(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 November 2001 (01.11.2001)

PCT

(10) International Publication Number
WO 01/81432 A1

(51) International Patent Classification[7]: C08F 4/16, 4/614

(21) International Application Number: PCT/KR00/01544

(22) International Filing Date:
28 December 2000 (28.12.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2000/21615 24 April 2000 (24.04.2000) KR

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(81) Designated States *(national)*: CN, ID, IN, JP, RU.

(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/81432 A1

(54) Title: CATALYST FOR PRODUCING AN ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE AND METHOD FOR PRODUCING AN ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE USING THE SAME

(57) Abstract: The present invention provides a catalyst for producing an ultra high molecular weight polyethylene and also a method for preparation of an ultra high molecular weight polyethylene with the use of said catalyst. The catalyst of the present invention is prepared by a process comprising: (i) producing a magnesium compound solution by contact-reacting a magnesium compound and an aluminum or boron compound with alcohol; (ii) contact-reacting the said solution with an ester compound containing at least one hydroxy group and a silicon compound containing an alkoxy group; and (iii) producing of a solid titanium catalyst by adding a mixture of a titanium compound and a silicon compound thereto. The catalyst prepared by the present invention has excellent catalytic activity, and it helps to produce an ultra-high molecular weight polyethylene with large bulk density and narrow particle distribution without too large and minute particles.

Catalyst for producing an ultra high molecular weight polyethylene and method for producing an ultra high molecular weight polyethylene using the same

Technical Field

The present invention relates to a catalyst for preparing an ultra high molecular weight polyethylene (UHMWPE) and also a method for preparing a UHMWPE with the use of that catalyst, and particularly relates to a solid complex titanium catalyst supported by a carrier containing magnesium for production of UHMWPE along with a preparation method by the use of that catalyst, of a UHMWPE with a large bulk density and narrow particle distribution with few untowardly large or small particles.

Background of the Invention and Prior Art

UHMWPE, a sort of polyethylene resin, having a molecular weight of at least 10^6g/mol or more, and, according to ASTM 4020, is defined as " linear polyethylene having a relative viscosity of 2.30 or more when measured in 100ml of 0.05% decahydronaphthalene solution at 135℃." Because UHMWPE has a larger molecular weight than the polyethylene for ordinary use, it has excellent characteristics in strength, wear resistance, self-lubricating ability, chemical resistance, and electrical properties. Owing to these excellent properties, UHMWPE can be considered a special raw material having high quality obtained from a common raw material.

UHMWPE prepared by the process of polymerization is so large in molecular weight it can not be prepared in pellets, as is the case for ordinary polyethylene, but in powder for commercial use. In powder form, the size and distribution of the polymer powders should be considered important. Thus the particle size distribution of the polymer, and the existence or absence of minute particles are the decisive factors for the quality of the catalyst used.

A magnesium-containing catalyst, based on titanium, for the

preparation of UHMWPE and its manufacturing process have been reported. A method making use of a magnesium solution intended to obtain a catalyst for polymerization of olefin having high bulk density has also been learned. US Patent No. 4,962,167 has disclosed the process of preparing a catalyst obtained by reacting what has been produced by reaction of a magnesium halide compound and a titanium alkoxide compound on one hand with what has been obtained by reaction of an aluminum halide and a silicon alkoxide compound on the other. The catalyst thus prepared provides a polymer of relatively high bulk density, but has to be improved, not to say the problems in the catalytic activity.

US Patent No. 5,587,440 disclosed a preparation method for a polymer with a narrow particle size distribution and a high bulk density by reducing a titanium(IV) halide to an organic aluminum compound and subjecting it to a post-treatment process, but this product has a demerit of relatively low catalytic activity.

As has been examined above, a preparation method for a catalyst with high polymerization activity to produce an UHMWPE having a high bulk density as well as narrow particle size distribution so that the polymer may have a reduced amount of untowardly big or minute particles, through a simple process though, is demanded to be developed.

To meet such a need, the present invention hereby intends to provide a method for preparation of a catalyst, which is excellent in its catalytic activity and can help produce a UHMWP having a high bulk density and, a narrow particle size distribution with few untowardly large or small particles; the method can be performed through a simple process by using raw materials of low cost. In addition, the detailed steps or processes for production of the catalyst, provided by the present invention, have never been known in any prior art.

Disclosure of Invention

An objective of the present invention is to provide a highly active catalyst for the production of UHMWPE, leading to production of a polymer

of high bulk density and such a narrow particle distribution as to evade too large or too small particles.

Another objective is to provide a UHMWPE by a simple yet practical production method and process. Still other objectives and advantages of the present invention will be seen more clearly by referring to the following descriptions and the claims of the present invention.

The catalyst of the present invention for UHMWPE production is characterized by comprising the following, simple yet effective steps: (i) forming a magnesium compound solution by contact-reacting a mixture of a halogenated magnesium compound and an aluminum or a boron compound with alcohol; (ii) reacting the formed magnesium compound solution with an ester compound having at least one hydroxy group and a silicon compound having an alkoxy group; and (iii) producing a solid titanium catalyst by adding a mixture of a titanium compound and a silicon compound thereto.

The kind of halogenated magnesium compounds which can be used in production of the catalyst in the present invention includes: dihalogenated magnesiums such as magnesium chloride, magnesium iodide, magnesium fluoride, or magnesium bromide; alkylmagnesium halides such as methylmagnesium halide, ethylmagnesium halide, propylmagnesium halide, butylmagnesium halide, isobutylmagnesium halide, hexylmagnesium halide, or amylmagnesium halide; alkoxymagnesium halides such as methoxymagnesium halide, ethoxymagnesium halide, isopropoxymagnesium halide, butoxymagnseium halide, or octoxymagnesium halide; and aryloxymagnesium halides such as phenoxymagnesium halide or methylphenoxymagnesium halide. Of the above-named compounds, a mixture of two or more can also be used, and these magnesium compounds can also be effective when they are used in the form of a complex with other metals.

The above-listed magnesium compounds can be represented by simple chemical formulae, but some magnesium compounds can not be

represented by simple formula, depending on their manufacturing process. In such cases they generally can be regarded as mixtures of these listed magnesium compounds. For instance, the following compounds can also be used in the present invention: as the compounds obtained by reacting a magnesium compound with a polysiloxane compound, a halogen-containing silane compopund, ester, or alcohol; the compounds obtained by reacting a magnesium metal with alcohol, phenol, or ether in the presence of halosilane, phosphor pentachloride, or thionyl chloride. The preferable magnesium compounds are magnesium halides, specifically, magnesium chloride, alkylmagnesium chloride, preferably including alkyl group having the number of 1~10 carbon atoms, alkoxymagnesium chlorides, preferably including alkoxy group having the number of 1~10 carbons; aryloxy magnesium chlorides, preferably including aryloxy group having the number of 6~20 carbons. The magnesium solution used in the present invention can be produced by using the aforesaid magnesium compounds in an alcohol in the presence or absence of a hydrocarbon solvent. The kinds of hydrocarbon solvent which can be used here include, for instance: aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decan or kerosene; alicyclic hydrocarbons such as cyclobenzene, methylcyclobenzene, cyclohexane, or methylcyclohexane; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, cumene, or cymene; and such halogenated hydrocarbons such as dichloropropane, dichloroethylene, trichloroethylene, carbon tetrachloride, or chlorobenzene.

As for the aluminum compound to be used together with the magnesium compound in the present invention is preferably one or more compounds chosen from the group consisting of: aluminum halides including aluminum fluoride, aluminum bromide, aluminum chloride or aluminum iodide; compounds having a general formula of $AlR^1_n (OR^2)_{3-n}$ (wherein, R^1 is hydrocarbon having 1~20 carbons or a halogen element, R^2 represents hydrocarbon having 1~20 carbons, and "n" means a natural number from 0 to 3) and; mixtures thereof. The compound represented by the general formula $AlR^1_n(OR^2)_{3-n}$ includes, for example aluminum triethoxide, aluminum triisopropoxide, aluminum tributoxide, or aluminum tri-2-ethylhexanoate, etc. can be used.

As for the boron compound to be used together with the magnesium compound in the production of the catalyst in the present invention, one or more compounds selected from a group consisting of boron halides including boron fluoride, boron chloride, or boron bromide; compounds represented by $BR^1_n(OR^2)_{3-n}$ (wherein R^1 is a hydrocarbon having 1~20 carbons or a halogen element, R^2 is hydrocarbon having 1~20 carbons, and "n" is a natural number from 0 to 3), and mixtures of these, are preferable. Particularly, the compounds represented by the general formula $BR^1_n(OR^2)_{3-n}$ includes for example, trimethylborate, triethylborate, tributylborate, triphenylborate, methylborondiethoxide, ethylborondiethoxide, ethylborondibutoxide, butylborondibutoxide, boron triethoxide, boron tributoxide, phenylboron diphenoxide, diethylboronethoxide, dibutylboronethoxide, diphenylboronphenoxide, diethoxyboronchloride, diethoxyboronbromide, diphenoxyboronchloride, ethoxyborondichloride, ethoxyborondibromide, butoxyborondichloride, phenoxyborondichloride, ethylethoxyboronchloride, etc. In order to obtain the catalyst effective in producing an UHMWPE of the present invention, having a high bulk density and a narrow particle distribution, the preferred molar ratio of the magnesium compound to the aluminum or boron compound is less than 1 : 0.25, more preferably 1 : 0.15.

For the conversion of the magnesium compound into a magnesium solution in the present invention, alcohol is used in the presence of hydrocarbon. The kinds of alcohol used in the process include alcohols having 1~20 carbons for example, methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, decanol, dodecanol, octadecylalcohol, benzylalcohol, phenylethylalcohol, isopropylbenzylalcohol, and cumylalcohol, and particularly alcohols having 1~12 carbons are preferred. Although the desired average size and the particle distribution of the catalyst can vary depending on the kind and the total amount of the alcohol used, and the kind of magnesium compound, the ratio of magnesium to alcohol, etc., but the total amount of the alcohol to obtain the magnesium solution is preferably, at least 0.5mol, more preferably about 1.0~20mols, still preferably about 2.0~10mols per 1 mol of the magnesium compound. The

reaction of the magnesium and the alcohol for the production of the magnesium compound solution is preferably performed in a hydrocarbon medium, the temperature preferably, though depending on the kinds and amount of the alcohol, being at about -25℃, preferably –10~200℃, and more preferably about 0~150℃, for about 15 minutes ~ 5 hours, preferably about 30 minutes ~ 4 hours.

As for the ester compound to be used in the present invention as an electron donor, may includes the followings, for example: unsaturated fatty acid esters containing at least one hydroxy group such as 2-hydroxy ethylacrylate, 2-hydroxy ethylmethacrylate, 2-hydroxy propylacrylate, 2-hydroxy propylmethacrylate, 4-hydroxy butylacrylate, or pentaerythritol triacrylate; aliphatic monoesters or polyesters containing at least one hydroxy group such as 2-hydroxy ethylacetate, methyl 3-hydroxy butyrate, ethyl 3-hydroxy butyrate, methyl 2-hydroxy isobutyrate, ethyl 2-hydoxy isobutyrate, methyl-3-hydroxy-2-methyl propionate, 2,2-dimethyl-3-hydroxy propionate, ethyl-6-hydroxy hexanoate, t-butyl-2-hydroxy isobutyrate, diethyl-3-hydroxy glutarate, ethyl lactate, isopropyl lactate, butylisobutyl lactate, isobutyl lactate, ethylmandelate, dimethyl ethyl tartrate, ethyl tartrate, dibutyl tartrate, diethyl citrate, triethyl citrate, ethyl 2-hydroxy caproate, or diethyl bis-(hydroxy methyl) malonate; aromatic esters containing at least one hydroxy group such as 2-hydroxy ethyl benzoate, 2-hydroxy ethyl salicylate, methyl 4-(hydroxy methyl) benzoate, methyl 4-hydroxy benzoate, ethyl 3-hydroxy benzoate, 4-methyl salicylate, ethyl salicylate, phenyl salicylate, propyl 4-hydroxy benzoate, phenyl 3-hydroxy naphthenoate, monoethylene glycol monobenzoate, diethylene glycol monobenzoate, triethylene glycol monobenzoate, etc. and; alicyclic esters containing at least one hydroxy group such as hydroxy butyl lactone. In order to obtain the catalyst effectively leading to the production of a UHMWPE having a high bulk density, a narrow particle distribution to obviate too large and small particles, the amount of the ester compound containing at least one hydroxy group should be 0.001~5mols to a mol of magnesium, preferably 0.01~2mols.

As for the silicon compound having an alkoxy group, which can be

used as another electron donor in the present invention, a compound which is represented by the general formula: $R_nSi(OR')_{4-n}$ (wherein R and R' are hydrocarbons having 1~12 carbons, and "n" is a natural number from 1 to 3) is preferred. In particular, compounds such as dimethyldimethoxysilane, dimethyldiethoxysilane, diphenyldimethoxysilane, methylphenylmethoxysilane, diphenyldiethoxysilane, ethyltrimethoxysilane, vinyltrimethoxysilane, methyltrimethoxysilane, phenyltrimethoxysilane, mehtyltriethoxysilane, ethyltriethoxysilane, vinyltriethoxysilane, butyltriethoxysilane, phenyltriethoxysilane, ethyltriisopropoxysilane, vinyltributoxysilane, ethylsilicate, butylsilicate, methyltriaryloxysilane can be used. In order to obtain the catalyst for production of an UHMWPE having a high bulk density and a narrow particle size distribution provided by the present invention, the amount of the above-said silicon compound having an alkoxy group should preferably be in the ratio of 0.05~3mols to a mol of the magnesium, more preferably the ratio 0.1~2mols. The temperature for the reaction of the liquid magnesium compound solution with an ester compound containing at least one hydroxy group and an alkoxy silicon compound is preferably 0~100℃, or more preferably 10~70℃.

For the catalyst in the present invention, the magnesium compound solution which has been reacted with an ester compound containing at least one hydroxy group and an alkoxy silicon compound is afterwards reacted with a liquid titanium compound represented by the general formula $Ti(OR)_aX_{4-a}$ (wherein R is a hydrocarbon, X is a halogen atom, "a" is a natural number $0 \leq a \leq 4$) and a silicon compound represented by the general formula R_nSiCl_{4-n} (wherein R is a hydrocarbon, "n" is a natural number $0 \leq n \leq 4$), to form a catalyst particles. Of the above general formulae, R represents an alkyl group having the number of 1~10 carbon atoms.

The kind of titanium compounds which satisfy the above general formula $Ti(OR)_aX_{4-a}$ includes, for example, tetra-halogenated titaniums such as $TiCl_4$, $TiBr_4$, and TiI_4; tri-halogenated alkoxy titaniums such as $Ti(OCH_3)Cl_3$, $Ti(OC_2H_5)Cl_3$, $Ti(OC_2H_5)Br_3$, and $Ti(O(i\text{-}C_4H_9)Br_3$;

dihalogenated alkoxy titaniums such as $Ti(OCH_3)_2Cl_2$, $Ti(OC_2H_5)_2Cl_2$. $Ti(O(i\text{-}C_4H_9))_2Cl_2$, and $Ti(OC_2H_5)_2Br_2$; and tetraalkoxy titaniums such as $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$, and $Ti(OC_4H_9)_4$. Mixtures of the above titanium compounds can also be used in the present invention. The preferred titanium compounds are halogen-containing compounds, and more preferred one is titanium tetrachloride.

The kind of silicon compounds which satisfy the above general formula R_nSiCl_{4-n} include, for example: tetrachlorosilicon; trichlorosilanes such as methyltrichlorosilane, ethyltrichlorosilane, and phenyltrichlorosilane; dichlorosilanes such as dimethyldichlorosilane, diethyldichlorosilane, diphenyldichlorosilane, and methylphenyldichloriosilane; and a monochloorsilane such as trimethylchlorosilane. The mixtures of these silicon compounds can also be used. The preferred silicon compound is silicon tetrachloride.

In order to obtain the catalyst effectively leading to the production of a UHMWPE with a high bulk density and a narrow particle size distribution, the amount of the mixture of a titanium compound and a silicon compound suitable for the formation of the catalyst particles is preferably 0.1~200mols to a mol of the magnesium compound, preferably 0.1~100 mols, and more preferably 0.2~80mols. The ratio of titanium compound to silicon compound in the mixture is preferably 1 : 0.05~0.95, or more preferably 1 : 1~0.8.

The shape and size of the solid catalyst component in the present invention may greatly vary depending on the condition of the reaction where the magnesium compound solution reacts with the mixture of titanium and silicon compounds. Therefore, the reaction of the magnesium compound solution with the mixture of titanium and silicon compounds is carried out at a sufficiently low temperature for the formation of solid components. Preferably, the contact reaction is carried out at -70℃ ~70℃, and more preferably at -50℃ ~ 50℃. After the contact reaction, the temperature is slowly raised and maintained at 50℃~150℃ for 30 minutes ~ 5 hours for sufficient reaction.

The solid catalyst particles obtained by the above-said reaction can be further reacted with a titanium compound. The titanium compound for this purpose is a titanium halide or a halogenated alkoxy titanium having 1 ~ 20 carbons of an alkoxy group. In some cases mixtures of these can also be used. Of these, a titanium halide or a halogenated alkoxy titanium having 1 ~ 8 carbons of an alkoxy group is preferred, and titanium tetrahalide is still more preferred.

The solid complex titanium catalyst produced by the method provided by the present invention is advantageously used in polymerization and copolymerization of ethylene. In especial, this catalyst is preferably used in polymerization of ethylene and also in copolymerization of ethylene with α -olepfins containing three or more carbons such as propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, and 1-hexene.

The polymerization reaction in the presence of the catalyst of the present invention is performed with the use of (i) the solid complex titanium catalyst of the present invention consisting of magnesium, titanium, halogen and an electron donor, and (ii) the organometalic compounds of Groups II and III in the periodic table.

The solid complex titanium catalyst of the present invention can also be pre-polymerized with ethylene or α -olefin, before being used in a polymerization reaction as a component. The pre-polymerization can be performed in the presence of the afore-said catalyst components, an organic aluminum compound such as triethylaluminum, and a hydrocarbon solvent like hexane, under the pressure conditions of ethylene or α -olefin at sufficiently low temperature. Pre-polymerization makes catalyst particles wrapped in polymers to maintain the shape of the catalyst, and thus helps to better the shape of the polymer after the polymerization. The ratio in weight of polymer to catalyst after the pre-polymerization is usually 0.1 : 1 ~20 : 1.

The organometalic compound useful in the present invention can be represented by the general formula MR_n, wherein M stands for metals of

Groups II or IIIA in the periodic table such as magnesium, calcium, zinc, boron, aluminum or potassium; "R" for alkali groups having 1 ~ 20 carbons such as methyl, ethyl, butyl, hexyl, octyl, and decyl; "n" for the atomic valence of metal atom. The example of the more preferred organometalic compounds include tri-alkylaluminums containing an alkyl group of 1 ~ six carbons such as triethylaluminum and tri-isobutylaluminum and mixtures thereof. In some cases, organic aluminum compounds containing one or more halogen or hydride groups for example ethylaluminum dichloride, diethylaluminum chloride, ethylaluminum sesquichloride, and diisobutylaluminum hydride can be used. Mixtures of these organometalic compounds can also be used.

The polymerization reaction in the present invention is performed in the gas phase or in bulk in the absence of an organic solvent, or carried out in liquid slurry in the presence of an organic solution. These reactions, however, are performed in the absence of oxygen, water, or any compounds that may act as a catalytic poison. In the case of liquid slurry polymerization, the suitable concentration of the solid complex titanium catalyst (i), in the polymerization reaction system, is about 0.001~5 mmols, more preferably about 0.001~0.5mmols in terms of the titanium atoms of the catalyst to one liter of the solvent. As for the solvent, alkanes and cycloalkanes such as pentane, hexane, heptane, n-octane, iso-octane, cyclohexane, and methylcyclohexane; alkylaromatics such as toluene, xylene, ethylbenzene, isopropylbenzene, ethyltoluene, n-propylbenzene, and diethylbenzene; halogenated aromatics such as chlorobenzene, chloronaphthalene, and ortho-dichlorobenzene; and mixtures thereof, can be useful. In the case of gas phase polymerization, the amount of the solid complex titanium catalyst (i) is about 0.001~5mmols, preferably about 0.001~1.0mmols, still preferably about 0.01~0.5mmols in terms of the titanium atoms in the catalyst to a liter of the polymerization reactor volume. The preferable concentration of the organometalic compound (ii) is about 1~2000mols to a mol of the titanium atoms in the catalyst (i), more preferably about 5~500mols, calculated by the organometalic atoms. That the concentration and amount of the solid complex catalyst are specified as above is to obtain a polymer having a large bulk density and a narrow particle distribution to admit the least possible

amount of too large and small particles.

To secure a high polymerization rate. the reaction is performed at a sufficiently high temperature regardless of the polymerization process itself. Generally, approximately 20~200℃ are preferred, and more preferably 20~95℃. The pressure of a monomer during polymerization is adequately the atmospheric ~ 100, and more preferably 2~50psi.

Now the present invention is described in further detail below, through the following examples of embodiment and comparative examples. But the present invention is not to be limited to these examples.

Best Mode for Carrying out the Invention

Example 1

A solid complex titanium catalyst was prepared through the following three steps:

Step (i)

Preparation of magnesium solution

Into a 1.0-L reactor equipped with a mechanic stirrer, substituted to nitrogen atmosphere, 9.5g of $MgCl_2$, 2.46g of aluminumtributoxide, and 400ml of decane were placed. After they were stirred at 300rpm, 80ml of 2-ethylhexane was added thereto. The temperature was raised to 120℃, then the reaction was allowed to continue for three hours. After the reaction, the obtained homogeneous solution was cooled to room temperature(25℃).

Step (ii)

Contact-reaction of the magnesium solution with ester containing hydroxy and an alkoxy silicon compound

To the said magnesium solution cooled to room temperature was added 1.2ml of 2-hydroxyethylmethacrylate and 10.0ml of silicontetraethoxide, and the solution was left to react for one hours.

Step (iii)

Treating a mixture of a titanium compound and a silicon compound

To the above solution cooled to room temperature (25℃), a mixture of 30ml of titanium tetrachloride and 30ml of silicon tetrachloride was added dropwise for one hour. After the dripping, the temperature of the reactor was raised to 80℃, taking one hour, then maintained at the temperature for another hour. After stirring, the supernatent of the solution was separated, and to the remained solid layer 300ml of decane and 100ml of titanium tetrachloride were instilled subsequently, the temperature was raised to 100℃ and kept there for two hours. After the reaction, the reactor was cooled to room temperature, and washed with 400ml of hexane until the un-reacted free titanium tetrachloride was completely removed. The titanium content of the thus prepared solid catalyst was 3.4%.

Polymerization

A 2 L high-pressure reactor was dried in an oven and assembled while hot. In order to make the inside of the reactor nitrogen atmosphere, nitrogen and vacuum were alternatively manipulated three times in the reactor. It was then instilled with 1,000ml of n-hexane, after which 1 mmol of triethylaluminum and 0.01mmol of the solid catalyst, in terms of titanium atoms. The temperature of the reactor was raised to 70℃ while stirring at 700rpm. While instilling the ethylene at the pressure of 110 psi, the polymerization was conducted for 1 hour. After the polymerization, the reactor was cooled to room temperature, an excessive amount of ethanol was added to the polymerized matter. The thus prepared polymer was then collected by separation, dried in a vacuum oven at 50℃ for at least six hours, finally to obtain UHMW polyethylene in the form of white powder.

The polymerization activity (polyethylene (kg)/catalyst (g)) was calculated as the weight ratio of the polymers produced (kg) per amount of the catalysts (g) used. The average size of the particles of the polymer was determined by a particle analyzer using laser (Mastersizer X, Malvern), and the particle distribution of the polymer was calculated by (d90-d10)/d50, wherin d10, d50, and d90 respectively means the sizes of the particles by each percentage, 10, 50, and 90, and d50 being defined as the median size. The results of the polymerization are given together with the bulk density (g/ml) and the intrinsic viscosity in Table 1 below.

Example 2

The catalyst was produced in the same way as in Example 1, except using 1.62g of aluminum triethoxide instead of the aluminum tributoxide in Step (i). The titanium content of the thus prepared catalyst was 3.2%. Polymerization was carried out under the same conditions as in Example 1, and the results are shown in Table 1 below.

Example 3

The catalyst was produced in the same way as in Example 1, except using 2.30g of boron tributoxide instead of the aluminum tributoxide in Step (i). The titanium content of thus prepared catalyst was 3.6%. Polymerization was carried out under the same conditions as in Example 1, and the results are shown in Table 1 below.

Example 4

The catalyst was produced in the same way as in Example 1, except using 1.46g of boron triethoxide instead of the aluminum tributoxide in Step (i). The titanium content of the thus prepared catalyst was 3.3%. Polymerization was carried out under the same conditions as in Example 1, and the results are shown in Table 1 below.

Example 5

The catalyst was produced in the same way as in Example 1, except using 1.30g of aluminum trichloride instead of the aluminum tributoxide Step (i). The titanium content of the thus prepared catalyst was 3.3%. Polymerization was carried out under the same conditions as in Example 1, and the results are shown in Table 1 below.

Example 6

The catalyst was produced in the same way as in Example 1, except using 4.92g of aluminum trichloride in Step (i) instead of 2.46g. The titanium content of the thus prepared catalyst was 3.4%. Polymerization was carried out under the same conditions as in Example 1, and the results are shown in Table 1 below.

Example 7

Using 2.4ml of 2-hydroxy ethylmethacrylate and 10.0ml of silicon tetraethoxide in Step (ii) of the process for preparing the catalyst in Example 1, the catalyst was prepared as in Example 1. The titanium content of the thus prepared catalyst was 3.8%. Polymerization was carried out under the same conditions as in Example 1, and the results are shown in Table 1 below.

Example 8

Using 1.2ml of 2-hydroxy ethylmethacrylate and 20.0ml of silicon tetraethoxide in Step (ii) of the process for preparing the catalyst in Example 1, the catalyst was prepared as in Example 1. The titanium content of the thus prepared catalyst was 3.9%. Polymerization was carried out under the same conditions as in Example 1, and the results are shown in Table 1 below.

Comparative Example 1

The catalyst was prepared as in Example 1 above, except using only

silicon tetraethoxide, without 2-hydroxy ethylmethacrylate in Step (ii) of the process for preparation of catalyst in Example 1. The titanium content of the thus prepared catalyst was 3.4%. Polymerization was carried out under the same conditions as in Example 1, and the results are shown in Table 1 below.

Comparative Example 2

The catalyst was prepared as in Example 1 above, except using only 2-hydroxy ethylmethacrylate, without silicon tetraethoxide in Step (ii) of the process for preparation of catalyst in Example 1. The titanium content of the thus prepared catalyst was 3.2%. Polymerization was carried out under the same conditions as in Example 1, and the results are shown in Table 1 below.

Comparative Example 3

The catalyst was prepared as in Example 1 above, except using 60ml of titanium tetrachloride only, without silicon tetrachloride in Step (iii) of the process for preparation of catalyst in Example 1. The titanium content of the thus prepared catalyst was 4.2%. Polymerization was carried out under the same conditions as in Example 1, and the results are shown in Table 1 below.

Comparative Example 4

The catalyst was prepared as in Example 1 above, except using no aluminum tributoxide in Step (i) of the process for preparation of catalyst in Example 1. The titanium content of the thus prepared catalyst was 3.8%. Polymerization was carried out under the same conditions as in Example 1, and the results are shown in Table 1 below.

[Table 1]

	Activity (P.E.(kg)/catayst(g))	Bulk Density (g/ml)	Intrinsic Viscosity (dl/g)	Aver. Particle Size (㎛)	Particle Size Distribution (span ratio)
Example 1	28.9	0.37	22.1	168.3	0.6
Example 2	29.8	0.38	23.8	154.9	0.6

Example 3	28.7	0.37	21.9	179.1	0.7
Example 4	27.4	0.38	19.3	152.4	0.5
Example 5	32.5	0.37	19.4	162.9	0.6
Example 6	30.6	0.36	19.6	158.4	0.6
Example 7	27.6	0.40	22.4	156.8	0.5
Example 8	28.8	0.40	21.6	150.7	0.6
Comparative Example 1	23.8	0.30	16.4	148.3	1.6
Comparative Example 2	22.4	0.26	18.7	136.7	1.8
Comparative Example 3	23.6	0.28	16.8	128.7	2.0
Comparative Example 4	21.2	0.29	18.1	129.7	1.4

As shown above, the catalyst prepared by the present invention is excellent in its catalytic activity, and makes possible to obtain an UHMW polyethylene which has high bulk density and such a narrow size distribution without too large and minute particles.

[What Is Claimed Is]

1. A catalyst for producing an ultra high molecular weight polyethylene, prepared by a process comprising:

(1) producing a magnesium compound solution by contact-reacting a mixture of a halogenated magnesium compound and an aluminum or a boron compound with alcohol;

(2) reacting the said solution with an ester compound having at least one hydroxy group and a silicon compound having an alkoxy group; and,

(3) reacting the above with a mixture of a titanium compound and a silicon compound, to obtain a solid titanium catalyst.

2. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 1, wherein said halogenated magnesium compound is one or more compounds selected from the group consisting of: dihalogenated magnesium such as magnesium chloride, magnesium iodide, magnesium fluoride, and magnesium bromide; alkylmagnesium halide such as methylmagnesium halide, ethylmagnesium halide, propylmagnesium halide, butylmagnesium halide, isobutylmagnesium halide, hexylmagnesium halide, and amylmagnesium halide; alkoxymagnesium halide such as methoxymagnesium halide, ethoxymagnesium halide, isopropoxymagnesium halide, butoxymagnesium halide, and octoxymagnesium halide; aryloxymagnesium halide such as phenoxymagnesium halide and methylphenoxymagnesium halide; and mixtures thereof, or a magnesium complex compound with another metals.

3. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 1, wherein said aluminum compound is one or more compounds selected from the group consisting of: aluminum halide such as aluminum fluoride, aluminum bromide, aluminum chloride, and aluminum iodide; a compound represented by the general formula $AlR^1_n(OR^2)_{3-n}$ (wherein R^1 stands for hydrocarbon having 1~20 carbons or a halogen atom, R^2 for hydrocarbon having 1~20 carbon atoms, and "n" for a natural number from 0 to 3); and mixtures thereof.

4. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 3, wherein said compound represented by the the general formula $AlR^1_n(OR^2)_{3-n}$ is aluminum triethoxide, aluminum triisopropoxide, aluminum tributoxide, or aluminum tri-2-ethylhexanoate.

5. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 1, wherein said boron compound is one or more compounds selected from the group consisting of: boron halide such as boron fluoride, boron chloride, and boron bromide; a compound represented by the general formula $BrR^1_n(OR^2)_{3-n}$ (wherein R^1 stands for hydrocarbon having 1~20 carbons or a halogen atom, R^2 for hydrocarbon having 1~20 carbons, and "n" for a natural number from 0 to 3); and mixtures thereof.

6. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 5, wherein the compound represented by the general formula $BR^1_n(OR^2)_{3-n}$ is trimethylborate, triethylborate, tributylborate, triphenylborate, methylborondiethoxide, ethylborondiethoxide, ethyldibutoxide, butylborondibutoxide, boron triethoxide, boron tributoxide, phenylborondiphenoxide, diethylboronethoxide, dibutylboronethoxide, diphenylboronphenoxide, diethoxyboronchloride, diethoxyboronbromide, diphenoxyboronchloride, ethoxyborondichloride, ethoxyborondibromide, butoxyborondichloride, phenoxyborondichloride, or ethylethoxyboronchloride.

7. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 1, characterized in that the molar ratio of the magnesium compound to the aluminum compound and the boron compound is 1 : 0.25 or less.

8. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 1, wherein said ester compound having at least one hydroxy group is: an unsaturated fatty acid ester such as 2-hydroxy ethylacrylate, 2-hydroxy ethylmethacrylate, 2-hyrdoxy propylacrylate, 2-hydroxy propylmethacrylate, 4-hydroxy butylacrylate, and pentaerythritol triacrylate; an aliphatic monoester or polyester such as 2-hydroxy ethylacetate,

methyl 3-hydroxy butyrate, ethyl 3-hydroxy butyrate, methyl 2-hydroxy isobutyrate, ethyl 2-hydroxy isobutyrate, methyl 3-hydroxy-2-methylpropionate, 2,2-dimethyl-3-hydroxy propionate, ethyl-6-hydroxy hexanoate, t-butyl-2-hydroxy isobutyrate, diethyl-3-hydroxy glutarate, ethyl lactate, isopropyl lactate, butyl isobutyl lactate, isobutyl lactate, ethyl mandelate, dimethyl ethyl tartrate, ethyl tartrate, dibutyl tartrate, diethyl citrate, triethyl citrate, ethyl 2-hydroxy caproate, and diethyl bis-(hydroxy methyl) malonate; an aromatic ester such as 2-hydroxy ethyl benzoate, 2-hydroxy ethyl salicylate, methyl 4-(hydroxy methyl)benzoate, methyl 4-hydroxy benzoate, ethyl 3-hydroxy benzoate, 4-methyl salicylate, ethyl salicylate, phenyl salicylate, propyl 4-hydroxy benzoate, phenyl 3-hydroxy naphthanoate, monoethylene glycol monobenzoate, diethylene glycol monobenzoate, and triethylene glycol monobenzoate; or an alicyclic ester such as hydroxy butyllactone.

9. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 1, wherein said silicon compound having an alkoxy group is a compound represented by the general formula: $R_nSi(OR')_{4-n}$ (here R and R stand for hydrocarbon containing 1 ~ 12 carbon atoms, "n" for a natural number 1 ~ 3).

10. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 9, wherein said compound represented by the general formula $R_nSi(OR')_{4-n}$ is dimethyldimethoxysilane, dimethyldiethoxysilane, diphenyldimethoxysilane, methylphenylmethoxysilane, diphenyldiethoxysilane, ethyltrimethoxysilane, vinyltrimethoxysilane, methyltrimethoxysilane, phenyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, vinyltriethoxysilane, butyltriethoxysilane, phenyltriethoxysilane, ethyltriisopropoxysilane, vinyltributoxysilane, ethylsilicate, butylsilicate, or methyltriaryloxysilane.

11. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 1, wherein the amount of said ester compound having at least one hydroxy group is 0.001~5mols per 1 mol of the magnesium, and the amount of said silicon compound having an alkoxy group is 0.05~3mols per 1

mol of the magnesium.

12. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 1, wherein the titanium compound is a compound represented by the general formula: $Ti(OR)_aX_{4-a}$ (R stands for a hydrocarbon group, X for halogen atome, and "a" for natural number $0 \leq a \leq 4$), and the silicon compound is a compound represented by the general formula: R_nSiCl_{n-4} (R stands for a hydrocarbon group, and "n" for a natural number $0 \leq n \leq 4$).

13. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 12, wherein said titanium compound is one or more compounds selected from the group consisting of: tetrahalogenated titanium such as $TiCl_4$, $TiBr_4$ and TiI_4; trihalogenated alkoxy titanium such as $Ti(OCH_3)Cl_3$, $Ti(OC_2H_5)Cl_3$, $Ti(OC_2H_5)Br_3$, and $Ti(O(i\text{-}C_4H_9)Br_3)$; dihalogenated alkoxy titanium such as $Ti(OCH_3)_2Cl_2$, $Ti(OC_2H_5)_2Cl_2$, $Ti(O(i\text{-}C_4H_9))_2Cl_2$, and $Ti(OC_2H_5)_2Br_3$; tetraalkoxy titanium such as $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$, or $Ti(OC_4H_9)_4$; and mixtures thereof, and wherein said silicon compound is one or more compounds selected from the group consisting of: silicon tetrachloride; trichlorosilane such as methyltrichlorosilane, ethyltrichlorosilane, and phenyltrichlorosilane; dichlorosilane such as dimethyldichlorosilane, diethyldichlorosilane, diphenyldichlorosilane, and mehtylphenyldichlorosilane; monochlorosilane such as trimethylchlorosilane; and mixtures thereof.

14. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 13, wherein the titanium compound is titanium tetrachloride, and the silicon compound is silicon tetrachloride.

15. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 1, wherein the amount of the mixture of the titanium compound and the silicon compound is 0.1~200mols per 1 mol of the magnesium compound, and the molar ratio of the titanium compound to the silicon compound in the mixture is 1 : 0.05~0.95.

16. A catalyst for producing an ultra high molecular weight polyethylene according to Claim 1, wherein the process further comprises reacting the solid titanium catalyst obtained from the Step (3) with a titanium compound.

17. A method for producing an ultra high molecular weight polyethylene, characterized in that a polymerization is performed by using the catalyst according to Claim 1 and an organometalic compound of metal of Groups II or III on the periodic table.

18. A method for producing an ultra high molecular weight polyethylene according to Claim 17, wherein said organometalic compound is one or more compounds selected from the group consisting of: compounds represented by the general formula, MR_n (wherein M represents a metal elements of Group II or IIIA in the periodic table such as magnesium, calcium, zinc, boron, aluminum, or potassium, R represents alkyl group having 1~20 carbons such as methyl, ethyl, butyl, hexyl, octyl, and decyl, and "n" means the atomic valences of the metal components); organoaluminum compound having one or more halogen or hydride groups, and mixtures thereof.

19. A method for producing an ultra high molecular weight polyethylene according to Claim 17 or 18, characterized in that the polymerization is either gas phase or liquid slurry polymerization; that in the case of liquid slurry polymerization, the concentration of the catalyst is 0.001~5mmols in terms of the titanium atoms in the catalyst per a liter of the solvent, and that in the case of gas phase polymerization, the quantity of the catalyst is 0.001~5mmols in terms of the titanium atoms in the catalyst per a liter of the polymerization reactor volume.

20. A method for producing an ultra high molecular weight polyethylene according to Claim 17 or 18, characterized in that, before using in the polymerization, the catalyst is pre-polymerized in the presence of a an organoaluminum such as triethylaluminum in a hydrocarbon solvent, under the ethylene or α -olefin pressure condition.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR00/01544

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C08F 4/16, C08F 4/614

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimun documentation searched (classification system followed by classification symbols)

IPC7 C08F 4/16, C08F 4/614

Documentation searched other than minimun documentation to the extent that such documents are included in the fileds searched

KOREAN PATENTS AND APPLICATIONS FOR INVENTIONS SINCE 1975

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search trerms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 98-082807 A (SAMSUNG GENERRAL CHEMICALS CO.,LTD.), 05 DECEMBER 1998(05.12.1998) SEE ABSTRACT AND CLAIM	1 - 5 17 - 20
Y	KR 98-082808 A (SAMSUNG GENERRAL CHEMICALS CO.,LTD.), 05 DECEMBER 1998(05.12.1998) SEE ABSTRACT AND CLAIM	1 - 5 17 - 20
Y	EP 0591922 A (MITSUI PETROCHEMICAL INDUSTRIES,LTD) 13.APRIL.1994(13.04.1994) SEE ABSTRACT AND CLAIM	1 - 6 17 - 20
A	JP 63-152608 A (MITSUI PETROCHEMICAL INDUSTRIES,LTD), 25 JUNE 1988 SEE THE WHOLE DOCUMENT	1 - 20
A	JP 08143618 A (SHOWA DENKO CO.,LTD.), 04 JUNE 1996 (04.06.1996) SEE THE WHOLE DOCUMENT	1 - 20
A	EP 0773237 A (MITSUI TOATSU CHEMICALS ,INCORPORATED), 14 MAY 1997 (14.05.1997) SEE THE WHOLE DOCUMENT	1 - 20

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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"Y" document of particular relevence; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 MARCH 2001 (12.03.2001)	13 MARCH 2001 (13.03.2001)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR00/01544

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0591922 A	13.04.1994	JP 06220120 A	09.08.1994
		US 5468703 A	21.11.1995
		US 5623033 A	22.04.1997