

PATENT SPECIFICATION

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(54) OLEFIN POLYMERIZATION CATALYST

(71) We, SUMITOMO CHEMICAL COMPANY, LIMITED, a Japanese company, of No. 15, Kitahama 5-Chome, Higashi-Ku, Osaka-Shi, Osaka, 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 catalyst for polymerizing olefins to produce highly stereospecific olefin polymers; the invention also relates to a process for preparing the catalyst and to a process for polymerizing olefins using such a catalyst.

It is well known that olefin polymers can be obtained in high yield by polymerizing olefins using a catalyst comprising a compound of a transition metal of Groups IV to VI of the Periodic Table according to Mendeleef and a metal or an organometallic compound containing a metal of Groups I to III of the Periodic Table, i.e., a so-called Ziegler-Natta catalyst, and that the polymers produced by such a polymerization process are generally in the form of a polymer slurry which contains amorphous polymer produced as a by-product in addition to the desired crystalline olefin polymer.

In such a polymerization process, the bulk density of the olefin polymers produced generally affects the productivity and an improvement in the bulk density is therefore desirable in order to increase the efficiency of the reactor used for the polymerization.

Also, in olefin polymers, the stereospecificity of the polymers greatly affects the mechanical properties of moulded products such as films, fibres and other articles prepared therefrom.

Furthermore, the by-production of amorphous polymer which is of less value commercially results in the waste of monomers and, in addition, necessitates the provision of equipment for the removal of such amorphous polymer thereby making the polymerization process uneconomical and disadvantageous from the industrial standpoint. Accordingly, it is considered that a polymerization process capable of producing polymer which is substantially free from amorphous polymer or which contains only a minimum amount of amorphous polymer is advantageous for the production of polymer on an industrial scale.

On the other hand, the polymer obtained by such a polymerization process contains residual catalyst which subsequently causes various problems such as instability and colouration of the olefin polymer, thus requiring equipment for its removal.

The above disadvantages associated with the conventional catalyst can be improved if the polymerization activity of the catalyst, i.e., unit weight of the olefin polymer produced per unit weight of the catalyst used for the olefin polymerization, can be increased, whereby the equipment required for the removal of the residual catalyst can be eliminated and the production cost of the olefin polymer can thus be reduced.

A typical solid catalyst which has conventionally been used for the polymerization of olefins is titanium trichloride. The titanium trichloride catalyst is generally prepared from titanium tetrachloride by (1) reduction with hydrogen, (2) reduction with aluminium metal at high temperature or (3) reduction with an organoaluminium compound at approximately room temperature.

Titanium trichloride obtained by the organoaluminium reduction of titanium tetrachloride has a β -type crystal structure, and the polymer produced by polymerizing olefins using a catalyst comprising a combination of the above β -type titanium trichloride and an organoaluminium compound poses a practical problem because of its low stereospecificity, i.e., its having a 70 to 80% content which is insoluble in boiling heptane.

We previously found, in published Japanese Patent Application No. 74594/75, that a solid catalyst which is useful for the production of a highly stereospecific olefin polymer can be prepared by treating a β -type titanium trichloride, which has previously been obtained by the reduction of titanium tetrachloride with an organoaluminium compound, with a certain type of complexing agent and subsequently

treating the resultant catalyst with a monoalkyl aluminium dihalide. Although the above solid catalyst provides olefin polymers having remarkably increased stereospecificity and bulk density, it still exhibits unsatisfactory catalytic activity during polymerization and, therefore, is disadvantageous in that the residual amount of the catalyst after polymerization is not negligible.

An object of the present invention is to provide an improved catalyst for the polymerization of olefins, which is capable of producing highly stereospecific olefin polymers containing a minimum amount of amorphous polymer and which greatly reduces the problem posed by residual catalyst.

According to the present invention there is provided a process for preparing a solid catalyst component for the polymerization of hydrocarbon olefins which comprises the steps of (1) reducing titanium tetrachloride with an organoaluminium compound represented by the following general formula (I):



wherein R represents a straight chain or branched chain alkyl group having from 1 to 18 carbon atoms, an alicyclic hydrocarbon group or an aromatic hydrocarbon group, X represents a halogen atom, and n has a value of from 1 to 3, inclusive, under conditions such that β -type titanium trichloride is produced, (2) contact-reacting the resultant β -type titanium trichloride with a complexing compound (A) selected from organic electron-donor compounds having at least one N, O, P or S atom in the molecule thereof, (3) contact-reacting the solid catalyst thus obtained with an organoaluminium compound represented by the following general formula (II):



wherein R and X have the previous significance, and m has a value of greater than 0 and less than 1.5, and (4) contact-reacting the resultant solid catalyst with a complexing compound (B) selected from organic electron-donor compounds having at least one N, O, P or S atom in the molecule thereof.

Examples of the organoaluminium compounds which may be used for the preparation of the β -type titanium trichloride are methyl aluminium dichloride, ethyl aluminium dichloride, *n*-propyl aluminium dichloride, methyl aluminium sesquichloride, ethyl aluminium sesquichloride, dimethyl aluminium chloride, diethyl aluminium chloride, di-*n*-propyl aluminium chloride, trimethyl aluminium, triethyl aluminium and triisobutyl aluminium, but the organoaluminium compound is not, of course, limited to the above specific examples.

The reduction reaction for producing a β -

type titanium trichloride can be carried out at a temperature of from about -100° to about 60°C , preferably from -30° to 30°C . Also, it is preferred to carry out the reduction reaction in the presence of an inert diluent such as hexane, heptane, octane or decalin.

The β -type titanium trichloride thus obtained is then treated with a complexing compound. The complexing compounds may be selected broadly from organic electron-donor compounds having at least one of N, O, P and S atoms in the molecule thereof such as alcohols, aldehydes, acids, acid anhydrides, ketones, esters, amides, imides, ethers, mercaptans, thioethers, nitriles, amines, lactams and phosphoric amides, but an amide, ether, thioether or amine generally provides better results, with ethers being particularly preferred.

Examples of the complexing agents which may be used for the treatment of the β -type titanium trichloride are N,N-dimethylformamide, N,N-dimethylacetamide, N,N-dimethyl propionamide, N,N,N',N'-tetramethylurea, diethyl ether, di-*n*-propyl ether, diisopropyl ether, di-*n*-butyl ether, diisobutyl ether, di-*tert*-butyl ether, di-*n*-amyl ether, diisoamyl ether, dineopentyl ether, di-*n*-hexyl ether, di-*n*-octyl ether, diphenyl ether, di-*o*-tolyl ether, di-*p*-tolyl ether, dicyclohexyl ether, diethyl sulphide, di-*n*-propyl sulphide, di-*n*-butyl sulphide, di-*tert*-butyl sulphide, diphenyl sulphide, trimethylamine, triethylamine, tri-*n*-butylamine, triphenylamine, pyridine, quinoline, sym-triazine, N,N-dimethylaniline, N,N-diethylaniline and N,N,N',N'-tetramethylethylenediamine. However, it is to be noted that the present invention is not limited to the use of the above-specified complexing agents.

The treatment of the β -type titanium trichloride with a complexing agent is advantageously carried out in the presence of a diluent. Examples of the diluents which may be used are inert hydrocarbon compounds such as hexane, heptane, octane and decalin.

The complexing agent may be used in an amount of from about 0.05 to about 3 moles, preferably 0.5 to 1.5 moles, per mole of titanium trichloride. The temperature for the treatment is preferably from about 0° to about 100°C .

As stated above, the solid resulting from treatment with the complexing agent is subsequently treated with an organoaluminium compound of the general formula (II).

Particularly preferred examples of the organoaluminium compounds which may be used in the above treatment are monoalkyl aluminium dihalides, but an appropriate mixture of a monoalkyl aluminium dihalide and another aluminium compound, for example, a mixture of a monoalkyl aluminium dihalide and an aluminium trihalide, a mixture of a monoalkyl aluminium dihalide and an alkyl

aluminum sesquihalide or the like, also provides satisfactory results.

On the other hand, organoaluminum compounds other than those represented by the above formula (II) or mixtures of such compounds, e.g., alkyl aluminum sesquihalides, dialkyl aluminum monohalides or trialkyl aluminums, do not exhibit the effect necessary to achieve the object of the present invention. Also, the catalysts prepared without effecting the treatment with a complexing agent exhibit less catalytic activity than that of the catalysts prepared in accordance with the process of this invention as shown in Comparative Example 2 to be presented hereinafter.

Typical examples of the organoaluminum compounds represented by the formula (II) which can be used in the present invention are methyl aluminum dichloride, ethyl aluminum dichloride, *n*-propyl aluminum dichloride, *n*-butyl aluminum dichloride, *n*-hexyl aluminum dichloride, *n*-octyl aluminum dichloride, phenyl aluminum dichloride, *o*-tolyl aluminum dichloride, cyclohexyl aluminum dichloride, methyl aluminum dibromide, ethyl aluminum dibromide, phenyl aluminum dibromide, methyl aluminum diiodide and ethyl aluminum diiodide. However, it is to be understood that other organoaluminum compounds defined by the above formula (II) may also be used and that the present invention is not limited to the above-listed specific compounds. These organoaluminum compounds can be used alone or as a combination of two or more thereof.

The treatment with the organoaluminum compound of the formula (II) may be effected in the presence or absence of a diluent. Examples of the diluent which may be used are an inert hydrocarbon compound such as hexane, heptane, octane or decalin.

The temperature for the treatment with the organoaluminum compounds is not critical, but a temperature of from about room temperature (about 20–30°) to about 200°C is preferably used.

The thus-obtained solid catalyst is further treated with a complexing agent. The complexing agent used in this treatment may be the same or different from that used in the previous treatment of the β -type titanium trichloride and is generally selected optionally from those used in the treatment of the β -type titanium trichloride. Better results can generally be obtained with an amide, ether, thioether or amine complexing agent. Of these agents, an ether-type complexing agent again provides particularly preferred results.

The treatment with the complexing agent may advantageously be carried out in the presence of a diluent. Examples of the diluent which may be used in this treatment are an inert hydrocarbon compound such as hexane, heptane, octane or decalin.

The amount of the complexing agent used

is not critical and can vary over a wide range of from about 0.001 to about 10 moles per mole of the titanium trichloride to be treated. However, generally, an amount of more than about 0.01 mole of the complexing agent per mole of the titanium trichloride is advantageously used since the treatment with the complexing agent in an amount less than about 0.01 mole sometimes results in unsatisfactory effects.

The treatment with the complexing agent may be carried out at a temperature of from about -78° to about 150°C, but neither the time nor the temperature required for the treatment is critical.

The solid catalyst in accordance with the present invention may be used in combination with an organoaluminum compound for the polymerization of olefins. The organoaluminum compound for the above purpose is preferably a dialkyl aluminum halide, particularly aluminum halide, particularly diethyl aluminum chloride.

The molar ratio of the solid catalyst and the organoaluminum compound used for the polymerization of olefins may vary widely from about 10 : 1 to about 1 : 200, preferably from 2 : 1 to 1 : 100. The concentration of the organoaluminum compound in the polymerization system may also vary widely from an extremely low concentration, i.e. 0.1 m mole/l to a high concentration, i.e., without using any diluent.

The polymerization is carried out at a temperature in the range of from -50° to about 200°C, but a polymerization temperature above about 100°C usually adversely affects the production of polymers having a high stereospecificity. The preferred polymerization temperature is therefore in the range of from about 0° to about 100°C. The polymerization pressure is not critical, but a pressure in the range of from about 3 to about 100 atm is preferred from industrial and economic standpoints. Polymerization may be effected in a continuous manner or a batch manner as well known to those skilled in the art.

The olefins which can be polymerized using the solid catalyst of this invention are straight chain or branched chain olefinic hydrocarbons having from 2 to 15 carbon atoms; the olefinic hydrocarbons may contain one or more aromatic hydrocarbon groups, and/or alicyclic hydrocarbon groups.

Typical examples of the olefinic hydrocarbons which can be polymerized are ethylene, propylene, butene-1, pentene-1, hexene-1, octene-1, decene-1, 3-methylpentene-1, 4-methylpentene-1, and styrene, but the application of the present invention is not limited to the above-specified olefinic hydrocarbons.

The solid catalyst of this invention can be used for both homopolymerization and copolymerization of the olefinic hydrocarbons. In copolymerization, the solid catalyst of this inven-

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tion is contacted with two or more different types of olefin in an admixed state to obtain a copolymer. In employing the solid catalyst in the copolymerization of two different types of olefin monomers, it is preferred that one of the two olefin monomers is used in a proportion of less than about 10 mole % with respect to the other olefin monomer in order to obtain a highly stereospecific copolymer.

The polymerization can be conducted by slurry polymerization using an inert solvent such as hexane, heptane, octane or decalin, or in the absence of a solvent.

The present invention will now be illustrated by the following Examples in which, unless otherwise indicated, all parts, percentages, ratios and the like are by weight.

EXAMPLE 1.

Catalyst Preparation 1

Preparation of β -type titanium trichloride

A 1 l reactor was purged with argon, and 200 cc of dried hexane and 50 cc of titanium tetrachloride were charged into the reactor followed by maintaining the mixture at a temperature of -5°C . A solution consisting of 150 cc of dried hexane and 58 cc of diethyl aluminium chloride was then added dropwise to the reactor at such a rate that the temperature of the reaction system was maintained below -3°C . After completion of the addition, the resultant mixture was stirred for an additional 30 minutes and, after the temperature of the mixture had been allowed to rise to 70°C , the stirring was continued for a further hour. The mixture was then allowed to stand to settle the precipitate and the supernatant liquid was removed. The resultant precipitate was washed with 150 cc of hexane to obtain 70 g of β -type titanium trichloride which contained 4.53% of aluminium.

Catalyst Preparation 2

Treatment of β -type titanium trichloride with complexing agent

67 g of the β -type titanium trichloride prepared as above were suspended in 500 cc of dried hexane, and 58.0 cc of di-*n*-butyl ether (a molar ratio of di-*n*-butyl ether to titanium trichloride of 1.0) was added to the suspension followed by stirring the mixture for 1 hour at a temperature of 40°C . After completion of the reaction, the supernatant liquid was removed, and the residual solid was washed 3 times with 150 cc portions of hexane and dried to obtain a solid catalyst (I).

Catalyst Preparation 3

Treatment of solid catalyst (I) with ethyl aluminium dichloride

A mixture of 65 g of the solid catalyst (I), obtained as above by the treatment with the complexing agent, and 100 cc of ethyl aluminium dichloride was stirred for 2 hours

while maintaining the mixture at a temperature of 90°C . The resultant solid was separated by centrifugation, washed 4 times with 500 cc portions of hexane and dried to obtain a solid catalyst (II).

Catalyst Preparation 4

Treatment of solid catalyst (II) with complexing agent

2.0 g of the solid catalyst (II) were suspended in 10 cc of dried hexane and 3.3 cc of di-*n*-butyl ether (a weight ratio of di-*n*-butyl ether to solid catalyst (II) of 1.25) was added to the suspension followed by stirring at room temperature (about $20-30^{\circ}\text{C}$) for one hour. After allowing the resultant mixture to stand, the liquid phase was removed, and the solid thus obtained was washed 3 times with 30 cc portions of hexane and dried to obtain the solid catalyst (III).

Polymerization of Propylene

Polymerization Process 1

A 5 l stainless steel autoclave equipped with a stirrer was purged with nitrogen and charged with 1.5 l of dried heptane, 4.5 g of diethyl aluminium chloride and 673 mg of the solid catalyst (III) prepared as described in the Catalyst Preparations 1 to 4. Hydrogen was then introduced into the autoclave to the pressure corresponding to a partial pressure of 0.16 kg/cm^2 . The temperature in the autoclave was elevated to 60°C , and propylene was introduced into the autoclave to a pressure of $6\text{ kg/cm}^2\text{G}$ and polymerized while keeping the pressure at $6\text{ kg/cm}^2\text{G}$ by introducing propylene monomer for 4 hours. After completion of the polymerization, introduction of the propylene monomer was stopped and propylene gas remaining in the autoclave was then purged and 100 cc of butanol was added to the polymerization system to decompose the catalyst. The polymer thus produced was separated by filtration using a Buchner funnel, washed 3 times with 500 cc portions of heptane and dried at 60°C under reduced pressure to obtain 945 g of polypropylene. The filtrate was subjected to a steam distillation to distill heptane whereby a small amount of amorphous polymer produced as by-product was recovered.

The polymerization activity of the solid catalyst (III) used above was 350 in terms of the polymerization rate (Rp) per 1 g of the solid catalyst (III), per 1 hour (g-polymer/g-catalyst (III) hr). The polymer content which was insoluble in boiling hexane in the resultant polymer was found to be 96.3%, including that the polymer was highly stereospecific. The polymer thus obtained had a bulk density of 0.45 and an intrinsic viscosity $[\eta]$ of 1.97 in tetralin at 135°C .

Polymerization Process 2

A 5 l stainless steel autoclave equipped with

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5 a stirrer was purged with nitrogen and charged with 4.5 g of diethyl aluminium chloride and 60.2 mg of the solid catalyst (III) prepared as described in the Catalyst Preparations 1 to 4. Hydrogen was then introduced into the autoclave to the pressure corresponding to a partial pressure of 0.53 kg/cm². 1.4 kg of liquid propylene was then introduced into the autoclave under pressure and polymerized while maintaining the autoclave at a temperature of 60°C for a period of 4 hours. After completion of the polymerization, unreacted gas was purged, and 100 cc of methanol were added to the polymerization system to decompose the catalyst. The polymer thus obtained was separated by filtration using a Buchner funnel, washed 3 times with 500 cc portions of heptane and dried at 60°C under reduced pressure to obtain 277 g of polypropylene.

10 The polymerization activity of the solid catalyst (III) used above was 1150 in terms of the polymerization rate (Rp). The polymer content which was insoluble in boiling hexane in the resultant polymer was found to be 96.2%, indicating that the polymer was highly stereospecific. The polymer had a bulk density of 0.47.

COMPARATIVE EXAMPLE 1.

30 Propylene was polymerized in the same manner as described in Polymerization Process 1 of Example 1 but using 1.512 g of a β -type titanium trichloride to obtain 750 g of a polypropylene.

35 In this procedure, the polymerization activity of the catalyst was found to be 124 in terms of the polymerization rate (Rp), indicating that the polymerization activity was low.

COMPARATIVE EXAMPLE 2.

40 Propylene was polymerized in the same manner as described in Polymerization Process 1 of Example 1 but using 1.603 g of the solid catalyst (I) prepared in Catalyst Preparation 2 above to obtain 765 g of a polypropylene.

45 In this procedure, the polymerization activity of the catalyst was found to be 118 in terms of the polymerization rate (Rp), and the polymer content which was insoluble in boiling heptane in the resultant polymer was 80.6%, indicating that the stereospecificity of the polymer was low.

COMPARATIVE EXAMPLE 3.

50 Propylene was polymerized in the same manner as described in Polymerization Process 1 of Example 1 but using 1.395 g of the solid catalyst (II) prepared in Catalyst Preparation 3 above to obtain 925 g of a polypropylene.

55 In this procedure, the polymerization activity of the catalyst was found to be 116 in terms of the polymerization rate (Rp) and the polymer content which was insoluble in boiling heptane of the resultant polymer was 96.2%. The bulk density of the polymer was 0.45.

COMPARATIVE EXAMPLES 4 to 6.

60 Solid catalysts were prepared under the same conditions as those used in the Catalyst Preparations 1 to 4 of Example 1 but using other organoaluminium compounds shown in Table 1 below in place of ethyl aluminium dichloride in the preparation of the solid catalyst (II), and propylene was polymerized in the same manner as described in Polymerization Process 1 of Example 1 using the resultant solid catalyst (II). The results obtained are shown in Table 1 below.

TABLE 1

Comparative Example Nos.	Organoaluminium compound	Rp	Insoluble in boiling heptane (%)	Bulk density (g/cc)
4	Triethyl aluminium	31	Amorphous	0.33
5	Diethyl aluminium chloride	145	80.2	0.35
6	Ethyl aluminium sesquichloride	119	79.5	0.35

EXAMPLES 2 to 9.

80 Propylene was polymerized in the same manner as described in Polymerization Process 1 of Example 1 using a solid catalyst (III) which was prepared as described in the Catalyst Preparations 1 to 4 but using the conditions shown in the following Table 2 for the di-n-butyl ether treatment of the solid catalyst (II). The results obtained are also shown in Table 2.

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TABLE 2

Example Nos.	Conditions for treatment			Polymer properties			
	Solid catalyst (II) (g)	Di- <i>n</i> -butyl ether (g)	Di- <i>n</i> -butyl ether	Temp. (°C)	Rp	Insoluble in boiling heptane (%)	Bulk density (g/cc)
			Solid Catalyst (II) (Weight Ratio)				
2	2.32	11.4	4.93	28	374	96.2	0.45
3	2.53	5.81	2.30	28	361	96.0	0.45
4	2.14	1.16	0.54	28	314	96.1	0.44
5	2.31	0.58	0.25	28	288	96.2	0.46
6	2.10	0.27	0.13	28	280	96.2	0.44
7	2.38	0.12	0.05	28	254	96.1	0.43
8	2.86	2.86	1.25	45	356	96.1	0.46
9	2.51	2.51	1.25	65	361	96.1	0.45

EXAMPLES 10 to 15.
Solid catalysts were prepared using the same conditions as described in Example 1 except for the use of different types of complexing agent as shown in the following Table 3.

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TABLE 3

Example No.	Treatment of β -type TiCl_3 with complexing agent		Treatment of solid catalyst (II) with complexing agent		Polymer properties	
	Complexing agent		Complexing agent		Insoluble in boiling heptane (%)	Bulk density (g/cc)
	Complexing agent	TiCl_3 (Molar ratio)	Complexing ratio	TiCl_3 (Weight ratio)		
10	<i>n</i> -Butyl ether	1.0	Diethyl ether	1.25	366	95.9
11	<i>n</i> -Butyl ether	1.0	Di- <i>n</i> -butyl sulphide	1.25	282	95.7
12	<i>n</i> -Butyl ether	1.0	Triethylamine	0.12	258	95.5
13	Di- <i>n</i> -butyl sulphide	1.0	Diethyl ether	1.25	279	93.1
14	Di- <i>n</i> -butyl sulphide	1.0	N_2N -Dimethylacetamide	0.23	249	93.4
15	Di- <i>n</i> -butyl sulphide	1.0	N_2N -Dimethylaniline	0.31	260	92.2

WHAT WE CLAIM IS:—

1. A process for preparing a solid catalyst component for the polymerization of hydrocarbon olefins which comprises the steps of (1) reducing titanium tetrachloride with an organo-aluminum compound represented by the following general formula (I):



wherein R represents a straight chain or branched chain alkyl group having from 1 to 18 carbon atoms, an alicyclic hydrocarbon group or an aromatic hydrocarbon group, X represents a halogen atom, and *n* has a value of from 1 to 3, inclusive, under conditions such that β -type titanium trichloride is produced, (2) contact-reacting the resultant β -type titanium trichloride with a complexing compound (A) selected from organic electron-

donor compounds having at least one, N,O,P or S atom in the molecule thereof, (3) contact-reacting the solid catalyst thus obtained with an organoaluminum compound represented by the following general formula (II):



wherein R and X have the previous significance, and *m* has a value of greater than 0 and less than 1.5, and (4) contact-reacting the resultant solid catalyst with a complexing compound (B) selected from organic electron-donor compounds having at least one N,O,P or S atom in the molecule thereof.

2. A process according to Claim 1, wherein said organo-aluminum compound used in the reduction step (1) is methyl aluminum dichloride, ethyl aluminum dichloride, *n*-propyl aluminum dichloride, methyl aluminum

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TABLE 3

Example No.	Treatment of β -type TiCl_3 with complexing agent		Treatment of solid catalyst (II) with complexing agent		Polymer properties	
	Complexing agent		Complexing agent		Insoluble in boiling heptane (%)	Bulk density (g/cc)
	Complexing agent	TiCl_3 (Molar ratio)	Complexing ratio	TiCl_3 (Weight ratio)		
10	<i>n</i> -Butyl ether	1.0	Diethyl ether	1.25	95.9	0.44
11	<i>n</i> -Butyl ether	1.0	Di- <i>n</i> -butyl sulphide	1.25	95.7	0.43
12	<i>n</i> -Butyl ether	1.0	Triethylamine	0.12	95.5	0.43
13	Di- <i>n</i> -butyl sulphide	1.0	Diethyl ether	1.25	93.1	0.41
14	Di- <i>n</i> -butyl sulphide	1.0	<i>N,N</i> -Dimethylacetamide	0.23	93.4	0.40
15	Di- <i>n</i> -butyl sulphide	1.0	<i>N,N</i> -Dimethylaniline	0.31	92.2	0.40

WHAT WE CLAIM IS:—

1. A process for preparing a solid catalyst component for the polymerization of hydrocarbon olefins which comprises the steps of (1) reducing titanium tetrachloride with an organo-aluminum compound represented by the following general formula (I):



wherein R represents a straight chain or branched chain alkyl group having from 1 to 18 carbon atoms, an alicyclic hydrocarbon group or an aromatic hydrocarbon group, X represents a halogen atom, and *n* has a value of from 1 to 3, inclusive, under conditions such that β -type titanium trichloride is produced, (2) contact-reacting the resultant β -type titanium trichloride with a complexing compound (A) selected from organic electron-

donor compounds having at least one, $\text{N}, \text{O}, \text{P}$ or S atom in the molecule thereof, (3) contact-reacting the solid catalyst thus obtained with an organoaluminum compound represented by the following general formula (II):



wherein R and X have the previous significance, and *m* has a value of greater than 0 and less than 1.5, and (4) contact-reacting the resultant solid catalyst with a complexing compound (B) selected from organic electron-donor compounds having at least one $\text{N}, \text{O}, \text{P}$ or S atom in the molecule thereof.

2. A process according to Claim 1, wherein said organo-aluminum compound used in the reduction step (1) is methyl aluminum dichloride, ethyl aluminum dichloride, *n*-propyl aluminum dichloride, methyl aluminum



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- sesquichloride, ethyl aluminium sesquichloride, dimethyl aluminium chloride, diethyl aluminium chloride, di-*n*-propyl aluminium chloride, trimethyl aluminium, triethyl aluminium or triisobutyl aluminium.
- 5 3. A process according to Claim 1 or 2, wherein the reduction step (1) is performed at a temperature of from -100 to 60°C in the presence of an inert solvent.
- 10 4. A process according to Claim 3 wherein the reduction step (1) is performed at a temperature of from -30 to +30°C.
- 5 5. A process according to Claim 3 or 4, wherein said inert solvent is hexane, heptane, octane or decalin.
- 15 6. A process according to any preceding claim, wherein said compound (A) and/or said compound (B) is selected from amides, ethers, thioethers and amines.
- 20 7. A process according to Claim 6, wherein said compound (A) and/or said compound (B) is selected from N,N-dimethylformamide, N,N-dimethylacetamide, N,N-dimethylpropionamide, N,N,N',N'-tetramethylurea, diethyl ether, di-*n*-propyl ether, diisopropyl ether, di-*n*-butyl ether, diisobutyl ether, di-*tert*-butyl ether, di-*n*-amyl ether, diisoamyl ether, diisopentyl ether, di-*n*-hexyl ether, di-*n*-octyl ether, diphenyl ether, di-*o*-tolyl ether, di-*p*-tolyl ether, dicyclohexyl ether, diethyl sulphide, di-*n*-propyl sulphide, di-*n*-butyl sulphide, di-*tert*-butyl sulphide, diphenyl sulphide, trimethylamine, triethylamine, tri-*n*-butylamine, triphenylamine, pyridine, quinoline, sym-triazine, N,N-dimethylaniline, N,N-diethylaniline and N,N,N',N'-tetramethylethylenediamine.
- 30 8. A process according to Claim 6, wherein each of said compound (A) and compound (B) is an ether.
- 35 9. A process according to any preceding claim, wherein step (2) is performed at a temperature of from 0 to 100°C using a molar ratio of from 0.05 to 3 moles of complexing agent per mole of titanium trichloride in the presence of a diluent.
- 40 10. A process according to Claim 9, wherein step (2) is performed using a molar ratio of from 0.5 to 1.5 moles on the same basis.
- 45 11. A process according to any preceding claim, wherein said organoaluminium compound used in step (3) is methyl aluminium dichloride, ethyl aluminium dichloride, *n*-propyl aluminium dichloride, *n*-butyl aluminium dichloride, *n*-hexyl aluminium dichloride, *n*-octyl aluminium dichloride, phenyl aluminium dichloride, *o*-tolyl aluminium dichloride, cyclohexyl aluminium dichloride, methyl aluminium dibromide, ethyl aluminium dibromide, phenyl aluminium dibromide, methyl aluminium diiodide or ethyl aluminium diiodide.
- 55 12. A process according to any preceding claim, wherein step (3) is performed at a temperature of from room temperature to 200°C.
- 60 13. A process according to any preceding claim, wherein step (4) is performed at a temperature of from -78° to +150°C at a molar ratio of from 0.001 to 10 moles of said complexing agent per mole of said solid catalyst in the presence of a diluent.
- 65 14. A process according to Claim 1 and substantially as hereinbefore described.
- 70 15. A process for preparing a solid catalyst component substantially as hereinbefore described with reference to any one of Examples 1 to 15.
- 75 16. A solid catalyst component for the polymerization of olefins when prepared by a process as claimed in any preceding claim.
- 80 17. A process for polymerizing olefins which includes contacting one or more olefinic hydrocarbon monomers having from 2 to 15 carbon atoms with a catalyst component as claimed in Claim 16 and an organo aluminium component at a temperature of from -50° to 200°C and at a pressure of from 3 to 100 atoms.
- 85 18. A process as claimed in Claim 17 and substantially as hereinbefore described.
- 90 19. A process for polymerizing olefinic hydrocarbon monomers substantially as hereinbefore described with reference to any one of Examples 1 to 15.
- 95 20. Olefinic hydrocarbon polymer or copolymer when prepared by a process as claimed in Claim 17, 18 or 19.

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