

PATENT SPECIFICATION

(11) 1 505 315

1 505 315

- (21) Application No. 5803/76 (22) Filed 13 Feb. 1976
 (31) Convention Application No. 50/017 934
 (32) Filed 14 Feb. 1975 in
 (33) Japan (JP)
 (44) Complete Specification published 30 March 1978
 (51) INT CL² C08F 10/04, 4/02, 4/66
 (52) Index at acceptance
 C3P 404 440 442 446 450 452 464 474 486 498 504 512
 526 534 538 542 546 574 578 GV



(54) OLEFIN POLYMERISATION PROCESS AND CATALYST FOR USE THEREIN

(71) We, MITSUI PETROCHEMICAL INDUSTRIES, LTD., a Japanese Body Corporate, of 2-5, 3-chome, Kasumigaseki, Chiyoda-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 performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing highly stereoregular polymers in high yields by homopolymerizing or copolymerizing an α -olefin containing at least 3 carbon atoms or copolymerizing an α -olefin containing at least 3 carbon atoms with not more than 10 mole % of ethylene and/or diolefins in the presence of a catalyst composed of a specific solid transition metal catalyst component and an organometallic compound of a metal of Groups I to III of the Periodic Table.

Some suggestions have already been made to homopolymerize or copolymerize α -olefins in the presence of a catalyst composed of (a) a transition metal catalyst component derived from a solid carrier, an electron donor and a titanium compound and (b) an organometallic compound of a metal of Groups I to III of the Periodic Table. The present invention is an improved invention of selective nature over the inventions previously suggested by one or more of the inventors of the present invention with or without co-workers.

One of the suggestions relates to the homopolymerization or copolymerization of olefins in the presence of a catalyst composed of (a) a transition metal catalyst component prepared by reacting a titanium or vanadium compound, a solid carrier of an adduct formed between a magnesium dihalide and an electron donor and a compound of Si or Sn selected from the group consisting of halogen compounds of Si, halogen compounds of Sn, organohalogen compounds of Si and organohalogen compounds of Sn, and (b) an organometallic compound catalyst component of a metal of Groups I to III of the Periodic Table (West German OLS 2,355,886 and U.K. Specifica-

tion No. 1452314). This suggestion exemplifies aliphatic alcohols, aliphatic carboxylic acids, aliphatic carboxylic acid esters, aromatic carboxylic acid esters, aliphatic ketones and aromatic ketones as the electron donor, but fails to disclose anything about the conjoint use of the carboxylic acid esters and active hydrogen-containing compounds such as the aforesaid alcohols and carboxylic acids. None of the working examples given in this suggestion show such a conjoint use.

A method for obtaining excellent stereoregular homopolymers or copolymers has also been known which comprises homopolymerizing or copolymerizing α -olefins containing at least 3 carbon atoms in the presence of a catalyst composed of (A) a titanium-containing solid catalyst component consisting of an organic complex derived from a magnesium halide, a specific silicon component, an organic carboxylic acid ester and a titanium compound, and (B) an organo-aluminum catalyst component (West German OLS 2,504,036 and U.K. Specification No. 1492618). This is also silent on the conjoint use of the carboxylic acid ester and the active hydrogen-containing compound such as the alcohols or carboxylic acids, and gives no specific working examples covering such conjoint use.

West German OLS 2,153,520, corresponding to French Laid-Open Patent Publication No. 2,113,313 and U.K. Specification No. 1335887, discloses a process for selectively preparing either an atactic polymer as a main product or a stereoregular polymer as a main product. This Patent Publication states that when a Ti catalyst component obtained by contacting a titanium compound with a mixture of an active-type magnesium halide and an anhydrous compound of an element of Groups I to IV, for example, Si or Sn, is used in the above process preferably in the form supported on a carrier and subsequently modified with an electron donor, a stereoregular polymer is obtained as a main product. This Publication, however, illustrates only SiO₂ and SnCl₂ as the anhydrous compound of Si or Sn. Furthermore, this Publication

50

55

60

65

70

75

80

85

90

95

discloses that ethers, thioethers, amines, phosphines, ketones and esters can be utilized as the electron donors, but does not exemplify any specific compounds that fall within the esters. The isotacticity of the polymer shown by the boiling n-heptane extraction residue in all of the Examples of the above Patent Publication is at most about 70%, and therefore, the process of this patent is far from satisfactory for preparing highly stereoregular polymers. On the other hand, the electron donor used in this patent for production of isotactic polymers is only N,N',N'',N'''-tetramethylethylenediamine. Moreover, only anhydrous lithium chloride and SiO₂ are actually disclosed in this publication as the anhydrous compound of an element of Groups I to IV.

We have made investigations with a view to providing an improved catalyst which can afford polymers of α -olefins with at least 3 carbon atoms having more improved stereoregularity in high yields, and can be prepared without the need for the time-consuming mixing-pulverizing means employed in the second suggestion cited above for preparing the titanium-containing solid catalyst component.

These investigations led to the present invention which provides a catalyst for use in homopolymerising or copolymerising α -olefins containing at least 3 carbon atoms or copolymerising said α -olefins with not more than 10 mole % of ethylene and/or diolefins, said catalyst consisting essentially of:

(a) a solid transition metal catalyst component prepared by reacting (1) a magnesium-containing reaction product obtained by contacting and reacting in any order (i) a magnesium halide, (ii) an organic active hydrogen-containing compound, (iii) an organic acid ester and (iv) a silicon or tin compound containing at least one halogen atom or hydrocarbon group bonded directly to silicon or tin, with (2) a titanium compound, and

(b) an organometallic compound of a metal of Groups I to III of the Periodic Table.

The invention also provides a process for preparing an α -olefin polymer which process comprises homopolymerising or copolymerising at least one α -olefin having at least 3 carbon atoms, or copolymerising such an α -olefin with not more than 10 mole % of ethylene and/or diolefins in the presence of a catalyst of the invention.

Examples of the α -olefins are propylene, 1-butene, 4-methyl-1-pentene and 3-methyl-1-butene, and examples of the diolefins include conjugated diolefins such as butadiene and non-conjugated dienes such as dicyclopentadiene, ethyldenenorbornene and 1,5-hexadiene.

The catalyst of this invention is composed of the following titanium-containing solid catalyst component (a) and organometallic

compound catalyst component (b).

Component (a) is prepared by reacting (1) a magnesium-containing reaction product obtained by contacting and reacting in any order (i) a magnesium halide, (ii) an organic active hydrogen-containing compound, (iii) an organic carboxylic acid ester, and (iv) a compound of Si or Sn containing at least one halogen atom or hydrocarbon group directly bonded to silicon or tin, with (2) a titanium compound.

Desirably, the magnesium halide (i) is a dihalide such as magnesium bromide, magnesium iodide or preferably magnesium chloride and preferably such a dihalide is as anhydrous as possible, but the inclusion of moisture is permissible to an extent such that the moisture does not substantially affect the performance of the catalyst. The dihalide may be one obtained by dehydrating a commercially available grade at 100 to 400°C. under reduced pressure prior to use.

The magnesium halide may also be a halogenated magnesium compound obtained by halogenating magnesium compounds such as Grignard reagents, magnesium salts of organic acids, or magnesium alcoholates. There can also be used products which are obtained by dissolving the magnesium halides described above in a polar solvent such as acetone or ether either alone or together with, for example,



(in which R is a hydrocarbon group, and n is a number greater than zero but not more than 3), or GeCl₄ which is soluble in the above solvent, and then evaporating off the solvent.

For convenience of use, the magnesium halide is preferably in the form of a powder having an average particle diameter of 1 to 50 microns. But when it is to be pulverized by a mechanical contacting treatment during catalyst preparation, powders of large particle size can also be used. The average particle diameter of 1 to 50 microns means that at least 80% by weight of the entire particles have a particle diameter of 1 to 50 microns.

Examples of the organic active hydrogen-containing compounds (ii) are aliphatic alcohols, preferably C₁₋₈, more preferably C₁₋₄, aliphatic alcohols such as methanol, ethanol, propanol or butanol; araliphatic alcohols or phenols, preferably benzyl alcohol, phenetyl alcohol, cumyl alcohol, triphenyl carbinol, o-cresol, m-cresol, 2,6-dimethylphenol or β -naphthol; primary amines such as ethylamine, n-butylamine, sec-butylamine or aniline; secondary amines such as diethylamine, di-n-butylamine, or diphenylamine; and thiols such as ethyl mercaptan or thiophenol; aliphatic carboxylic acids such as acetic acid, propionic acid, valeric acid or acrylic acid; acid amides or acid imides of said aliphatic carboxylic acids such as formamide, acetamide or pro-

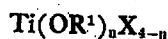
pionamide. Of these active hydrogen-containing compounds, preferred are the above-mentioned C_1-C_8 aliphatic alcohols, and most preferred are C_1-C_4 aliphatic alcohols.

Examples of the organic carboxylic acid esters (iii) include esters formed between C_1-C_8 , preferably C_1-C_4 , saturated or unsaturated aliphatic carboxylic acids which may optionally be substituted by a halogen atom and alcohols selected from C_1-C_8 , preferably C_1-C_4 , saturated or unsaturated aliphatic primary alcohols optionally substituted by halogen atoms, C_6-C_8 , preferably C_6-C_8 , saturated or unsaturated alicyclic alcohols and C_1-C_4 saturated or unsaturated aliphatic primary alcohols substituted by C_6-C_{10} , preferably C_6-C_8 , aromatic groups; esters formed between C_7-C_{12} , preferably C_7-C_{10} , aromatic monocarboxylic acids and alcohols selected from C_1-C_8 , preferably C_1-C_4 , saturated or unsaturated aliphatic primary alcohols optionally substituted by halogen atoms, C_6-C_8 , preferably C_6-C_8 , saturated or unsaturated alicyclic alcohols and C_1-C_4 saturated or unsaturated aliphatic primary alcohols substituted by C_6-C_{10} , preferably C_6-C_8 , aromatic groups; and alicyclic carboxylic acid esters, such as methyl cyclopentanecarboxylate, methyl hexahydrobenzoate, ethyl hexahydrobenzoate, methyl hexahydrotoluate and ethyl hexahydrotoluate.

Specific examples of the organic carboxylic acid esters (iii) include methyl acetate, ethyl acetate, ethyl propionate, methyl chloroacetate, methyl cyclohexanecarboxylate, methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, methyl toluate, ethyl toluate, butyl toluate, ethyl p-ethyl benzoate, methyl anisate, ethyl anisate, and ethyl chlorobenzoate. Of these, C_1-C_4 alkyl esters of benzoic acid or nuclearly substituted benzoic acid are preferred. The use of methyl benzoate, ethyl benzoate, methyl toluate or ethyl toluate is most preferred.

The Si or Sn compound (iv) containing at least one halogen atom or hydrocarbon group directly bonded to silicon or tin may also contain a hydrogen atom or an alkoxy group. Specific examples of the Si or Sn compound are silicon tetrahalides, tetraalkyl silicons, silicon alkylhalides, silicon alkyl hydrides, tin tetrahalides, tin dihalides, tin alkyl halides, and tin hydride halides. Of these, the silicon tetrahalides and tin tetrahalides, such as silicon tetrachloride or tin tetrachloride, are preferred. In the compound (iv), the alkyl group is preferably one containing 1 to 4 carbon atoms, and the halogen atom is preferably chlorine.

The titanium compound (2) to be reacted with the magnesium-containing reaction product (1) preferably is a compound of the formula



wherein X is a halogen atom such as chlorine or bromine, R^1 is an alkyl group such as a C_1-C_4 alkyl group, and n is 0 or an integer from 1 to 4.

Specific examples of such titanium compounds (2) are titanium tetrahalides such as titanium tetrachloride, titanium tetrabromide or titanium tetraiodide, alkoxy titanium trihalides such as methoxy titanium trichloride, ethoxy titanium trichloride, n-butoxy titanium tribromide; dialkoxy titanium dihalides such as dimethoxy titanium dichloride, diethoxy titanium dichloride, di-n-butoxy titanium dichloride or diethoxy titanium dibromide; trialkoxy titanium monohalides such as trimethoxy titanium chloride, triethoxy titanium chloride, tri-n-butoxy titanium chloride and triethoxy titanium bromide; and tetraalkoxy titaniums such as tetramethoxy titanium, tetraethoxy titanium and tetra-n-butoxy titanium. Of these, the titanium tetrahalides, especially titanium tetrachloride, are preferred.

The molar ratio of the compounds (i)/(ii)/(iii)/(iv)/(2) used for the preparation of the catalyst component (a) is preferably $1/(20-0.1)/(20-0.005)/(at\ at\ least\ 0.01)/(3-0.1)/(20-0.2)/(100-0.1)$.

The preferred order of addition of these catalyst ingredients and the method of contacting will be described below.

There are many modes in the sequence of addition and the method of addition, for example, addition of one time, portionwise addition, or addition of the ingredients in the form of an adduct, and only some of them will be described below.

(1) The magnesium halide (i) is pre-treated with the organic active hydrogen-containing compound (ii) and the organic acid ester (iii). Then, the treated product is reacted with the silicon or tin compound (iv). The reaction product is preferably washed with an inert solvent, and then treated by being suspended in the titanium compound (2) or a solution thereof in an inert solvent.

(2) The magnesium halide (i) is pre-treated with the organic active hydrogen-containing compound (ii). The pre-treated product is reacted with the silicon or tin compound (iv), and the resulting reaction product is treated with the organic acid ester (iii). The ester-treated product is preferably washed with an inert solvent, and then treated by being suspended in the titanium compound (2) or a solution thereof in an inert solvent.

In the above pre-treating operation, the magnesium halide can be pre-treated with a compound selected from organic active hydrogen-containing compounds, organic acid esters and silicon or tin compounds by various methods capable of permitting the contacting of these compounds. The most preferred method, however, is one comprising suspend-

(9)

ing the magnesium halide in an inert hydrocarbon such as hexane, heptane, benzene, toluene or kerosene, adding the organic active hydrogen-containing compound and the silicon or tin compound to the suspension, stirring the mixture, and contacting the mixture with the organic acid ester. Usually, treatment at room temperature suffices, but it is generally preferred to perform the treatment at elevated temperatures. The upper limit of the treating temperature is usually below the lowest point of the boiling points at atmospheric pressure or decomposition points of the suspension, and the active hydrogen-containing compounds, the organic esters, and the silicon or tin compounds used for catalyst preparation. The upper limit can, in some cases, be set at a higher level by employing elevated pressures.

Usually, temperatures of about 0°C. to about 100°C. are used for the above treatment.

The magnesium halide so pre-treated is preferably suspended in an inert solvent such as hydrocarbons, and the silicon or tin compound or a solution thereof in an inert solvent is added to the suspension. Generally, the reaction proceeds sufficiently at room temperature, and heating is not required. It is generally advantageous however to carry out the reaction at elevated temperatures, since it promotes the reaction. The reaction product contains unreacted materials, and therefore, is preferably washed with an inert solvent prior to contact with the titanium compound.

The reaction of the magnesium halide so treated with the titanium compound (the supporting reaction) can be carried out by contacting the treated magnesium halide with the titanium compound preferably in the presence of an inert solvent, for example at room temperature to 200°C. for 10 minutes to 5 hours. Then, the unreacted titanium compound is removed by filtration or decantation, and then washed with a suitable inert solvent such as hexane, heptane or kerosene to remove the unsupported titanium compound as much as possible.

The organometallic compound catalyst component (b) may, for example, be selected from trialkyl aluminums, alkyl aluminum halides, alkyl aluminum alkoxides, alkyl aluminum aryloxides, alkyl aluminum hydrides, dialkyl zincs, dialkyl magnesiums, and alkyl magnesium halides, in which the alkyl is preferably of 1 to 12 carbon atoms, and the halogen is preferably chlorine, bromine or iodine. Specific examples include triethyl aluminum, diethyl aluminum hydride, tripropyl aluminum, tributyl aluminum, diethyl aluminum chloride, diethyl aluminum bromide, diethyl aluminum ethoxide, diethyl aluminum ethoxychloride, and ethyl aluminum sesquichloride. Of these, the trialkyl aluminums such as triethyl aluminum or tributyl alu-

minum, the dialkyl aluminum hydrides such as diisobutyl aluminum hydride, and the dialkyl aluminum halides such as diethyl aluminum chloride are preferred.

The polymerization process of the present invention can be carried out in the presence or absence of a liquid inert organic solvent. For example, the homopolymerization or copolymerization in accordance with the process of this invention can be carried out in the liquid phase in the presence of a liquid olefin, or it can be carried out in the vapor phase for example in a fluidized catalyst bed. Preferably, the polymerization of olefins in accordance with this invention is carried out in an inert organic liquid medium, e.g. an inert organic solvent. The amount of the transition metal catalyst component (a) is preferably 0.0001 to 1.0, more preferably 0.001 to 0.5, milligram-atoms of titanium per liter of the inert organic liquid medium. The amount of the organometallic compound catalyst component (b) is preferably such that the ratio of the metal atom of Groups I to III to Ti metal atom is 1/1 to 2000/1, more preferably 1/1 to 300/1.

The olefin polymerization reaction using the catalyst of this invention can be performed in the same way as in the case of olefin polymerization using conventional Ziegler-type catalysts. The reaction is carried out in the substantial absence of oxygen and water. A suitable inert organic liquid medium, for example, an aliphatic hydrocarbon such as hexane, heptane or kerosene, is used, and an olefin and the catalyst, and if desired, another olefin and/or diolefin are fed into the medium, and then the polymerization is carried out.

The polymerization temperature may usually be 20 to 200°C., preferably 50 to 180°C. Generally, the reaction is carried out at a pressure of 1 to 50 Kg/cm², preferably 2 to 20 Kg/cm². Preferably, the reaction is performed at an elevated pressure. The control of the molecular weight distribution by the conjoint use of the catalyst composition of this invention and hydrogen is effective both for a batchwise process and for a continuous process in the preparation of homopolymers or copolymers in accordance with this invention.

The following Examples and Comparative Examples illustrate the present invention.

Example 1.

Preparation of catalyst component (a). Commercially available anhydrous magnesium chloride (0.1 mole) was suspended in 0.3 liter of kerosene, and 0.6 mole of ethanol and 0.1 mole of ethyl benzoate were added to the suspension at room temperature. The mixture was stirred for 1 hour, and 0.6 mole of silicon tetrachloride was added dropwise at room temperature, followed by stirring the mixture for 1 hour. The solid portion of the

(11)

resulting product was collected, and washed thoroughly with kerosene. The solid product was suspended in 0.3 liter of a kerosene solution containing 30 ml of titanium tetrachloride, and the reaction was carried out at 80°C. for 2 hours. After the reaction, the supernatant liquid was removed by decantation, and the solid portion was washed with fresh kerosene. The resulting solid contained 38.5 mg of titanium and 595 mg of chlorine on the atomic basis per gram thereof.

Polymerization.

An autoclave with an available volume of 2 liters was charged with 0.75 liter of kerosene, 0.375 millimole of triethyl aluminum and 0.0375 millimoles calculated as titanium atom, of the catalyst component (a) prepared by the method set forth in the previous section. The mixture was heated to 70°C. Propylene was polymerized for 3 hours while feeding it into the autoclave so that the total pressure was maintained at 7 Kg/cm². The solid com-

ponent of the resulting product was collected by filtration, washed with hexane, and then dried to afford a 365 g of polypropylene as a white powder. The polymer has a boiling n-heptane extraction residue of 95.3% and an apparent density of 0.31 g/ml. On the other hand, concentration of the liquid portion gave 12.7 g of a solvent-soluble polymer.

The catalyst used had an average specific polymerization activity of 480 PP-g/Ti-mH. hr.atm.

Examples 2 to 11.

A catalyst component (a) was prepared in the same way as in Example 1 except that the combination of the alcohol, ester and silicon or tin compound was changed. Propylene was polymerized in the same way as in Example 1 using 0.05 millimole/liter, calculated as titanium atom, of the catalyst component (a) and each of the various organo-aluminium compounds shown in Table 1. The results are shown in Table 1.

25

30

35

40

TABLE 1

Catalyst component (a)										Results of polymerization					
Materials										Properties					
Alcohol of Phenyl			Ester		Si or Sn compound			Amount supported		Yield (g)			Extraction residue of powder (%)	Apparent density (g/ml)	Average specific polymerization activity (PP-g/Ti, mM.hr.atm)
Name	mole		Name	mole	Name	mole	Ti (mg/g)	Cl (mg/g)	Powdery polymer	Soluble polymer					
Ex-ample															
2	Ethanol	0.6	Ethyl benzoate	0.1	SiCl ₄ H	0.6	39.5	585	343	12.7	94.9	0.30	452		
3	Iso-propanol	0.6	Methyl benzoate	0.1	SiCl ₄	0.6	41.5	575	356	14.5	94.3	0.30	470		
4	Octanol	0.6	Ethyl O-toluate	0.1	SiCl ₄	0.6	40.6	580	335	14.4	94.4	0.30	444		
5	Ethanol	0.6	Ethyl benzoate	0.2	SnCl ₄	0.5	40.5	570	315	10.0	94.4	0.29	413		
6	Ethanol	0.5	Ethyl benzoate	0.2	Sn(C ₂ H ₅) ₄	0.5	36.4	596	306	14.5	94.9	0.29	407		
7	Ethanol	0.6	Ethyl o-toluate	0.04	SiCl ₄ (O ₂ H ₅)	0.4	40.0	585	308.5	14.4	94.0	0.30	410		
8	Ethanol	0.6	„	0.04	SiCl ₄ (O-o-tolyl)	0.4	46.0	570	320.5	16.1	94.2	0.29	428		
9	Cumyl alcohol*	0.3	„	0.04	SiCl ₄	0.4	46.3	574	351.5	13.1	94.7	0.29	463		
10	o-Cresol*	0.3	„	0.04	SiCl ₄	0.4	45.8	570	349	16.1	94.7	0.29	464		
11	2,6-Dimethyl-phenol*	0.3	„	0.04	SiCl ₄	0.4	45.7	575	307	12.1	94.9	0.29	405		

* The reaction between magnesium chloride and the alcohol was carried out at 100°C.

Example 12.

Preparation of catalyst component (a).

Commercially available anhydrous magnesium chloride (0.1 mole) was suspended in 0.3 liter of kerosene, and at room temperature, 0.4 mole of ethanol was added to the suspension. Then, 0.4 mole of silicon tetrachloride was added dropwise at room temperature, and the mixture was stirred for 1 hour. Then, 0.15 mole of ethyl benzoate was added, and the temperature was raised to 70°C. The mixture was stirred for 1 hour. The supernatant liquid was washed thoroughly with fresh kerosene. Then, 30 ml of titanium tetrachloride was added, and the mixture was heated to 100°C. and stirred for 2 hours. After the reaction, the mixture was decanted and the supernatant was washed thoroughly with fresh kerosene. The solid obtained by the reaction contained 36.5 mg of titanium and 600 mg of chlorine calculated at atoms per gram thereof.

Polymerization.

Propylene was polymerized under the same conditions as in Example 1 except that 0.0375 millimole of the catalyst component (a) was used and 0.375 millimole of triisobutyl aluminum was used instead of 0.375 millimole of triethyl aluminum. As a result, 309 g of a white powdery polymer and 11.2 g of a solvent-soluble polymer were obtained. The powdery polymer had a boiling n-heptane extraction residue of 94.6%, and an apparent density of 0.31 g/ml. The average specific polymerization activity was 407 PP-g/Ti.mM.hr.atm.

Comparative Example 1.

When propylene was polymerized using a catalyst prepared in the same way as in Example 1 except that ethyl benzoate was not used, 138 g of a white powdery polymer and 76 g of a solvent-soluble polymer were obtained. The powdery polymer had a boiling n-heptane extraction residue of only 71.3% and an apparent density of less than 0.1 g/ml. The average specific polymerization activity was 272 PP-g/Ti.mM.hr.atm.

Comparative Example 2.

Propylene was polymerized in the same way as in Example 1 using a catalyst prepared in the same way as in Example 1 except that ethyl benzoate was used instead of the ethanol, and the reaction of it with the anhydrous magnesium chloride was carried out at 180°C. As a result, 73.8 g of a powder polymer and 16.8 g of a solvent-soluble polymer were obtained. The powdery polymer had a boiling n-heptane extraction residue of only 85.1% and an apparent density of 0.15 g/ml. The average specific polymerization activity was 58 PP-g/Ti.mM.hr.atm.

WHAT WE CLAIM IS:—

1. A catalyst for use in homopolymerising or copolymerizing α -olefins containing at least 3 carbon atoms or copolymerising said α -olefins with not more than 10 mole % of ethylene and/or diolefins, said catalyst consisting essentially of:

(a) a solid transition metal catalyst component prepared by reacting (1) a magnesium-containing reaction product obtained by contacting and reacting in any order (i) a magnesium halide, (ii) an organic active hydrogen-containing compound, (iii) an organic acid ester and (iv) a silicon or tin compound containing at least one halogen atom or hydrocarbon group bonded directly to silicon or tin, with (2) a titanium compound, and

(b) an organometallic compound of a metal of Groups I to III of the Periodic Table.

2. A catalyst according to claim 1 wherein the active hydrogen-containing compound (ii) is an aliphatic alcohol, araliphatic alcohol, phenol, primary amine, secondary amine, aliphatic carboxylic acid, acid amide of such acid or acid imide of such acid.

3. A catalyst according to claim 1 or 2 wherein the organic acid ester (iii) is an ester formed between a C_1-C_8 saturated or unsaturated aliphatic carboxylic acid which is unsubstituted or is substituted by a halogen atom and an alcohol selected from C_1-C_8 saturated or unsaturated aliphatic primary alcohols optionally substituted by halogen atoms, C_3-C_8 saturated or unsaturated alicyclic alcohols and C_1-C_4 saturated or unsaturated aliphatic primary alcohols substituted by C_6-C_{10} aromatic groups; an ester formed between a C_1-C_{12} aromatic monocarboxylic acid and an alcohol selected from C_1-C_8 saturated or unsaturated aliphatic primary alcohols optionally substituted by halogen atoms, C_3-C_8 saturated or unsaturated alicyclic alcohols and C_1-C_4 saturated or unsaturated aliphatic primary alcohols substituted by C_6-C_{10} aromatic groups; or an alicyclic carboxylic acid ester from methyl cyclopentanecarboxylate methyl hexahydrobenzoate, ethyl hexahydrobenzoate, methyl hexahydrotoluate and ethyl hexahydrotoluate.

4. A catalyst according to claim 1, 2 or 3 wherein said silicon or tin compound (iv) is a silicon tetrahalide, tin tetrahalide, tetraalkyl silicon, silicon alkyl halide, silicon alkyl hydride, tin alkyl-halide or tin hydride halide.

5. A catalyst according to any one of the preceding claims wherein titanium compound (2) is a compound of the formula



wherein X is a halogen atom, R^1 is an alkyl



* C L M S *

1,505,315

7

Example 12.

Preparation of catalyst component (a).

Commercially available anhydrous magnesium chloride (0.1 mole) was suspended in 0.3 liter of kerosene, and at room temperature, 0.4 mole of ethanol was added to the suspension. Then, 0.4 mole of silicon tetrachloride was added dropwise at room temperature, and the mixture was stirred for 1 hour. Then, 0.15 mole of ethyl benzoate was added, and the temperature was raised to 70°C. The mixture was stirred for 1 hour. The supernatant liquid was washed thoroughly with fresh kerosene. Then, 30 ml of titanium tetrachloride was added, and the mixture was heated to 100°C. and stirred for 2 hours. After the reaction, the mixture was decanted and the supernatant was washed thoroughly with fresh kerosene. The solid obtained by the reaction contained 36.5 mg of titanium and 600 mg of chlorine calculated at atoms per gram thereof.

Polymerization.

Propylene was polymerized under the same conditions as in Example 1 except that 0.0375 millimole of the catalyst component (a) was used and 0.375 millimole of triisobutyl aluminum was used instead of 0.375 millimole of triethyl aluminum. As a result, 309 g of a white powdery polymer and 11.2 g of a solvent-soluble polymer were obtained. The powdery polymer had a boiling n-heptane extraction residue of 94.6%, and an apparent density of 0.31 g/ml. The average specific polymerization activity was 407 PP-g/Ti.mM.hr.atm.

Comparative Example 1.

When propylene was polymerized using a catalyst prepared in the same way as in Example 1 except that ethyl benzoate was not used, 138 g of a white powdery polymer and 76 g of a solvent-soluble polymer were obtained. The powdery polymer had a boiling n-heptane extraction residue of only 71.3% and an apparent density of less than 0.1 g/ml. The average specific polymerization activity was 272 PP-g/Ti.mM.hr.atm.

Comparative Example 2.

Propylene was polymerized in the same way as in Example 1 using a catalyst prepared in the same way as in Example 1 except that ethyl benzoate was used instead of the ethanol, and the reaction of it with the anhydrous magnesium chloride was carried out at 180°C. As a result, 73.8 g of a powder polymer and 16.8 g of a solvent-soluble polymer were obtained. The powdery polymer had a boiling n-heptane extraction residue of only 85.1% and an apparent density of 0.15 g/ml. The average specific polymerization activity was 58 PP-g/Ti.mM.hr.atm.

WHAT WE CLAIM IS:—

1. A catalyst for use in homopolymerising or copolymerizing α -olefins containing at least 3 carbon atoms or copolymerising said α -olefins with not more than 10 mole % of ethylene and/or diolefins, said catalyst consisting essentially of:

(a) a solid transition metal catalyst component prepared by reacting (1) a magnesium-containing reaction product obtained by contacting and reacting in any order (i) a magnesium halide, (ii) an organic active hydrogen-containing compound, (iii) an organic acid ester and (iv) a silicon or tin compound containing at least one halogen atom or hydrocarbon group bonded directly to silicon or tin, with (2) a titanium compound, and

(b) an organometallic compound of a metal of Groups I to III of the Periodic Table.

2. A catalyst according to claim 1 wherein the active hydrogen-containing compound (ii) is an aliphatic alcohol, araliphatic alcohol, phenol, primary amine, secondary amine, aliphatic carboxylic acid, acid amide of such acid or acid imide of such acid.

3. A catalyst according to claim 1 or 2 wherein the organic acid ester (iii) is an ester formed between a C_1-C_8 saturated or unsaturated aliphatic carboxylic acid which is unsubstituted or is substituted by a halogen atom and an alcohol selected from C_1-C_8 saturated or unsaturated aliphatic primary alcohols optionally substituted by halogen atoms, C_3-C_8 saturated or unsaturated alicyclic alcohols and C_1-C_4 saturated or unsaturated aliphatic primary alcohols substituted by C_6-C_{10} aromatic groups; an ester formed between a C_7-C_{12} aromatic monocarboxylic acid and an alcohol selected from C_1-C_8 saturated or unsaturated aliphatic primary alcohols optionally substituted by halogen atoms, C_3-C_8 saturated or unsaturated alicyclic alcohols and C_1-C_4 saturated or unsaturated aliphatic primary alcohols substituted by C_6-C_{10} aromatic groups; or an alicyclic carboxylic acid ester from methyl cyclopentanecarboxylate methyl hexahydrobenzoate, ethyl hexahydrobenzoate, methyl hexahydrotoluate and ethyl hexahydrotoluate.

4. A catalyst according to claim 1, 2 or 3 wherein said silicon or tin compound (iv) is a silicon tetrahalide, tin tetrahalide, tetraalkyl silicon, silicon alkyl halide, silicon alkyl hydride, tin alkyl-halide or tin hydride halide.

5. A catalyst according to any one of the preceding claims wherein titanium compound (2) is a compound of the formula



wherein X is a halogen atom, R^1 is an alkyl

14

8

1,505,315

8

- group and n is 0 or an integer from 1 to 4.
- 5 6. A catalyst according to any one of the preceding claims wherein the molar ratio of the compounds (i)/(ii)/(iii)/(iv)/ (2) used in preparing the solid transition metal catalyst component (a) is $1/(20-0.1)/(20-0.005)/$ (at least 0.1)/(at least 0.1).
- 10 7. A catalyst according to any one of the preceding claims wherein the component (b) is an organometallic compound of aluminium, magnesium or zinc.
- 15 8. A catalyst according to claim 7 wherein the component (b) is a trialkyl aluminium, alkyl aluminium halide, alkyl aluminium alkoxide, alkyl aluminium aryloxy, alkyl aluminium hydride, dialkyl zinc, dialkyl magnesium or alkyl magnesium halide, in which component each alkyl contains 1 to 12 carbon atoms and any halogen is chlorine, bromine or iodine.
- 20 9. A catalyst according to claim 1 substantially as described in any one of Examples 1 to 12.
- 25 10. A process for preparing an α -olefin polymer which comprises homopolymerising or copolymerising at least one α -olefin containing at least 3 carbon atoms or copolymerising such an olefin with not more than 10 mole % of ethylene and/or diolefins in the presence of a catalyst as claimed in any one of the preceding claims.
- 30 11. A process according to claim 10 wherein the polymerisation or copolymerisation is carried out in an inert organic liquid medium using the component (a) in an amount of 0.0001 to 1.0 milligram-atoms of titanium per liter of the inert organic liquid medium and the component (b) in an amount such that the ratio of said metal of Groups I to III/Ti (as metal atom ratio) is 1/1 to 1000/1.
- 35 12. A process according to claim 10 substantially as described in any one of Examples 1 to 12.
- 40 13. An α -olefin polymer prepared by a process as claimed in claim 10, 11 or 12.
- 45

J. A. KEMP & CO.,
Chartered Patent Agents,
14 South Square, Gray's Inn,
London, WC1R 5EU.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



* C L M S *