylbenzoate, methyl anisate, ethyl anisate, ethyl ethoxybenzoate, diethyl phthalate, dibutyl phthalate, diheptyl phthalate, γ -butyrolactone, 15 α -valerolactone, coumarine, phthalide, ethylene carbonate, cellosolve acetate, cellosolve isobutyrate and cellosolve benzoate, etc.; (f) inorganic acid esters, such as silicates such as ethyl silicate, butyl silicate, phenyl-triethoxysilane, etc.; (g) acid halides having 2 20 to 15 carbon atoms, such as acetyl chloride, benzoyl chloride, toluyloic chloride, anisic chloride, phthaloyl chloride, phthaloyl isochloride and the like; (h) ethers having 2 to 20 carbon atoms, such as methyl ether, ethyl ether, isopropyl ether, butyl ether, amyl ether, 25 tetrahydrofuran, anisole, diphenyl ether and the like; (i) acid amides, such as acetic amide, benzoic amide, toluyloic amide and the like; (j) amines, such as monomethylamine, monoethylamine, diethylamine, tributylamine, piperidine, tribenzylamine, aniline, 30 pyridine, picoline, tetramethylethylenediamine and the like; and (k) nitriles, such as acetonitrile, benzonitrile, tolunitrile and the like. One or more of these electron donors can be used in preparing the solid catalyst component. Among them, preferred are organic 35 acid esters and acid halides, particularly preferably phthalic acid esters, phthalic acid halides, and cellosolve acetate.

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The amounts of the above respective components used may be at any desired level, so long as the advantages inherent in the present invention can be attained, but, generally speaking, the following ranges are preferred.

5 The amount of the titanium compound used may be within the range of 1×10^{-4} to 1000, preferably 0.01 to 10, in terms of molar ratio relative to the amount of the magnesium compound used. When a compound as the halogen source is used, its amount used may be within the range
10 of 1×10^{-2} to 1000, preferably 0.1 to 100, in terms of a molar ratio relative to magnesium used, irrespective of whether the titanium compound and/or the magnesium compound may contain a halogen or not.

15 The amount of the silicon, aluminum, boron, wolfram or molybdenum compound when used may be within the range of 1×10^{-3} to 100, preferably 0.01 to 10, in terms of a molar ratio to the amount of the above magnesium compound used.

20 The amount of the electron donor compound when used may be within the range of 1×10^{-3} to 10, preferably 0.01 to 5, in terms of a molar ratio relative to the amount of the above magnesium compound used.

25 The solid component for preparing the Sub-component (i) may be prepared from the titanium source, the magnesium source and the halogen source, and further optionally other components such as an electron donor according to methods mentioned below.

30 (a) A method in which a magnesium halide optionally together with an electron donor is contacted with a titanium compound.

(b) A method in which alumina or magnesia is treated with a phosphorus halide compound, and the product is contacted with a magnesium halide, an electron donor, a titanium halide-containing compound.

35 (c) A method in which the solid component obtained by contacting a magnesium halide with a titanium tetraalkoxide and a specific polymeric silicon compound

As the polymeric silicon compound, those represented by the following formula are suitable:

$$\left(\begin{array}{c} \text{H} \\ | \\ \text{--- Si --- O ---} \\ | \\ \text{R} \end{array} \right)_n$$

Among them, methylhydrogenpolysiloxane, 1,3,5,7-
15 tetramethylcyclotetrasiloxane, 1,3,5,7,9-pentamethyl-
cyclopentacyclopentasiloxane, ethylhydrogenpolysiloxane,
phenylhydrogenpolysiloxane, and cyclohexylhydrogen
polysiloxane are preferred.

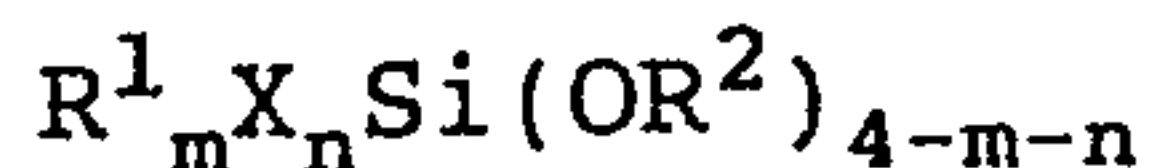
(e) A method in which an organomagnesium compound such as Grignard reagent, etc. is reacted with a halogenating agent, a reducing agent, etc., and then the
30 reaction product is contacted with an electron donor and a titanium compound.

35 Among these methods, method (c), (d) and (f) are
preferable.

Sub-component (ii)

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Sub-component (ii) for preparing the Component (A) is a silicon compound expressed by a formula



wherein R^1 is a hydrocarbyl group of 1 to 20 carbon atoms, R^2 is a hydrocarbyl group of 1 to 20 carbon atoms which is the same as or different from R^1 , X is a halogen atom, and m and n are each numbers satisfying equations $0 \leq m \leq 3$, $0 \leq n \leq 3$ and $0 \leq (m+n) \leq 3$.

R^1 and R^2 have 1 to 20, preferably 1 to 10, carbon atoms and may be in a branched or straight configuration, respectively.

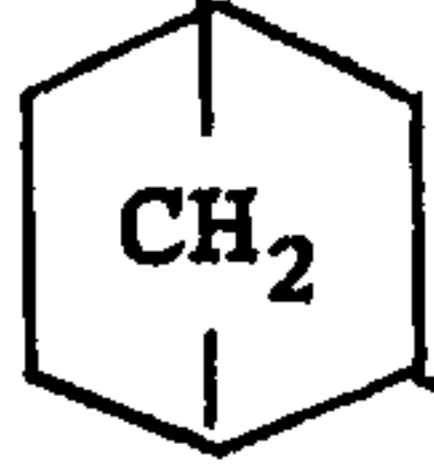
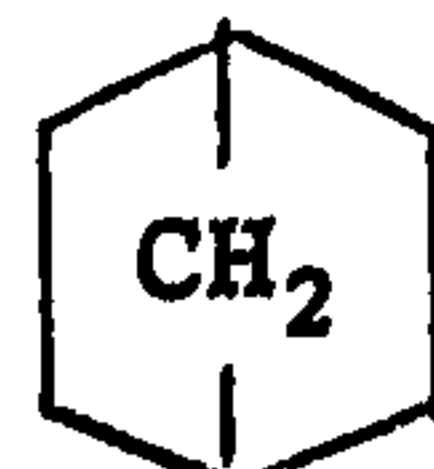
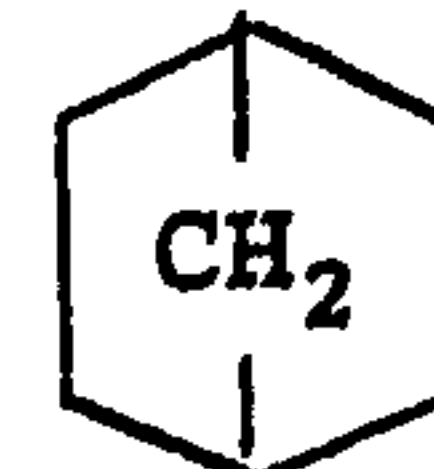
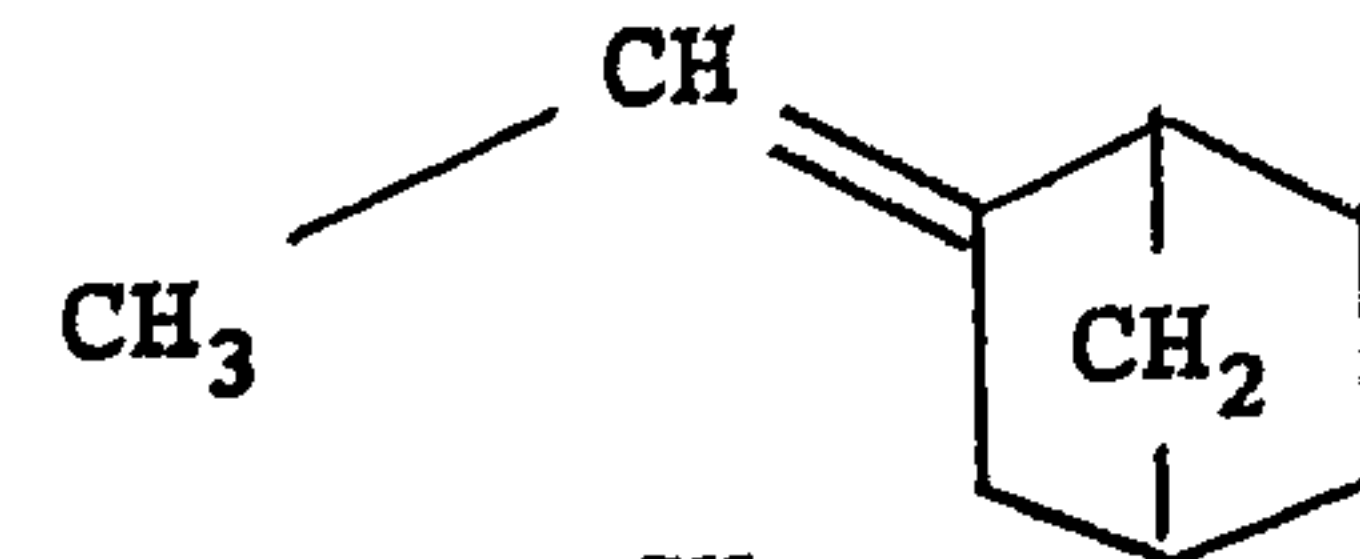
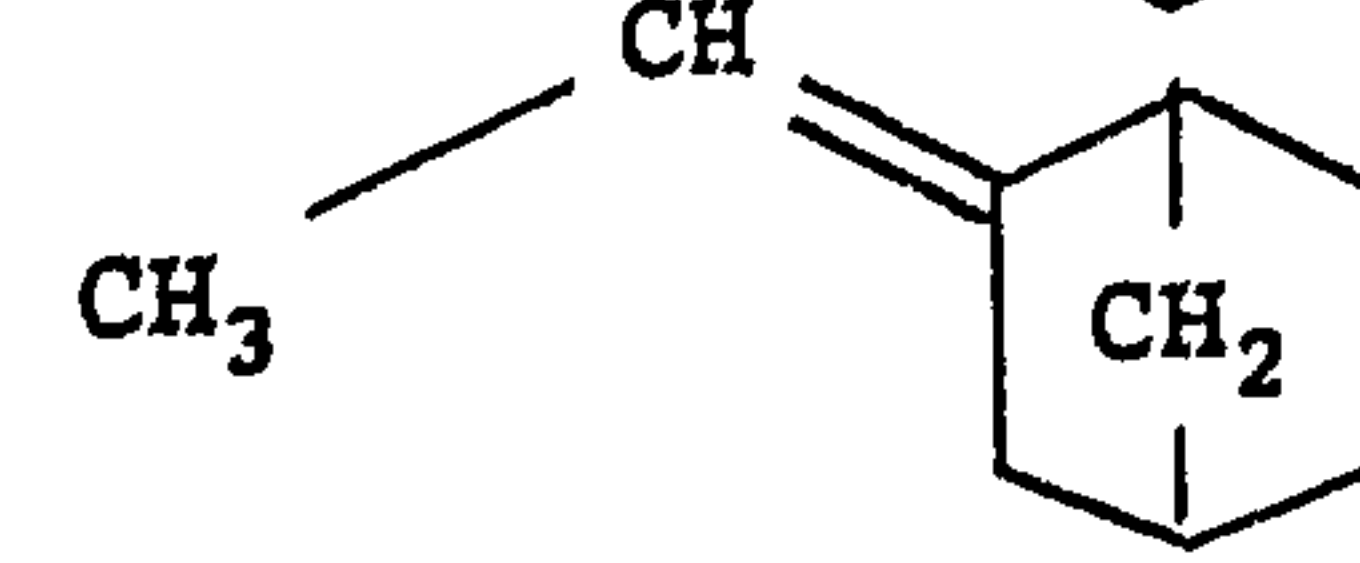
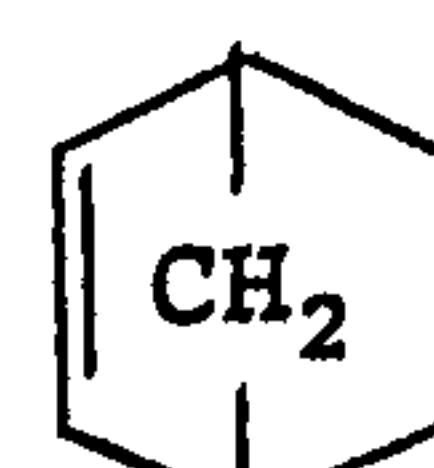
X is preferably a chlorine atom at least from an economical point of view.

R^2 may be an aliphatic hydrocarbyl group, and preferably is a hydrocarbyl group of 1 to 4 carbon atoms.

Specific examples of the silicon compounds may include:

- (CH₃)Si(OCH₃)₃,
- (CH₃)Si(OC₂H₅)₃,
- 20 (C₂H₅)₂Si(OCH₃)₂,
- (i-C₃H₇)₂Si(OCH₃)₂,
- (n-C₆H₁₃)Si(OCH₃)₃,
- (i-C₃H₇)Si(OC₂H₅)₃,
- (i-C₄H₉)₂Si(OCH₃)₂,
- 25 (C₆H₁₁)₂Si(OCH₃)₂,
- (C₆H₁₁)(CH₃)Si(OCH₃)₂,
- (C₆H₁₁)₂Si(OCH₃)₂,
- (C₆H₁₁)(CH₃)Si(OCH₃)₂,
- (C₅H₄)₂Si(OCH₃)₂,
- 30 (C₅H₄)(CH₃)Si(OCH₃)₂,
- (C₂H₅)Si(OC₂H₅)₃,
- (n-C₁₀H₂₁)Si(OC₂H₅)₃,
- Cl(CH₂)₃Si(OCH₃)₃,
- Si(OCH₃)₄,
- 35 Si(OC₂H₅)₃Cl,
- (C₂H₅)₂Si(OC₂H₅)₂,

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- $(C_{17}H_{35})Si(OCH_3)_3$,
 $Si(OC_2H_5)_4$,
 $(C_6H_5)Si(OCH_3)_3$,
 $Si(OCH_3)_2Cl_2$,
 5 $(C_6H_5)_2Si(OCH_3)_2$,
 $(C_6H_5)(CH_3)Si(OCH_3)_2$,
 $(C_6H_5)Si(OC_2H_5)_3$,
 $(C_6H_5)_2Si(OC_2H_5)_2$,
 $NC(CH_2)_2Si(OC_2H_5)_3$,
 10 $(C_6H_5)(CH_3)Si(OC_2H_5)_2$,
 $(n-C_3H_7)Si(OC_2H_5)_3$,
 $(CH_3)Si(OC_3H_7)_3$,
 $(C_6H_5)(CH_2)Si(OC_2H_5)_3$,
 15  $Si(OC_2H_5)_3$,
 20  $Si(CH_3)(OC_2H_5)_2$,
 $Si(CH_3)(OCH_3)_2$,
 25  $Si(OCH_3)_3$,
 30  $Si(OC_2H_5)_3$,
 35  $Si(OCH_3)_3$,
 $(CH_3)_3CSi(CH_3)(OCH_3)_2$,
 $(CH_3)_3CSi(HC(CH_3)_2)(OCH_3)_2$

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- $(\text{CH}_3)_3\text{CSi}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2,$
 $(\text{C}_2\text{H}_5)_3\text{CSi}(\text{CH}_3)(\text{OCH}_3)_2,$
 $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{CHSi}(\text{CH}_3)(\text{OCH}_3)_2,$
 $((\text{CH}_3)_2\text{CHCH}_2)_2\text{Si}(\text{OCH}_3)_2,$
 5 $(\text{C}_2\text{H}_5)(\text{CH}_3)_2\text{CSi}(\text{CH}_3)(\text{OCH}_3)_2,$
 $(\text{C}_2\text{H}_5)(\text{CH}_3)_2\text{CSi}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2,$
 $(\text{CH}_3)_3\text{CSi}(\text{OCH}_3)_3,$
 $(\text{CH}_3)_3\text{CSi}(\text{OC}_2\text{H}_5)_3,$
 $(\text{C}_2\text{H}_5)_3\text{CSi}(\text{OC}_2\text{H}_5)_3,$
 10 $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{CHSi}(\text{OCH}_3)_3,$
 $(\text{C}_2\text{H}_5)(\text{CH}_3)_2\text{CSi}(\text{OCH}_3)_3,$
 $(\text{C}_2\text{H}_5)(\text{CH}_3)_2\text{CSi}(\text{OC}_2\text{H}_5)_3,$
 $(\text{C}_2\text{H}_5)_3\text{CSi}(\text{OC}_2\text{H}_5)_3,$
 $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{CHSi}(\text{OCH}_3)_3,$
 15 $((\text{CH}_3)_3\text{C})_2\text{Si}(\text{OCH}_3)_2.$

It is preferable that R^1 has a branch at the carbon atom adjacent to the silicon atom. The branch may preferably be an alkyl group or a cycloalkyl group. More preferably, the carbon atom adjacent to the silicon atom, namely α -carbon atom, is a secondary or tertiary carbon atom in a branched hydrocarbyl group having 3 to 20 carbon atoms. Most preferably, the carbon atom connected with the silicon atom is a tertiary carbon atom in a branched hydrocarbyl group having 4 to 10 carbon atoms.

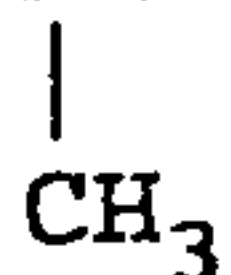
25 Sub-component (iii)

Sub-component (iii) for preparing a solid catalyst component in accordance with the present invention is an organometal compound of a metal of the Group I to III of the Periodic Table.

30 Examples of the metals include lithium, magnesium, aluminum and zinc, but aluminum is representable.

The compounds are organometal compounds and thus have at least one organic radical-metal bonding. The organic radical may typically be a hydrocarbyl group of 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms, more preferably 1 to 6 carbon atoms.

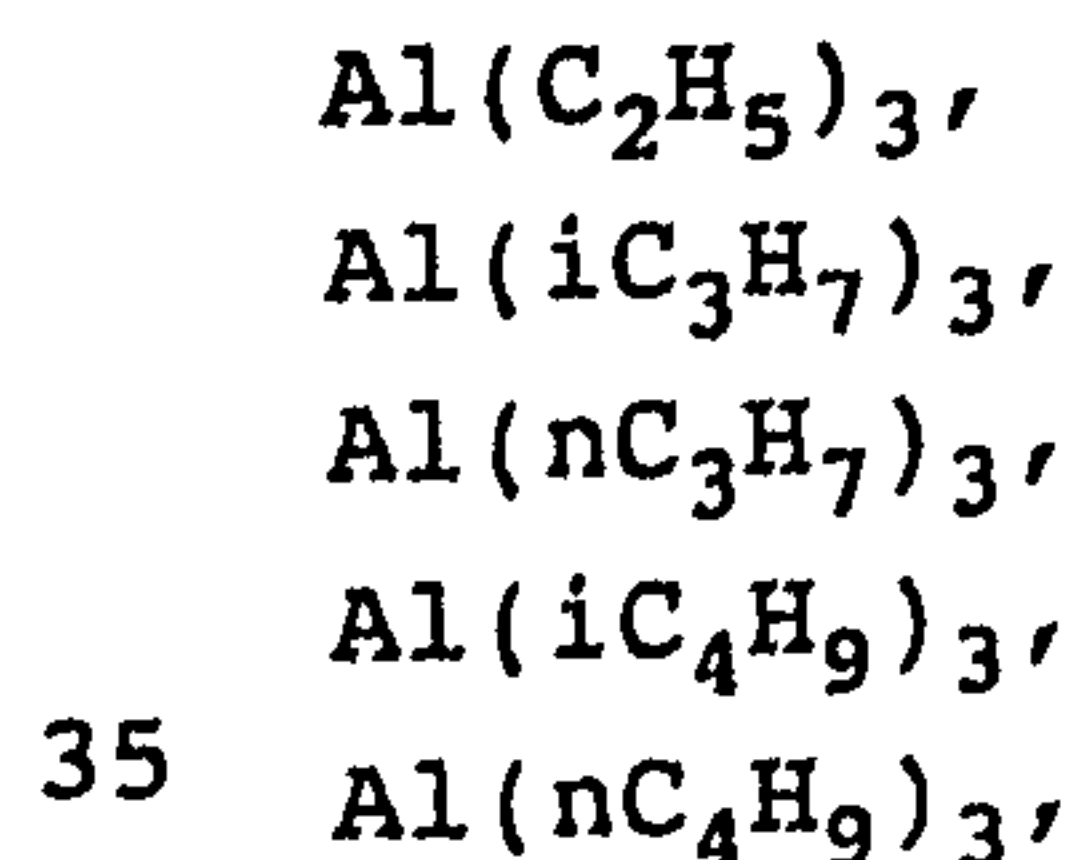
The remaining valence of the metal in question other than those satisfied by an organic radical, if any, can be satisfied by a hydrogen atom, a halogen atom, hydrocarbyloxy group of 1 to 10, preferably 1 to 6, carbon atoms, or the metal itself with an oxygen bridge therebetween such as-O-Al-



methylalminoxanes.

Specific examples of such organometal compounds may include: (a) organolithium compounds, e.g. methyllithium, n-butyllithium, sec.-butyllithium, tert.-butyllithium and the like; (b) organomagnesium compounds, e.g. diethylmagnesium, ethylbutylmagnesium, dibutylmagnesium, dihexylmagnesium, hexylethylmagnesium, ethylmagnesium chloride, ethylmagnesium bromide, butylmagnesium chloride, tert.-butylmagnesium bromide, and the like; (c) organozinc compounds, e.g. diethylzinc, dimethylzinc, dibutylzinc, and the like; (d) organoaluminum compounds, e.g. trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, diethylaluminum chloride, diethylaluminum hydride, diethylaluminum ethoxide, ethylaluminum sesquichloride, ethylaluminum dichloride, methylaluminumoxane, and the like. Among these, organoaluminum compounds and organozinc compounds, especially the former, are preferable.

The most preferable are organoaluminum compounds and further examples of organoaluminum compounds may be found in the examples of organoaluminum compounds as the Component (B) which will be given hereinbelow, but include:



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- $\text{Al}(\text{C}_5\text{H}_{11})_3$,
 $\text{Al}(\text{nC}_6\text{H}_{13})_3$,
 $\text{Al}(\text{C}_8\text{H}_{17})_3$,
 $\text{Al}(\text{C}_{10}\text{H}_{21})_3$,
5 $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$,
 $\text{Al}(\text{iC}_4\text{H}_9)_2\text{Cl}$,
 $\text{Al}(\text{C}_2\text{H}_5)_2\text{H}$,
 $\text{Al}(\text{iC}_4\text{H}_9)_2\text{H}$,
 $\text{Al}(\text{C}_2\text{H}_5)_2(\text{OC}_2\text{H}_5)$.

10 Preparation of the Component (A)

The contacting method and conditions for the Sub-components (i) to (iii) can be as desired, so long as the advantages inherent in the present invention can be attained, but generally the following conditions are
 15 preferred. The contact temperature may be about -50 to 200°C , preferably 0 to 100°C . As the contacting method, there may be employed the mechanical method wherein a rotating ball mill, a vibrating ball mill, a jet mill, a medium stirring pulverizer or the like is used and the
 20 method in which contact is effected with stirring under the presence of an inert diluent. As the inert diluent to be used, aliphatic or aromatic hydrocarbons and halohydrocarbons, polysiloxane, etc. may be exemplified.

The contacting order and the contacting time of the
 25 Sub-components (i) to (iii) in preparing the component (A) of the present invention may be any desired one, so long as the advantages inherent in the present invention are attained.

Specific orders of such contact may include those as
 30 shown below, where the symbol "+" indicates a contact between the components flanking the symbol, and a washing or rinsing processing can be interposed between the contacts.

- (a) {Sub-component (i) + Sub-component (ii)} + Sub-
 35 component (iii);
 (b) {Sub-component (i) + Sub-component (iii)} + Sub-
 component (ii);

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(c) Sub-component (i) + {Sub-component (ii) + {Sub-component (iii)}} + {Sub-component (ii) + Sub-component (iii)};

5 (d) {Sub-component (ii) + Sub-component (iii)} + Sub-component (i);

(e) Sub-component (i) + Sub-component (ii) + Sub-component (iii).

The quantitative ratio of the Sub-components (i) to (iii) can be any desired one, so long as the advantages
10 inherent in the present invention can be attained, but generally preferred to be within the following ranges.

The quantitative ratio of the Sub-component (i) to (ii) may be within the range of 0.01 to 1000, preferably 0.1 to 100, in terms of the atomic ratio
15 (silicon/titanium) of the silicon of the Sub-component (ii) to the titanium component constituting the Sub-component (i).

The Sub-component (iii) is used in an amount within the range of 0.01 to 100, preferably 0.1 to 30, in terms
20 of the atomic ratio of the metals {(Sub-component (iii)/titanium(Sub-component (i)))}.

Modification of the Component (A) can be applied provided that the advantages inherent in the present invention may not be impaired.

25 One of the modification comprises use of another component other than Sub-components (i) to (iii) during the process for preparing Component (A), such as methylhydrogenpolysiloxane, ethyl borate, aluminum triisopropoxide, aluminum trichloride, silicon
30 tetrachloride, a tetra-valent titanium compound of a formula: $Ti(OR^9)_{4-s}X_s$ where R^9 is a hydrocarbyl group preferably of 1 to 6 carbon atoms, X is a halogen atom, and s is $0 \leq s \leq 4$, a tri-valent titanium compound, wolfram hexachloride, molybdenum pentachloride and the
35 like.

The contact product of the Sub-components (i) to (iii) is washed amply with an inert hydrocarbon solvent

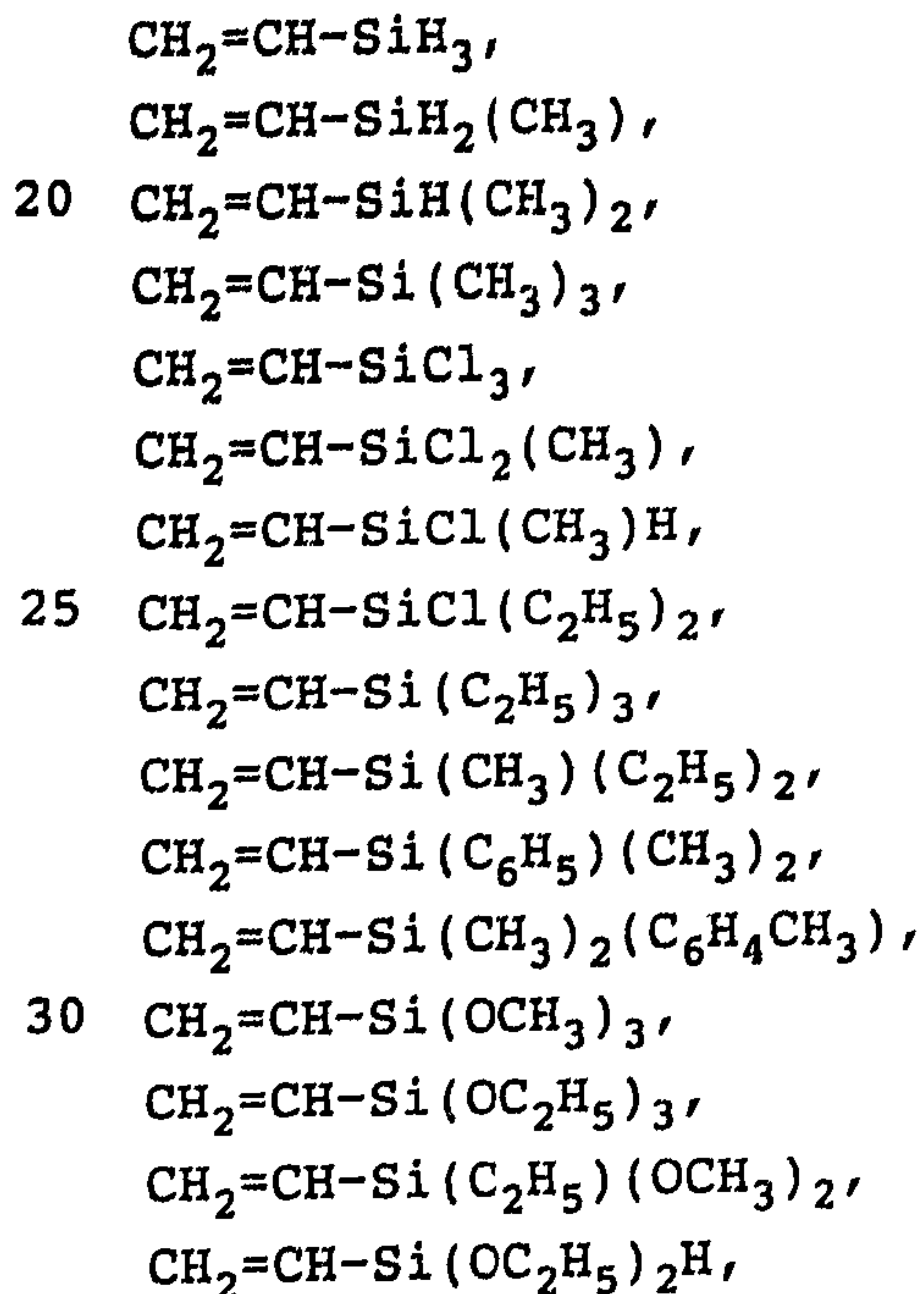
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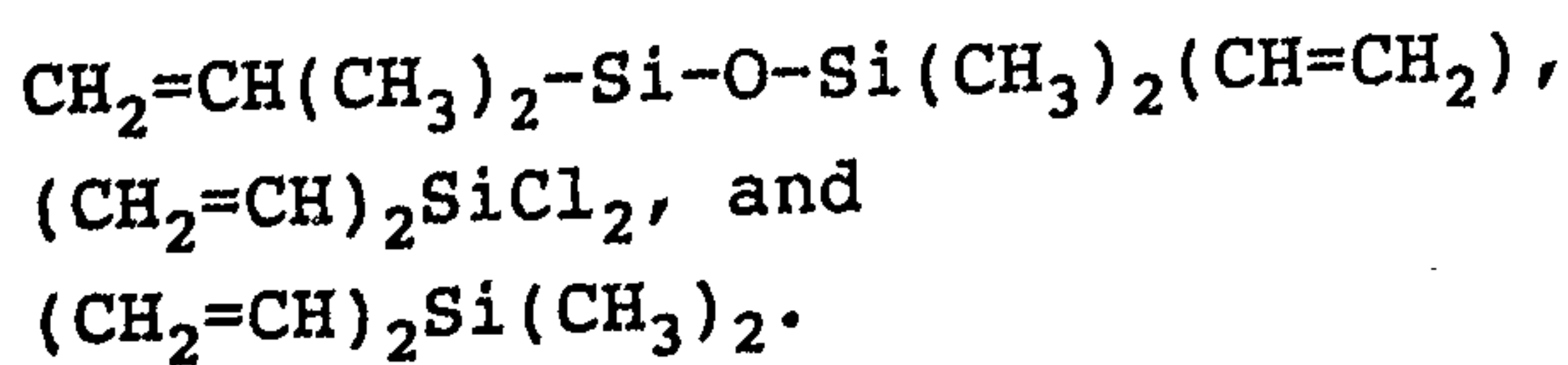
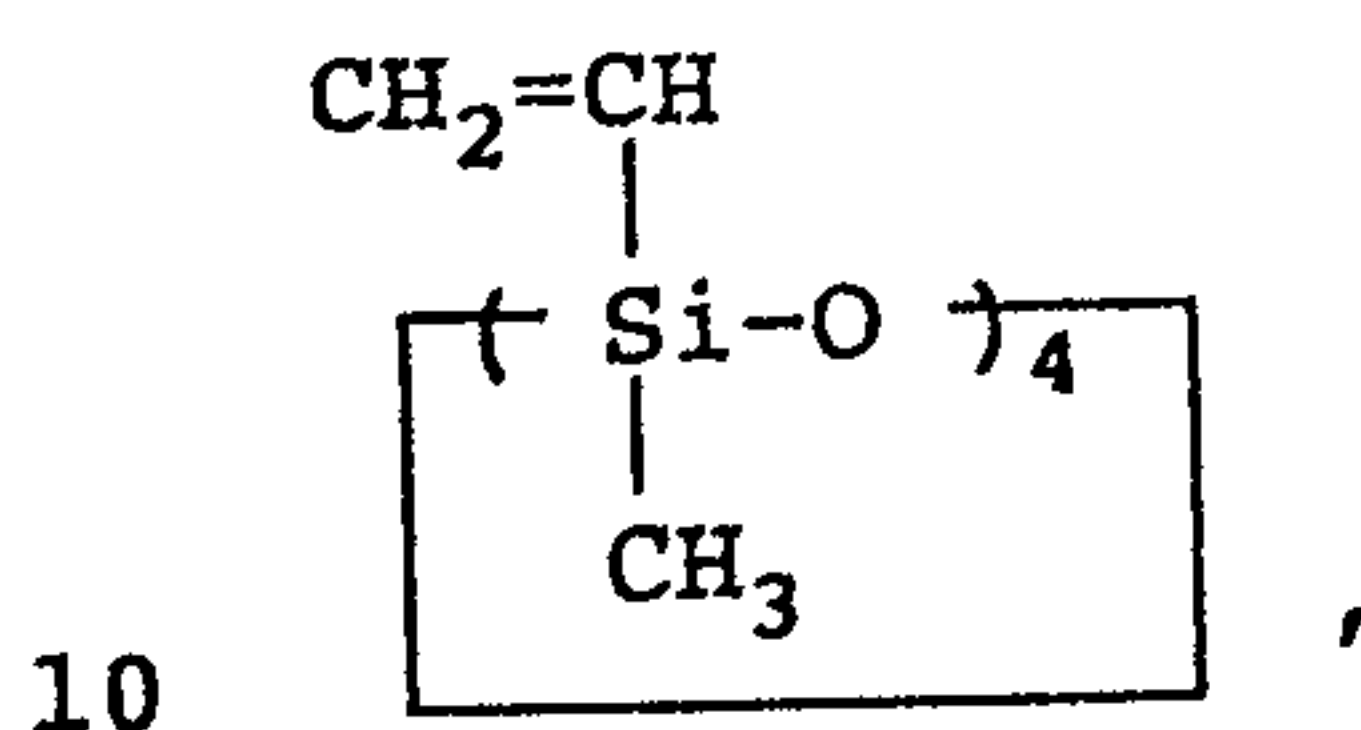
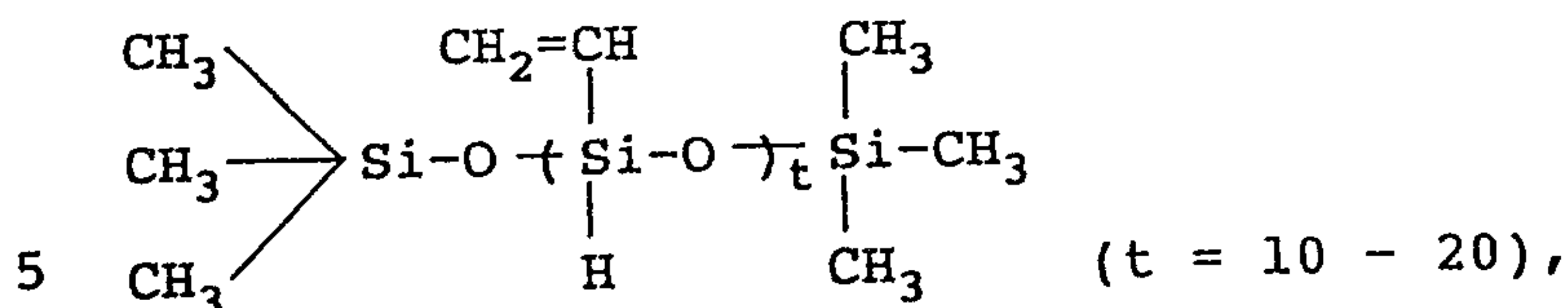
to form the Component (A). Particular examples of the inert hydrocarbon solvent include those conventionally used in preparing the transition metal components for Ziegler catalysts such as, for example, hexane, heptane, 5 octane, decane, cyclohexane and toluene.

One typical example of the optional component for modifying the Component (A) is a group of vinylsilane compounds.

Examples of vinylsilane compounds are derivatives of 10 monosilane (SiH_4) such that at least one of the hydrogen atoms has been replaced by vinyl group ($\text{CH}_2=\text{CH}-$) and one or some of the remaining hydrogen atoms has been replaced by a halogen atom, preferably a chlorine atom, an alkyl, preferably one having 1 to 12 carbon atoms, an alkoxy, 15 preferably one having 1 to 12 carbon atoms, or an aryl, preferably phenyl.

Specific examples of vinylsilane compounds include:





Preferable vinylsilane compounds are those having no oxygen atoms, and more preferable vinylsilane compounds are vinylalkylsilanes and vinylchlorosilanes.

The amount of the vinylsilane compounds is 0.001 to 1000, preferably 0.01 to 100, in terms of mole ratio to the titanium component of the component (i).

20 Component (B)

The component (B) is an organoaluminum compound represented by a formula



wherein R^3 indicates a hydrocarbyl group of up to 5 carbon atoms, preferably up to 4 carbon atoms, and p is a number satisfying an equation $0 \leq p \leq 1$.

Examples of the organoaluminum compounds for Component (B) include: $\text{Al}(\text{C}_2\text{H}_5)_3$, $\text{Al}(\text{CH}_3)_3$, $\text{Al}(\text{iC}_3\text{H}_7)_3$, $\text{Al}(\text{n-C}_3\text{H}_7)_3$, $\text{Al}(\text{C}_2\text{H}_5)_2\text{H}$, $\text{Al}(\text{nC}_3\text{H}_7)\text{H}$, $\text{Al}(\text{iC}_4\text{H}_9)_3$, $\text{Al}(\text{n-C}_4\text{H}_9)_3$, and $\text{Al}(\text{iC}_4\text{H}_9)_2\text{H}$. These can be used in admixture.

30 Making up of a catalyst

The catalysts in accordance with the present invention may be made up by contacting Components (A) and (B) or (A), (B) and an optional component each other at once, or step-wisely or portion-wisely, within or outside

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a polymerization vessel in the absence or presence of an α -olefin to be polymerized.

The amount of the Component (B) used is, in accordance with one of the features of the present invention, no higher than 1, more preferably less than 1, but not less than 0.001, still preferably 0.001 to 1, more preferably 0.01 to 0.5, in terms of mole ratio of Al/Ti of the Component (B)/Component (A).

The Components (A) and (B) can be introduced to the place where they are contacted in any suitable way, but it may be preferred to bring it into contact each in a dispersion in an aliphatic hydrocarbon such as hexane or heptane before or after they are introduced into a polymerization vessel.

15 [II] Polymerization of olefins

The polymerization of olefins in accordance with the present invention is characterized by, inter alia, the temperature used, which is 150°C or higher.

The upper limit of the polymerization temperature may be around 300°C. The preferable temperature range may be 150 to 250°C.

Not only are the catalysts of the present invention applicable to ordinary slurry polymerization but they may also be used for liquid-phase, solventless polymerization wherein substantially no solvent is used, solution polymerization and vapor-phase polymerization, in a continuous or a batch-wise fashion. The catalysts in accordance with the present invention can be used not only in continuous polymerization and batchwise polymerization but also in the polymerization wherein a preliminary polymerization is conducted in which a small amount of an α -olefin is polymerized by the catalyst. In the case of slurry polymerization, aliphatic or aromatic hydrocarbons such as hexane, heptane, pentane, cyclohexane, benzene, toluene and kerosene are used alone or in combination as the polymerization solvent. The polymerization may be practiced under any pressure,

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preferably under a pressure of atmospheric to 1000 kg/cm²G, preferably atmospheric to 150 kg/cm², and hydrogen can be used additionally as the molecular-weight control agent.

- 5 The olefins to be polymerized with the catalyst systems of the present invention are represented by the general formula:



- 10 wherein R¹⁰ is a hydrocarbyl group which has 1 to 10, preferably 1 to 6, carbon atoms and may be in a linear or branch structure.

- Specific examples of such olefins may include propylene, butene-1, pentene-1, hexene-1, 3-methylbutene-1 and 4-methylpentene-1. Preference is given to
15 propylene, 3-methylbutene-1 and 4-methylpentene-1, propylene being more preferable. These α -olefin can be used in combination.

- The poly α -olefins thereby obtained are characterized by their molecular weight distribution
20 which is broader than that in poly α -olefins produced at a temperature of 80°C or lower.

[EXPERIMENTAL EXAMPLES]

Example-1

[Preparation of Component (A)]

- 25 Into a flask purged with nitrogen was introduced 200 ml of dehydrated and deoxygenated n-heptane, and subsequently 0.4 mol of MgCl₂ and 0.8 mol of Ti(O-nC₄H₉)₄ and the reaction was carried out at 95°C for 2 hours. After completion of the reaction, the temperature was
30 lowered to 40°C, followed by addition of 48 ml of methylhydrogenpolysiloxane (of 20 centistokes) and the reaction was carried out for 3 hours. The solid component formed was washed with n-heptane.

- 35 Into a flask purged with nitrogen was introduced 50 ml of n-heptane purified similarly as described above, and the solid component synthesized above was introduced in an amount of 0.24 mol as calculated on Mg atom. Then,

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a mixture of 25 ml of n-heptane with 0.8 mol of SiCl_4 was introduced into the flask at 30°C over 30 minutes, and the reaction was carried out at 90°C for 4 hours. After completion of the reaction, the product was washed with
5 n-heptane.

Into a flask purged with nitrogen was introduced 50 ml of amply purified n-heptane, and then 5 g of the solid component obtained above, Sub-component (i), was introduced. Next, 2.4 ml of $(\text{CH}_3)_3\text{CSi}(\text{CH}_3)(\text{OCH}_3)_2$ as the
10 silicon compound of the Sub-component (ii), 2.0 ml of vinyltrimethylsilane as an optional component, and 3.0 g of triethylaluminum of the Sub-component (iii) were respectively introduced and contacted at 30°C for 2 hours.

15 The solid product obtained was thoroughly washed with n-heptane to provide the Component (A), which was found upon analysis on its portion to contain 2.50% by weight of titanium. The content of $(\text{CH}_3)_3\text{CSi}(\text{CH}_3)(\text{OCH}_3)_2$ was 17.6% by weight.

20 [Polymerization of propylene]

Into a stainless steel autoclave with a stirring and a temperature control means of 1.5 liter capacity were introduced 500 ml of amply dehydrated and deoxygenated n-paraffin, 3.0 mg of triethylaluminum as Component (B) and
25 100 mg of the above synthesized Component (A), the Al/Ti mole ratio being 0.5. Polymerization of propylene was conducted at a temperature of 170°C and under a pressure of 9 $\text{Kg/cm}^2\text{G}$ for 2 hours, after which the polymer solution obtained was subjected to treatment with
30 methanol to separate the polymer from the n-paraffin and the polymer obtained was dried.

A polymer in a yield of 37.4 g was obtained.

The polymer had a content of the fraction soluble in xylene at 20°C , which is hereinbelow referred to as CXS,
35 was 1.76% by weight.

The polymer had a molecular weight distribution such that the Q-value, which is a ratio of M_w/M_n where M_w

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stands for weight average molecular weight and M_N stands for number average molecular weight, upon the gel permeation chromatography was 7.1.

Example-2

5 [Preparation of Component (A)]

Into a flask purged with nitrogen was introduced 200 ml of dehydrated and deoxygenated n-heptane, and subsequently 0.4 mol of $MgCl_2$ and 0.8 mol of $Ti(O-nC_4H_9)_4$ and the reaction was carried at 95°C for 2 hours. After
10 completion of the reaction, the temperature was lowered to 40°C, followed by addition of 48 ml of methylhydrogenpolysiloxane (of 20 centistokes) and the reaction was carried out for 3 hours. The solid component formed was washed with n-heptane.

15 Into a flask purged with nitrogen was introduced 50 ml of n-heptane purified similarly as described above, and the solid component synthesized above was introduced in an amount of 0.24 mol as calculated on Mg atom. Then, a mixture of 25 ml of n-heptane with 0.4 mol of $SiCl_4$ was
20 introduced into the flask at 30°C over 30 minutes, and the reaction was carried out at 70°C for 3 hours. After completion of the reaction, the product was washed with n-heptane.

Then, 0.024 mole of phthaloyl chloride in 25 ml of
25 n-heptane was introduced into the flask at 90°C for 30 minutes and the reaction was conducted at 90°C for 1 hour. The product was then washed with n-heptane. 20 ml of $SiCl_4$ was then introduced and reacted at 80°C for 6 hours, after which the product was washed with n-heptane.
30 The solid product produced was found to contain 1.21% by weight of titanium.

Into a flask purged with nitrogen was introduced 50 ml of thoroughly purified n-heptane, and then 5 g of the solid component obtained above, Sub-component (i), was
35 introduced. Next, 1.2 ml of $(CH_3)_3CSi(CH_3)(OCH_3)_2$ as the silicon compound of the Sub-component (ii), 1.2 ml of divinyl dimethylsilane as an optional component and 1.7 g

of triethylaluminum of the Sub-component (iii) were respectively introduced and contacted at 30°C for 2 hours. After completion of the contact, the product was amply washed with n-heptane to provide a component (A),
5 which was found to contain 0.89% by weight of titanium. The content of $(\text{CH}_3)_3\text{CSi}(\text{CH}_3)(\text{OCH}_3)_2$ was 9.6% by weight.

[Polymerization of propylene]

Polymerization of propylene was conducted as in Example-1 except for the use of 2.1 mg of
10 triethylaluminum as Component (B). The polymer obtained was in an amount of 61.4 g and had the CXS of 1.01% by weight, the MFR of 45.3 g/10 min. and the Q-value upon GPC analysis of 7.0.

Examples 3 to 6

15 Polymerization of propylene was conducted in which Component (A) prepared in Example-2 was used and under the conditions which are set forth in Table-1.

The results obtained are set forth in Table-1.

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Table-1

Example No.	Polymeri- zation temp. (°C)	Component (B) and amount used		H ₂ introduced (vol %)	Polymer yield (g)	CXS (% by wt.)	Q-value (M _W /M _N)
			Al/Ti (mole)				
3	170	(iC ₄ H ₉) ₃ Al	1.0	0	55.2	1.20	7.7
4	160	(C ₂ H ₅) ₃ Al	0.3	10	99.8	0.98	6.5
5	150	(iC ₄ H ₉) ₃ Al	0.7	0	43.2	1.16	7.2
6	200	(C ₂ H ₅) ₃ Al	0.1	0	21.4	1.38	6.3

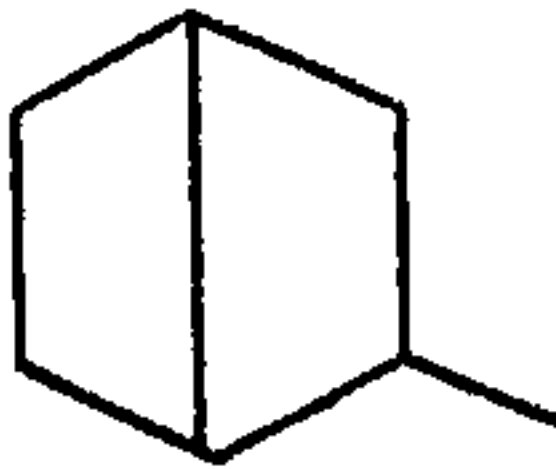
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Example 7

[Preparation of Component (A)]

Thirty (30) stainless steel balls of 12 mm diameter were loaded into a 0.47-liter ball mill, in which 20 g of anhydrous MgCl_2 and 2.2 ml of dibutyl phthalate were introduced for a 48-hour ball milling. Upon completion of this ball milling, 15 g of the milled composition was introduced into a flask which had been purged with nitrogen, and 50 ml of TiCl_4 was added to the flask wherein contact took place at 100°C for 2 hours. After completion of the contact, the contact product was thoroughly washed with n-heptane to give Sub-component (i).

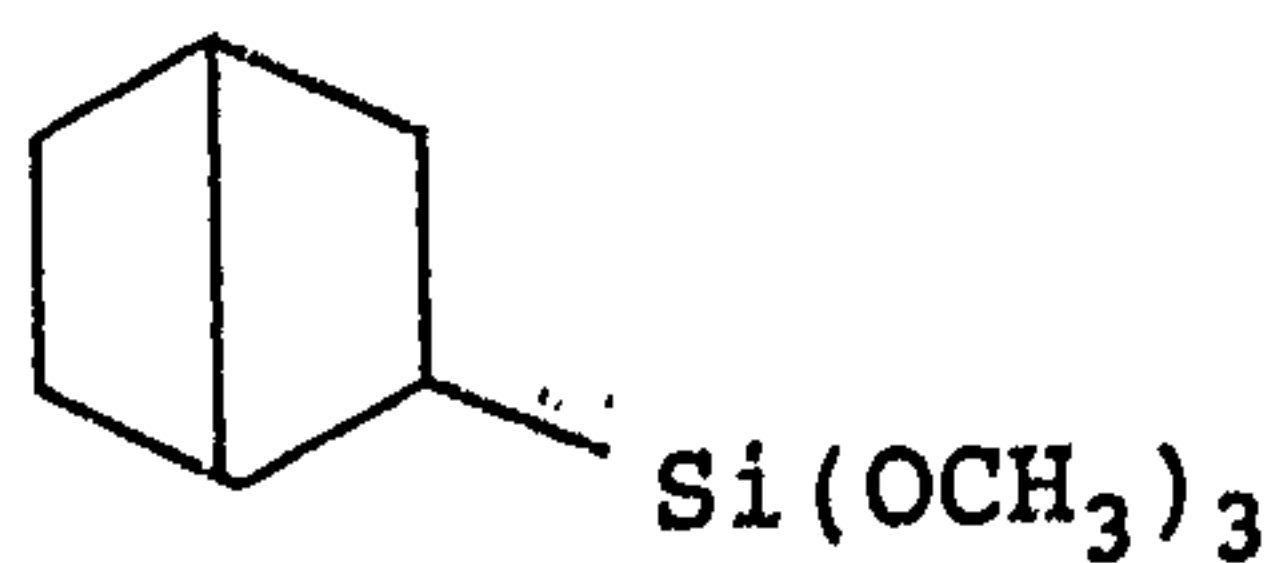
Next, 50 ml of thoroughly purified n-heptane were introduced into a flask which had been purged with nitrogen. Subsequently, 5 g of the Sub-component (i)

obtained as above, 2.4 ml of  as Sub-component

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(ii), 0.3 ml of TiCl_4 , 1.5 g of $\text{Al}(\text{C}_2\text{H}_5)_3$ and 0.5 g of $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}$ as Sub-component (iii) were introduced thereinto for a 2-hour contact at 20°C . After the completion of this contact, the product was thoroughly washed with n-heptane to obtain the component (A), which was formed to contain 2.8% by weight of titanium and 9.2% by weight of the silicon compound as Sub-component (ii), namely

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[Polymerization of propylene]

Polymerization of propylene was conducted as in Example-1 except for the use of 3.3 mg of $(C_2H_5)_3Al$ as the Component (B), Al/Ti mole ratio being 0.5.

The polymer obtained was in an amount of 41.7 g and had the CXS of 1.96% by weight and the Q-value of 7.7.

Example 8

[Preparation of Component (A)]

10 Into a flask purged with nitrogen of a 500 ml capacity was introduced 10 g of $Mg(OC_2H_5)_2$, 100 ml of n-heptane, and subsequently 30 ml of $TiCl_4$ and, after the temperature was raised to 70°C, 3.8 ml of di-n-octyl phthalate, and the temperature was then raised to 100°C
15 and the contact was continued for 3 hours. The product of the contact was thoroughly washed with n-heptane to give sub-component (i).

Into a flask purged with nitrogen were introduced 50 ml of thoroughly purified n-heptane, 5 g of the sub-
20 component (i), 1.8 ml of $(iC_3H_7)_2Si(OCH_3)_2$ as sub-component (ii), 0.5 ml of vinyltrichlorosilane as an optional component and 2.1 g of $Al(C_2H_5)_3$ as sub-component (iii), followed by contact with each other at 30°C for 2 hours. The contact product was then
25 thoroughly washed with n-heptane to give Component (A), which was found to contain 1.9% by weight of titanium and 10.6% by weight of the silicon compound as the sub-component (ii).

[Polymerization of propylene]

30 Polymerization of propylene was conducted as in Example-1 except for the use of 1.4 mg of $Al(C_2H_5)_3$, the mole ratio of Al/Ti being 0.3, and for the temperature of 180°C.

The polymer obtained was in an amount of 54.4 g and
35 had CXS of 1.58% by weight and Q of 7.7.

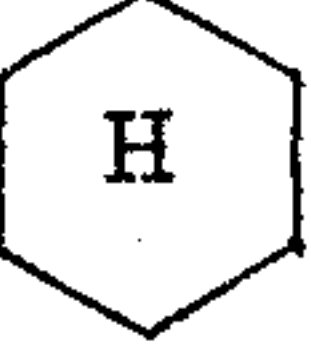
Example 9

[Preparation of Component (A)]

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Into a flask of 1 liter capacity purged with thoroughly purified nitrogen was introduced 15 g of filings of metallic magnesium followed by thorough drying. 315 ml of di-n-butylether and, then, 78 ml of n-butyl chloride were introduced and contacted with each other at 50°C for 3 hours to form a solution of n-butylmagnesium chloride in di-n-butyl ether, to which 69 ml of SiCl_4 was added drop-wise at 15°C for 2 hours, followed by contact with each other at 20°C for 2 hours. After the contact, the solid product formed was washed with n-heptane. 5 g of the solid product thus obtained was sampled, to which 2.6 ml of cellosolve acetate was added, followed by contact with each other at 80°C for 2 hours. After the contact, the solid product was thoroughly washed with n-heptane. To the solid product was added 50 ml of TiCl_4 , followed by contact with each other at 100°C for 4 hours. After the contact, the solid product was thoroughly washed with n-heptane to give sub-component (i).

Into a flask purged with nitrogen was introduced 50 ml of thoroughly purified n-heptane, and the sub-component (i) obtained above was introduced. Next, 0.25

ml of TiCl_4 , 2.5 ml of () $(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$ as the silicon compound of sub-component (ii) and 3 g of triethylzinc as sub-component (iii) were respectively introduced and contacted at 40°C for 3 hours. The solid product obtained was thoroughly washed with n-heptane to provide the Component (A), which was found to contain 2.7% by weight of titanium and 8.3% by weight of the silicon compound as sub-component (ii).

[Polymerization of propylene]

Polymerization of propylene was conducted as in Example 1 except for the use of 0.48 mg of $\text{Al}(\text{C}_2\text{H}_5)_3$, the mole ratio of Al/Ti being 0.075 and for the temperature of 220°C.

The polymer was obtained in an amount of 11.4 g and had CXS of 1.62% by weight and Q of 7.1.

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Comparative Example 1

Polymerization of propylene was conducted as in Example 1 except for the use of 3,000 mg of $\text{Al}(\text{C}_2\text{H}_5)_3$ of Component (B), the mole ratio of Al/Ti being 50. The
5 polymer was obtained in an amount of only 1.2 g.

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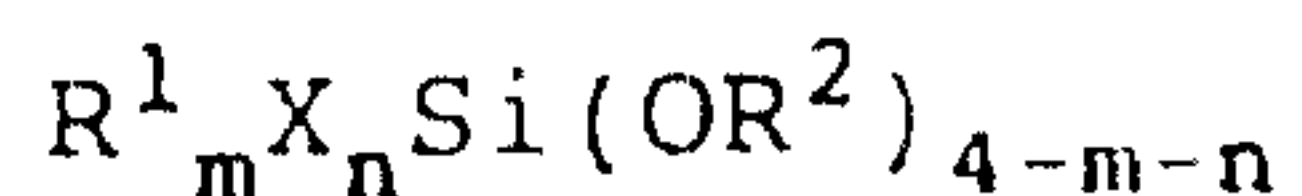
What is claimed is:

1. A process for producing α -olefin polymers which comprises contacting at a temperature of 150°C to 300°C an α -olefin with a catalyst thereby to polymerize the olefin, the catalyst comprising:

Component (A) which is a solid catalyst component for Ziegler catalysts, which solid catalyst component is obtained by contacting the following Sub-components (i) to (iii):

Sub-component (i) which is a solid catalyst component for Ziegler-type catalysts comprising titanium, magnesium and a halogen as the essential components;

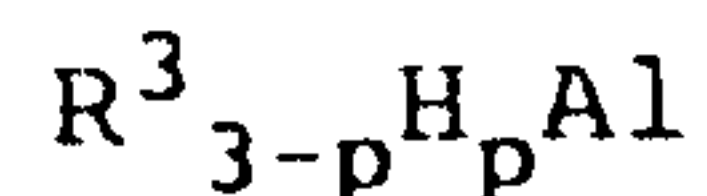
Sub-component (ii) which is a silicon compound represented by a formula



wherein R^1 indicates a hydrocarbyl group of 1 to 20 carbon atoms, R^2 which may be the same as or different from R^1 indicates a hydrocarbyl group of 1 to 20 carbon atoms, X indicates a halogen atom, and m and n are each numbers satisfying equations $0 \leq m \leq 3$, $0 \leq n \leq 3$ and $0 \leq (m+n) \leq 3$; and

Sub-component (iii) which is an organometal compound of a metal of the Groups I to III of the Periodic Table; and

Component (B) which is an organoaluminum compound represented by a formula



wherein R^3 indicates a hydrocarbyl group of up to 5 carbon atoms and p is a number satisfying an equation $0 \leq p \leq 1$;

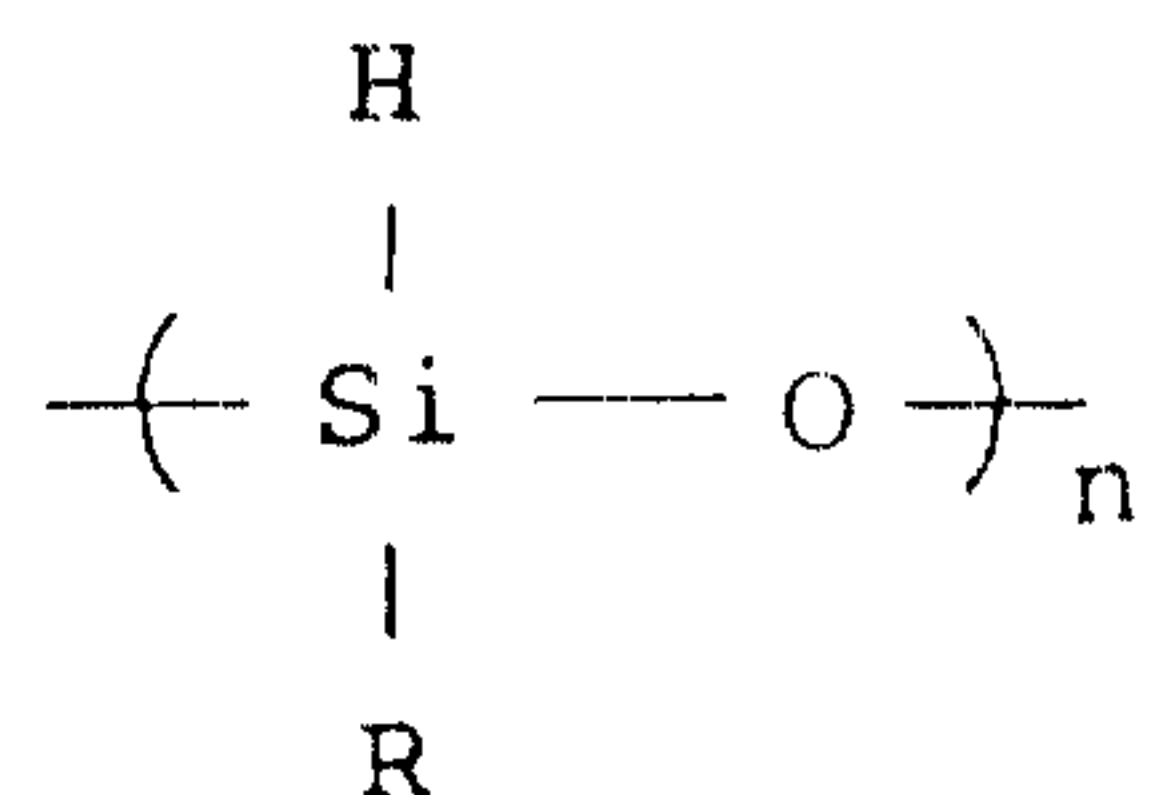
wherein the mole ratio of the Al in Component (B) to the Ti in Component (A) is equal to or less than 1.

2. The process as claimed in claim 1, wherein the polymerization temperature is within the range of 150 to 250°C.

3. The process as claimed in claim 1, wherein the α -olefin has a formula: $R-CH=CH_2$ wherein R is a linear or branched hydrocarbyl group of 1 to 6 carbon atoms.

4. The process as claimed in claim 1, wherein the Sub-component (i) is a product prepared by a method selected from the group of:

(i) a method in which a solid component obtained by contacting a magnesium halide with a titanium tetraalkoxide and a polymeric silicon compound is contacted with a titanium halide compound and/or a silicon halide compound, the polymeric silicon compound represented by the formula



wherein R is a hydrocarbyl group having about 1 to 10 carbon atoms, n is a polymerization degree such that the viscosity of the polymeric silicon compound may be 1 to 100 centistokes;

(ii) a method in which a magnesium compound is dissolved in a titanium tetraalkoxide and an electron donor, and the solid component precipitated from the solution upon addition thereto of a halogenating agent or a titanium halide compound is contacted with a titanium compound; and

(iii) a method in which an alkoxymagnesium compound is contacted with a halogenating agent and/or a titanium compound in the presence or absence of an electron donor.

5. The process as claimed in claim 4, wherein the halogenating agent is selected from the group of silicon halides, aluminum halides and halogen compounds of phosphorus.

6. The process as claimed in claim 1, wherein the silicon compound of the Sub-component (ii) is such that the R^1 is a branched chain hydrocarbyl group of 3 to 20 carbon atoms whose α -carbon is secondary or tertiary.

7. The process as claimed in claim 1, wherein the Sub-component (iii) is an organoaluminum compound.

8. The process as claimed in claim 1, wherein the proportions of the Sub-components (i), (ii) and (iii) are:

the Si/Ti atomic ratio of Sub-component (ii)/Sub-component (i) being 0.01 to 1000;

the metal of Group I-III/Ti atomic ratio of Sub-component (iii)/Sub-component (i) being 0.01 to 100.

9. The process as claimed in claim 1, wherein the Component (B) has the substituent R^3 which has up to 4 carbon atoms.

10. The process as claimed in claim 1, wherein the Component (B) is such that the p in the formula is zero.

11. The process as claimed in claim 1, wherein the mole ratio of the Al in Component (B) to the Ti in Component (A) is lower than 1.

12. The process as claimed in claim 1, wherein the mole ratio of the Al in Component (B) to the Ti in Component (A) is 0.01 to 0.5.