



PROCESS FOR PRODUCING SOLID CATALYST FOR
USE IN POLYMERIZATION OF OLEFINS

1

This invention relates to a process for producing a solid catalyst used in the production of olefin polymers, and more particularly to a process for producing a novel solid catalyst having a very high polymerizing activity per solid catalyst and per titanium atom which is for use in producing olefin polymers containing only very small amounts of catalyst residues and amorphous polymers and having excellent mechanical properties and processability.

As a process for producing polymers of α -olefins such as propylene, butene-1 and the like, the process using the so-called Ziegler-Natta catalyst constituted of a transition metal compound belonging to Group IV to Group VI of the periodic table and an organometallic compound belonging to Group I to Group III is generally well known. Particularly, in the industrial production of α -olefin polymers, titanium trichloride catalysts are widely used.

In this production process, however, amorphous polymers are formed as a by-product in addition to the valuable highly stereospecific α -olefin polymers.



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1 These amorphous polymers are not valuable
industrially and exercise a greatly adverse influence
upon the mechanical properties of α -olefin polymers in
the form of e.g. films, fibers or other processed
5 products or shaped articles.

Further, formation of the amorphous product
brings about a loss in starting monomer. At the same
time, it indispensably requires equipment for removing
the amorphous polymers, and thereby brings about a very
10 large industrial disadvantage.

Accordingly, if formation of such amorphous
polymers can be prevented or suppressed to a low degree,
it will bring about a very great merit.

On the other hand, in α -olefin polymers
15 produced according to such a polymerization process,
catalyst residues remain and cause various problems as regards
stability and processability of α -olefin polymers. Thus,
it becomes necessary to provide equipment for removing
catalyst residues and stabilizing the polymers.

20 These difficulties can be overcome by enhancing the
catalyst activity represented by the weight of formed
 α -olefin polymer per unit weight of catalyst, by which
the equipment for removing a catalyst residue becomes
unnecessary and the production cost of α -olefin polymers
25 can be reduced.

As production process of titanium trichloride,
1) reduction of titanium tetrachloride with hydrogen,
followed by activation of the reduced product by its

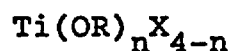


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1 pulverization in ball mill, 2) reduction of titanium
tetrachloride with metallic aluminum, followed by
activation of the reduced product by its pulverization in
ball mill, 3) reduction of titanium tetrachloride with an
5 organoaluminum compound at a temperature of -30 to 30°C,
followed by heat-treatment of the reduced solid product at
a temperature of 120 to 180°C, etc. can be referred to.

However, titanium trichloride produced by these
processes is not satisfactory in catalyst activity and
10 stereospecificity.

In Japanese Patent Publication No. 53-3356, a
process which comprises reducing titanium tetrachloride
with an organoaluminum compound to obtain a reduced solid
material, followed by treating the reduced solid material
15 with a complexing agent and further reacting it with
titanium tetrachloride is mentioned. Further, in Japanese
Patent Application Kokai (Laid-Open) No. 59-126401, a
process which
comprises reducing a titanium compound represented by the
20 following general formula:



with an organoaluminum compound, followed by treating the
reduced product with a mixture consisting of an ether
compound and titanium tetrachloride is mentioned. If an α -
25 olefin is polymerized with a catalyst system comprising a
solid catalyst component obtained according to these



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1 processes and an organoaluminum compound, however, catalyst
activity is not yet satisfactorily high, though the result-
ing α -olefin polymer has a high stereo- specificity.

It is also known that titanium trichloride can
5 be synthesized by reducing titanium tetrachloride with an
organomagnesium compound such as a Grignard reagent.

The present inventors previously proposed a
process which comprises reducing titanium tetrachloride
with an organomagnesium compound to obtain a solid product
10 and treating said solid product with a Lewis acid
(Japanese Patent Publication No. 57-24361) and a process
which comprises reducing an alkoxytitanium compound with
an organomagnesium compound in the presence of an organic
silicon compound having Si-O bond to obtain a solid
15 product and treating said solid product with a mixture
consisting of an ester compound and an ether compound
(Japanese Patent Application Kokai (Laid-Open) No.
61-287904).

The catalysts obtained by these processes cannot
20 yet give α -olefin polymer having a satisfactory
stereospecificity, though they exhibit a high catalytic
activity in the polymerization of α -olefins.

In view of the above-mentioned situation, the
25 problem to be solved by this invention, or the object of
this invention, is to provide a process for producing a
solid catalyst for use in the polymerization of olefins



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- 1 having so high a catalytic activity and so high a
stereospecificity as to make the removal of catalyst
residue and amorphous polymer unnecessary.

By the use of the solid catalyst of this
5 invention, the following effects can be achieved.

- (1) Since catalytic activity per solid catalyst and
per titanium atom is very high, the contents of halogen
atom and titanium atom in the resulting polymer, closely
related to color, stability and corrosive property of the
10 resulting polymer, can be made quite low without practis-
ing any particular procedure for removing catalyst
residue. That is, the equipment for removing catalyst
residue becomes unnecessary and production cost of olefin
polymer can be reduced.

- 15 (2) Since the decrease in catalytic activity and
stereospecificity in the lapse of polymerization time is
very small, formation of polymer per unit quantity of
catalyst can be increased by prolonging the polymerization
time.

20 Further, the following effects are also
expectable.

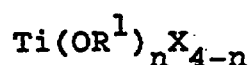
- (3) The use of the solid catalyst of this invention
makes it possible to produce an α -olefin polymer having
a very high stereospecificity. In other words, the
25 formation of amorphous polymer as by-product is very
small. Accordingly, an α -olefin polymer excellent in
mechanical properties can be produced without removing
amorphous polymer.



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- 1 (4) Since the formation of polymer soluble in
polymerization solvent, or a polymer having a low
stereospecificity, is very small, process troubles such as
deposition of polymer onto reactor wall, pipings, flash
5 hopper, etc. do not occur. Further, since formation of
soluble polymer is very small, the starting monomer can be
utilized effectively.

This invention relates to a trivalent titanium
compound-containing solid catalyst for use in the
10 production of olefin polymers which comprises treating a
solid product, obtained by reducing a titanium compound
represented by the following general formula:



- (R¹ represents hydrocarbon group having 1 to 20 carbon
15 atoms, x represents halogen atom, and n represents a
number satisfying 0 < n ≤ 4) with an organomagnesium
compound in the presence of an organic silicon compound
having Si-O bond(s), with an ester compound, followed by
treating it with a mixture consisting of an ester compound
20 and titanium tetrachloride or a mixture consisting of an
ester compound, an ether compound and titanium tetra-
chloride.

By the use of the catalyst system of this
invention, the above-mentioned object of this invention
25 can be achieved.



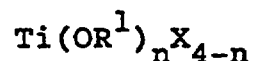
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Figure 1 is a flow chart diagram for facilitating understanding of this invention. This flow chart diagram is nothing other than a typical embodiment of this invention, and it does not limit this invention.

Hereunder, this invention will be explained more concretely.

(a) Titanium compound

10 Titanium compound used in this invention is represented by the following general formula:



(R¹ represents hydrocarbon group having 1 to 20 carbon atoms, X represents halogen atom, and n represents a number satisfying 0 < n ≤ 4).

Concrete examples of R¹ include alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, hexyl, heptyl, octyl, decyl, dodecyl and the like; aryl groups such as phenyl, cresyl, xylyl, naphthyl and the like; cycloalkyl groups such as cyclohexyl, cyclopentyl and the like; allyl groups such as propenyl and the like; and aralkyl groups such as benzyl and the like. Among them, alkyl groups having 2 to 18 carbon atoms and aryl groups having 6 to 18 carbon atoms are preferable, and straight chain alkyl groups having 2



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1 to 18 carbon atoms are particularly preferable. It is
 also possible to use two or more kinds of titanium
 compounds having different OR^1 group.

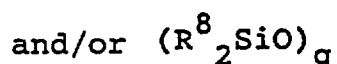
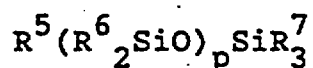
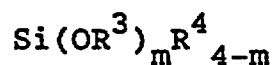
Examples of the halogen atom represented by X
 5 include chlorine, bromine and iodine. Among them,
 chlorine gives a particularly good result.

The value of "n" in the titanium compound
 represented by general formula $Ti(OR^1)_nX_{4-n}$ is a value
 satisfying $0 < n \leq 4$, preferably $2 \leq n \leq 4$, and
 10 particularly $n = 4$.

As the synthetic method of titanium compound
 represented by general formula $Ti(OR^1)_nX_{4-n}$ ($0 < n \leq 4$),
 any of the known methods can be adopted. For example, a
 method of reacting $Ti(OR^1)_4$ with TiX_4 at a desired ratio,
 15 or a method of reacting TiX_4 with the corresponding
 alcohol at a desired ratio can be adopted.

(b) Organic silicon compound having Si-O bond(s)

The organic silicon compounds having Si-O bond(s)
 which can be used in this invention include those
 20 represented by the following general formulae:



wherein R^3 represents hydrocarbon group having 1 to 20



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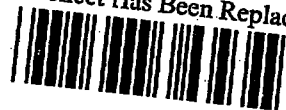
- 1 carbon atoms; R^4 , R^5 , R^6 , R^7 and R^8 each represents hydrocarbon group having 1 to 20 carbon atoms or hydrogen atom; m represents a number satisfying $0 < m \leq 4$; p represents an integer of 1 to 1,000; and q represents an
5 integer of 2 to 1,000.

Concrete examples of the organic silicon compound include tetramethoxysilane, dimethyldimethoxysilane, tetraethoxysilane, triethoxyethylsilane, diethoxydiethylsilane, ethoxytriethylsilane, tetraisopropoxysilane, diisopropoxydiisopropylsilane,
10 tetrapropoxysilane, dipropoxydipropylsilane, tetrabutoxysilane, dibutoxydibutylsilane, dicyclopentoxymethylsilane, diethoxydiphenylsilane, cyclohexyloxytrimethylsilane, phenoxytrimethylsilane,
15 tetraphenoxysilane, triethoxyphenylsilane, hexamethyldisiloxane, hexaethyldisiloxane, hexapropyldisiloxane, octaethyltrisiloxane, dimethylpolysiloxane, diphenylpolysiloxane, methylhydropolysiloxane, phenylhydropolysiloxane, and the like.

- 20 Among these organic silicon compounds alkoxy-silane compounds represented by general formula $Si(OR^3)_m R^4_{4-m}$ wherein m satisfies $1 \leq m \leq 4$ are preferable, and tetraalkoxy-silane compounds satisfying $m = 4$ are particularly preferable.

- 25 (c) Organomagnesium compound

As the organomagnesium compound of this invention, arbitrary types of organomagnesium compounds having magnesium-carbon bond can be used. Particularly,



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1 Grignard compounds represented by general formula R^9MgX
(R^9 represents hydrocarbon group having 1 to 20 carbon
atoms and X represents halogen atom), dialkylmagnesium
compounds and diarylmagnesium compounds represented by
5 general formula $R^{10}R^{11}Mg$ (R^{10} and R^{11} each represents
hydrocarbon group having 1 to 20 carbon atoms) are
preferably usable. In these formulas, R^9 , R^{10} and R^{11} ,
which may be identical or different from one another,
represent alkyl, aryl, aralkyl and alkenyl groups having 1
10 to 20 carbon atoms such as methyl, ethyl, propyl,
isopropyl, butyl, sec-butyl, tert-butyl, amyl, isoamyl,
hexyl, octyl, 2-ethylhexyl, phenyl, benzyl and the like.

Concrete examples of the organomagnesium
compounds are as follows. Thus, examples of the Grignard
15 compounds include methylmagnesium chloride, ethylmagnesium
chloride, ethylmagnesium bromide, ethylmagnesium iodide,
propylmagnesium chloride, propylmagnesium bromide,
butylmagnesium chloride, butylmagnesium bromide, sec-
butylmagnesium chloride, sec-butylmagnesium bromide,
20 tert-butylmagnesium chloride, tert-butylmagnesium bromide,
amylmagnesium chloride, isoamylmagnesium chloride,
phenylmagnesium chloride, phenylmagnesium bromide, and the
like. Examples of the compounds represented by $R^{10}R^{11}Mg$
include diethylmagnesium, dipropylmagnesium, diisopropyl-
25 magnesium, dibutylmagnesium, di-sec-butylmagnesium,
di-tert-butylmagnesium, butyl-sec-butylmagnesium,
diamylmagnesium, diphenylmagnesium, and the like.



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1 As the solvent used in the synthesis of the
above-mentioned organomagnesium compounds, ethereal
solvents such as diethyl ether, dipropyl ether,
diisopropyl ether, dibutyl ether, diisobutyl ether, diamyl
5 ether, diisoamyl ether, dihexyl ether, dioctyl ether,
diphenyl ether, dibenzyl ether, phenetole, anisole,
tetrahydrofuran, tetrahydropyran and the like can be
used. Apart from them, hydrocarbon solvents such as
hexane, heptane, octane, cyclohexane, methylcyclohexane,
10 benzene, toluene, xylene and the like or mixture of the
ethereal solvent and the hydrocarbon solvent are also
usable. The organomagnesium compound is preferably used
in the state of an ethereal solution. As the ether
compound used for this purpose, an ether compound having 6
15 or more carbon atoms in molecule or an ether compound
having cyclic structure is used.

From the viewpoint of catalytic performance, it
is particularly preferable to use a Grignard compound
represented by R^9MgCl in the state of an ethereal
20 solution.

Hydrocarbon-soluble complexes formed between the
above-mentioned organomagnesium compound and an organo-
metallic compound are also usable. As examples of said
organometallic compound, organic compounds of Li, Be, B,
25 Al and Zn can be referred to.

(d) Ester compound

As the ester compound of this invention, mono-
and poly-valent carboxylic esters including aliphatic



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- 1 carboxylic esters, olefinic carboxylic esters, alicyclic carboxylic esters and aromatic carboxylic esters can be used.

Concrete examples of said ester compounds include

- 5 methyl acetate, ethyl acetate, phenyl acetate, methyl propionate, ethyl propionate, ethyl butyrate, ethyl valerate, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl benzoate, butyl benzoate, methyl toluate, ethyl toluate, ethyl anisate, diethyl succinate,
10 dibutyl succinate, diethyl malonate, dibutyl malonate, dimethyl maleate, dibutyl maleate, diethyl itaconate, dibutyl itaconate, monoethyl phthalate, dimethyl phthalate, methyl ethyl phthalate, diethyl phthalate, dipropyl phthalate, diisopropyl phthalate, dibutyl
15 phthalate, diisobutyl phthalate, diheptyl phthalate, dioctyl phthalate, diphenyl phthalate and the like.

- Among these ester compounds, olefinic carboxylic esters such as methacrylic esters, maleic esters and the like and phthalic esters are preferable, and phthalic
20 diesters are particularly preferable.

(e) Ether compound

- As the ether compounds which can optionally be used in this invention, diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, diamyl ether, diisoamyl
25 ether, dineopentyl ether, dihexyl ether, dioctyl ether, methyl butyl ether, methyl isoamyl ether, ethyl isobutyl ether and the like are preferable, among which dibutyl ether and diisoamyl ether are particularly preferable.



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1 (f) Synthesis of solid catalyst

The solid catalysts of this invention are synthesized by treating a solid product obtained by reducing a titanium compound with an organomagnesium compound in the presence of an organic silicon compound with an ester compound and thereafter treating it with a mixture comprising an ester compound and titanium tetrachloride or a mixture comprising an ester compound, an ether compound and titanium tetrachloride.

10 The synthetic reaction is carried out in an atmosphere of inert gas such as nitrogen, argon or the like.

In the first step, a titanium compound is reduced with an organomagnesium compound. The reduction may be carried out by any of a method which comprises adding an organomagnesium compound to a mixture of a titanium compound and an organic silicon compound, and a method which comprises, inversely, adding a mixture of a titanium compound and an organic silicon compound to a solution of an organomagnesium compound. Among these two methods, the method of adding an organomagnesium compound to a mixture comprising a titanium compound and an organic silicon compound is more preferable from the viewpoint of catalytic activity.

25 Preferably, the titanium compound and organic silicon compound are used after dissolving or diluting them with an appropriate solvent.



1 As the solvent used for this purpose, the followings can be referred to: aliphatic hydrocarbons such as hexane, heptane, octane, decane and the like; aromatic hydrocarbons such as toluene, xylene and the like;
5 alicyclic hydrocarbons such as cyclohexane, methylcyclohexane, decalin and the like; and ether compounds such as diethyl ether, dibutyl ether, diisoamyl ether, tetrahydrofuran and the like.

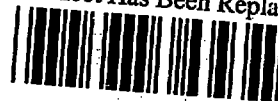
 The reduction is carried out at a temperature
10 ranging from -50 to 70°C, preferably from -30 to 50°C, and particularly preferably from -25 to 35°C. If temperature of the reduction is too high, the catalyst activity decreases.

 It is also possible to synthesize the solid
15 product by reduction in the presence of a porous material such as inorganic oxide, organic polymer or the like so as to impregnate the porous material with the solid product.

 As said porous material, those having a pore
volume of 0.3 ml/g or more as measured at a pore radius of
20 200 to 2,000 angstroms and having a mean particle diameter of 5 to 300 microns are preferable.

 As said porous inorganic oxide, SiO_2 , Al_2O_3 , MgO , TiO_2 , ZrO_2 , $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, $\text{MgO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ and the like can be referred to.

25 As said porous organic polymer, polystyrene type, polyacrylic ester type, polymethacrylic ester type, polyacrylonitrile type, polyvinyl chloride type and polyolefin type polymers can be referred to. Their



1 typical examples include polystyrene, styrene-divinyl-
benzene copolymer, styrene-N,N'-alkylenedimethacrylamide
copolymer, styrene-ethylene glycol dimethacrylate
copolymer, polymethyl acrylate, polyethyl acrylate, methyl
5 acrylate-divinylbenzene copolymer, ethyl acrylate-divinyl-
benzene copolymer, polymethyl methacrylate, methyl
methacrylate-divinylbenzene copolymer, polyethylene glycol
dimethacrylate, polyacrylonitrile, acrylonitrile-
divinylbenzene copolymer, polyvinyl chloride, polyvinyl-
10 pyrrolidine, polyvinylpyridine, ethylvinylbenzene-
divinylbenzene copolymer, polyethylene, ethylene-methyl
acrylate copolymer, polypropylene and the like. Among
these porous materials, SiO_2 , Al_2O_3 and polystyrene type
polymers are particularly preferable.

15 Although the time period of dropping is not
critical, it is usually in the range from about 30 minutes
to about 6 hours. After completion of the reduction, a
post-reaction may be carried out optionally at a tempera-
ture of 20 to 120°C.

20 The amount of organic silicon compound is in the
range of 1 to 50, preferably 3 to 30, and particularly 5
to 25, as expressed in terms of atomic ratio of silicon
atom to titanium atom (Si/Ti) in titanium compound.

 The amount of the organomagnesium compound is in
25 the range of 0.1 to 10, preferably 0.2 to 5.0, and
particularly 0.5 to 2.0, as expressed in terms of atomic
ratio of the sum of titanium atom and silicon atom to
magnesium atom (Ti+Si/Mg).



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1 The solid product obtained by the reduction is separated from liquid and several times washed with inert hydrocarbon solvent such as hexane, heptane or the like.

 The solid product thus obtained contains
5 trivalent titanium, magnesium and hydrocarbyloxy group, and it is generally amorphous or very weakly crystalline. From the viewpoint of catalytic performance, amorphous structure is more desirable than the other.

 The solid product obtained by the above-
10 mentioned procedure is then treated with an ester compound.

 The amount of ester compound is 0.1 to 50 moles, preferably 0.3 to 20 moles, and particularly 0.5 to 10 moles, per one mole of titanium atom in the solid product.

 Per one mole of magnesium atom in the solid
15 product, the ester compound is used in an amount of 0.01 to 1.0 mole, and preferably 0.03 to 0.5 mole. If the amount of ester compound is too large, destruction of particle takes place.

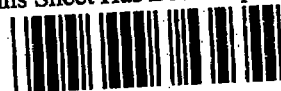
 The treatment of the solid product with the
20 ester compound can be practised according to any known methods such as slurry method, mechanical pulverization using ball mill, and the like, so far as both the materials can be contacted together. However, mechanical pulverization is undesirable from the industrial point of
25 view because a large amount of fine powder is formed in the solid catalyst component which makes particle size distribution broad. Preferably, both the materials are contacted together in the presence of a diluent.



1 As the diluent, aliphatic hydrocarbons such as
pentane, hexane, heptane, octane and the like, aromatic
hydrocarbons such as benzene, toluene, xylene and the
like, alicyclic hydrocarbons such as cyclohexane,
5 cyclopentane and the like, and halogenated hydrocarbons
such as 1,2-dichloroethane, monochlorobenzene and the like
can be used. Among them, aromatic hydrocarbons and
halogenated hydrocarbons are particularly preferable.

 The diluent is used in an amount of 0.1 ml to
10 1,000 ml and preferably 1 ml to 100 ml, per one gram of
the solid product. Temperature of the treatment is -50°C
to 150°C , and preferably 0 to 120°C . Duration of the
treatment is 10 minutes or longer, and preferably 30
minutes to 3 hours. After completion of the treatment,
15 the solid material is separated from liquid and several
times washed with inert hydrocarbon solvent to obtain an
ester-treated solid product.

 In the next step, the ester-treated solid
product is treated with a mixture of ester compound and
20 titanium tetrachloride. This treatment is preferably
carried out in the state of a slurry. As the solvent used
for the slurry formation, aliphatic hydrocarbons such as
pentane, hexane, heptane, octane, decane and the like,
aromatic hydrocarbons such as toluene, xylene and the
25 like, alicyclic hydrocarbons such as cyclohexane,
methylcyclohexane, decalin and the like, and halogenated
hydrocarbons such as dichloroethane, trichloroethane,
monochlorobenzene, dichlorobenzene, trichlorobenzene and



- 1 the like can be referred to. Among them, halogenated hydrocarbons and aromatic hydrocarbons are preferable.

Concentration of the slurry is preferably 0.05 to 0.7 g solid/ml solvent, and particularly 0.1 to 0.5 g
5 solid/ml solvent. The reaction temperature is 30 to 150°C, preferably 45 to 120°C, and particularly 60 to 100°C. Though the reaction time is not critical, it is usually 30 minutes to 6 hours..

- As the method for feeding the ester-treated
10 solid product, the ester compound and titanium tetrachloride, any of a method of adding ester compound and titanium tetrachloride to ester-treated solid and a method of inversely adding ester-treated solid to a solution containing ester compound and titanium
15 tetrachloride may be adopted.

- In the method of adding ester compound and titanium tetrachloride to ester-treated solid, a method of adding ester compound and thereafter adding titanium tetrachloride or a method of simultaneously adding ester
20 compound and titanium tetrachloride are desirable. A method of adding a previously prepared mixture of ester compound and titanium tetrachloride to ester-treated solid is particularly preferable.

- The reaction between ester-treated solid product
25 and ester compound and titanium tetrachloride may be repeated twice or more. From the viewpoint of catalyst activity and stereospecificity, it is preferable to carry out the reaction using a mixture of ester compound and



1 titanium tetrachloride at least twice.

The amount of the ester compound is 0.02 to 30 moles, preferably 0.05 to 15 moles, and particularly 0.1 to 5 moles, per one mole of titanium atom in the solid
5 product.

The amount of titanium tetrachloride is 1 to 1,000 moles, preferably 3 to 500 moles and particularly 10 to 300 moles, per one mole of titanium atom in the solid product. Per one mole of ester compound, the amount of
10 titanium tetrachloride is 30 to 1,000 moles, preferably 50 to 700 moles, and particularly 100 to 500 moles.

The treatment of an ester-treated solid product with a mixture of ester compound and titanium tetrachloride may optionally be carried out in the presence of
15 an ether compound. Said ether compound is used in an amount of 100 moles or less, preferably 50 moles or less and particularly 20 moles or less, per one mole of titanium atom in the solid product.

The trivalent titanium compound-containing solid
20 catalyst obtained according to the above-mentioned process is separated from liquid, several times washed with inert hydrocarbon such as hexane, heptane or the like, and then put to use for polymerization.

From the viewpoint of catalyst activity and
25 stereospecificity, it is preferable to wash the solid catalyst after separated from liquid, with a large amount of halogenated hydrocarbon solvent such as monochlorobenzene or the like or aromatic hydrocarbon solvent such



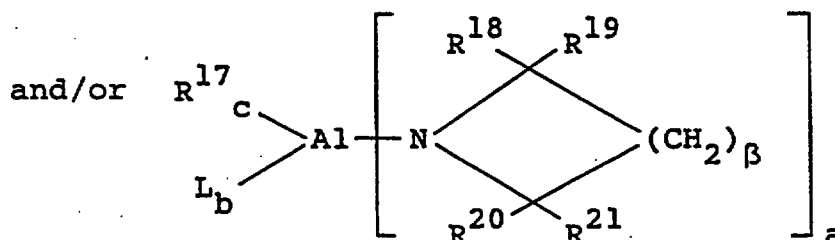
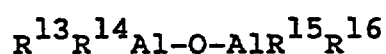
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1 as toluene or the like at a temperature of 50 to 120°C at
 least once and thereafter wash it several times with
 aliphatic hydrocarbon solvent such as hexane or the like,
 and thereafter to use it for polymerization.

5 The solid catalyst of this invention is used for
 polymerization of olefin in combination with an organo-
 aluminum compound and, if desired, additionally with an
 electron donor. Concrete examples of such
 organoaluminum compounds and electron donors
 10 will be shown below.

(g) Organoaluminum compounds

The organoaluminum compounds used in this
 invention in combination with the above-mentioned solid
 catalyst contain at least one aluminum-carbon bond
 15 in their molecule. The following general formulae represent
 typical examples of said organoaluminum compounds:



wherein R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} and
 R^{21} each represents hydrocarbon group having 1 to 20
 carbon atoms; Y and L each represents halogen atom,

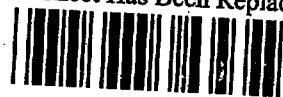


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- 1 hydrogen atom or alkoxy group; γ represents a number satisfying $2 \leq \gamma \leq 3$; β represents a number of 2 or 3; a represents a number satisfying $0 < a < 1$; b represents a number satisfying $0 \leq b < 3$; and c represents a number
5 satisfying $1 \leq c < 3$; provided that $(a+b+c)$ is equal to 3.

- Concrete examples of the organoaluminum compound include trialkylaluminums such as triethylaluminum, triisobutylaluminum, trihexylaluminum and the like;
10 dialkylaluminum hydrides such as diethylaluminum hydride, diisobutylaluminum hydride and the like; mixture of trialkylaluminum and dialkylaluminum halide; mixture of trialkylaluminum and alkylaluminum alkoxide; and alkylalumoxanes such as tetraethyldialumoxane, tetra-
15 butyldialumoxane and the like. Sterically hindered alkylaluminum amides synthesized by reacting an organoaluminum compound such as triethylaluminum, triisobutylaluminum, diethylaluminum halide and the like with an amine compound such as 2,2,5,5-tetramethyl-
20 pyrrolidine, 2,2,6,6-tetramethylpiperidine and the like are also included.

- Among these organoaluminum compounds, trialkyl-
aluminums, mixture of trialkylaluminum and dialkylaluminum halide, alkylalumoxanes and sterically hindered
25 alkylaluminum amides are preferable, and triethylaluminum, triisobutylaluminum, mixture of triethylaluminum and diethylaluminum chloride, tetraethyldialumoxane, reaction product of triethylaluminum and 2,2,6,6-tetramethyl-



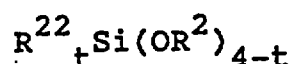
1 piperidine and reaction product of triethylaluminum and
2,2,5,5-tetramethylpyrrolidine are particularly preferable.

The amount of the organoaluminum compound can be
varied in as a wide range as 1 to 1,000 moles per one mole
5 of titanium atom in solid catalyst. Preferably, the
amount of organomagnesium compound is in the range of 5 to
600 moles per one of titanium atom in solid catalyst.

(h) Electron donor

The electron donor optionally used at the time
10 of polymerization is selected from organic silicon
compounds having Si-OR²bond(s) (R² is hydrocarbon group
having 1 to 20 carbon atoms) or Si-N-Cbond(s), aromatic
carboxylic ester compounds and sterically hindered amines.

As said organic silicon compound, alkoxysilane
15 compounds represented by the following general formula:



(R²² and R² represent hydrocarbon group having 1 to 20
carbon atoms and t represents a number satisfying 0 ≤ t ≤
3) are preferably used.

20 As said aromatic carboxylic ester compound,
methyl benzoate, ethyl benzoate, propyl benzoate,
isopropyl benzoate, butyl benzoate, phenyl benzoate,
methyl toluene, ethyl toluate, methyl anisate, ethyl
anisate, monoethyl phthalate, dimethyl phthalate, methyl
25 ethyl phthalate, diethyl phthalate, dipropyl phthalate,



1 diisopropyl phthalate, dibutyl phthalate, diisobutyl
phthalate, diheptyl phthalate, dioctyl phthalate, diphenyl
phthalate and the like can be referred to.

As the sterically hindered amine, 2,6-substi-
5 tuted piperidines, 2,5-substituted pyrrolidines, and
substituted methylenediamine compounds such as N,N,N',N'-
tetramethylmethylenediamine and the like can be referred
to.

Among these electron donor, alkoxysilane
10 compounds represented by the general formula $R^{22}_t(OR^2)_{4-t}$
and 2,6-substituted piperidines give a particularly good
result.

Concrete examples of said alkoxysilane compounds
include tetramethoxysilane, methyltrimethoxysilane,
15 dicyclohexyldimethoxysilane, diisobutyldimethoxysilane,
dioctadecyldimethoxysilane, dimethyldimethoxysilane,
cyclohexyltrimethoxysilane, isobutyltrimethoxysilane,
octadecyltrimethoxysilane, ethyltrimethoxysilane,
phenyltrimethoxysilane, phenylmethyldimethoxysilane,
20 tetraethoxysilane, methyltriethoxysilane, ethyltriethoxy-
silane, vinyltriethoxysilane, phenyltriethoxysilane,
diphenyldimethoxysilane, diphenyldiethoxysilane,
butyltriethoxysilane, tetrabutoxysilane, vinyltributoxy-
silane, diethyldiethoxysilane and the like can be referred
25 to. As example of 2,6-substituted piperidine, 2,2,6,6-
tetramethylpiperidine and the like can be referred to.

The electron donor is used in an amount of 0.01
to 5 moles, preferably 0.03 to 3 moles and particularly



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1 0.05 to 1.0 mole, per one mole of aluminum atom in
organoaluminum compound.

(i) Polymerization of olefin

The method for feeding the catalyst components
5 into polymerization reactor is not critical, so far as
they are fed in a moisture-free state in an inert gas such
as nitrogen, argon or the like.

The solid catalyst, the organoaluminum compound
and the electron donor (optional component) may be fed
10 either separately or after a previous contact between two
of them.

The polymerization can be practised in a wide
temperature range from -30°C to $+300^{\circ}\text{C}$, preferably -5 to
200 $^{\circ}\text{C}$. Though pressure of the polymerization is not
15 critical, a pressure of about 3 to 2,000 atmospheres is
preferable from the viewpoint of industrial applicability
and economy. The mode of polymerization may be any of
continuous system and batch system. Slurry polymerization
and solution polymerization using inert hydrocarbon
20 solvent such as propane, butane, pentane, hexane, heptane
and octane, liquid phase polymerization in the absence of
solvent, and gas phase polymerization are all adoptable, too.

Next, the olefins to which this invention is
applicable are those having 2 or more carbon atoms.
25 Concrete examples of such olefin include ethylene,
propylene, butene-1, pentene-1, hexene-1, 3-methyl-
pentene-1, 4-methylpentene-1, octene-1, decene-1,
dodecene-1 and the like, though this invention is by no



1 means limited by these compounds. The polymerization of
this invention may be any of homopolymerization and
copolymerization. In the copolymerization, two or more
kinds of olefins are mixed together and they are contacted
5 with catalyst in this state to obtain a copolymer. A
heteroblock copolymerization carrying out the polymeriza-
tion in two or more steps can also be carried out easily.
A chain transfer agent such as hydrogen and the like may
be added for the purpose of regulating molecular weight of
10 the resulting polymer.

Next, this invention will be illustrated in more
detail by way of the following examples and comparative
examples.

Example 1

15 (A) Synthesis of the organomagnesium compound

After replacing the inner atmosphere of a one
liter flask equipped with a stirrer, a reflux condenser, a
dropping funnel and a thermometer with argon gas, 32.0 g
of sliced metallic magnesium for Grignard reaction was
20 charged into the flask. Into the dropping funnel were
charged 120 g of butyl chloride and 500 ml of dibutyl
ether, and their about 30 ml was dropped onto the
magnesium placed in the flask to start a reaction. After
start of the reaction, they were continuously dropped at
25 50°C over a period of 4 hours. After completion of the
dropping, the reaction was continued for an additional one
hour at 60°C. Then, the reacted solution was cooled to



1 room temperature, and the solid material was filtered off.

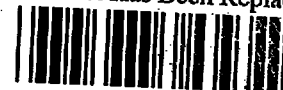
The butylmagnesium chloride dissolved in dibutyl ether was hydrolyzed with 1N sulfuric acid and excessive sulfuric acid was back-titrated with 1N sodium hydroxide
5 solution to determine the concentration of butylmagnesium chloride, using phenolphthalein as indicator. As the result, its concentration was 2.1 moles/liter.

(B) Synthesis of solid product

After replacing the inner atmosphere of a 500 ml
10 flask equipped with a stirrer and a dropping funnel with argon gas, 240 ml of hexane, 5.4 g (15.8 mmoles) of tetrabutoxytitanium and 61.4 g (295 mmoles) of tetraethoxy-
silane were charged to form a homogeneous solution. Then, 150 ml of the organomagnesium compound synthesized in (A)
15 was slowly dropped thereinto from the dropping funnel over a period of 4 hours, while keeping the inner temperature of the flask at 5°C. After dropping it, the mixture was stirred at room temperature for an additional one hour. The solid product was separated from liquid, thrice washed
20 with each 240 ml portions of hexane and dried under reduced pressure to obtain 45.0 g of a brown colored solid product.

The solid product contained 1.7% by weight of titanium atom, 33.8% of ethoxy group and 2.9% by weight of
25 butoxy group.

In the wide angle X ray diffraction pattern of this solid product by Cu-K α ray, no clear diffraction peak was observable at all, demonstrating its amorphous



1 structure.

(C) Synthesis of ester-treated solid product

After replacing inner atmosphere of a 100 ml flask with argon gas, 8.6 g of the solid product

5 synthesized in (B), 43 ml of toluene and 5.8 ml (22 mmoles) of diisobutyl phthalate were charged and reacted at 95°C for one hour.

After the reaction, the solid material was separated from liquid and thrice washed with each 35 ml
10 portions of toluene.

(D) Synthesis of solid catalyst (activating treatment)

After completing the washing step in (C), 21 ml of toluene, 0.48 ml (1.8 mmoles) of diisobutyl phthalate and 12.8 ml (116 mmoles) of titanium tetrachloride were
15 charged into the flask and reacted at 95°C for 3 hours.

After the reaction, the solid product was separated from liquid and washed at that temperature twice with each 43 ml portions of toluene. The above-mentioned treatment using a mixture of diisobutyl phthalate and titanium
20 tetrachloride was repeated once more under the same conditions as above and the solid was thrice washed with each 43 ml portions of hexane to obtain 6.6 g of an other colored solid catalyst.

The solid catalyst thus obtained contained 2.1%
25 by weight of titanium atom, 20.2% by weight of magnesium atom and 17.3% by weight of phthalic ester.

(E) Polymerization of propylene

After replacing the inner atmosphere of a 3



1 liter agitation type autoclave made of stainless steel
with argon gas, 2.6 mmoles of triethylaluminum, 0.39 mmole
of phenyltrimethoxysilane and 7.1 mg of the solid catalyst
synthesized in (C) were charged and hydrogen was
5 introduced until its partial pressure reached 0.33
kg/cm². Then, 780 g of liquefied propylene was charged,
temperature of autoclave was elevated to 80°C, and
polymerization was continued for 2 hours at 80°C. After
the polymerization, the unreacted monomer was purged. The
10 resulting polymer was dried under reduced pressure at 60°C
for 2 hours to obtain 116 g of powdery polypropylene.

This means that the yield (grams) of polypro-
pylene per one gram of solid catalyst component (herein-
after, abbreviated to PP/cat) was 16,300. Proportion (%
15 by weight) of cold xylene-soluble component in the total
polymer (hereinafter referred to as "CXS") was 1.3. Bulk
density (g/ml) of the powdery polypropylene (hereinafter
referred to as BD) was 0.42.

Example 2

20 (A) Synthesis of ester-treated solid products

After replacing inner atmosphere of a 100 ml
flask with argon gas, 6.5 g of the solid product
synthesized in Example 1 (B), 16.2 ml of toluene and 4.3
ml (16 mmoles) of diisobutyl phthalate were charged and
25 reacted at 95°C for one hour.

After the reaction, the solid was separated from
liquid and thrice washed with each 33 ml portions of



1 toluene.

(B) Synthesis of solid catalyst

After completing the washing step of (A), 16.2 ml of toluene, 0.36 ml (1.3 mmoles) of diisobutyl
5 phthalate, 2.2 ml (13 mmoles) of butyl ether and 38.0 ml (346 mmoles) of titanium tetrachloride were charged into the flask and reacted at 95°C for 3 hours. After the reaction, the solid was separated from liquid at 95°C and twice washed at that temperature with each 33 ml portions
10 of toluene, after which the above-mentioned treatment using a mixture of diisobutyl phthalate, butyl ether and titanium tetrachloride was repeated once more under the same conditions as above and the solid was thrice washed with each 33 ml portions of hexane to obtain 5.0 g of an
15 ocher colored solid catalyst.

The solid catalyst contained 2.1% by weight of titanium atom. 19.9% by weight of magnesium atom and 12.7% by weight of phthalic ester.

(C) Polymerization of propylene

20 Propylene was polymerized in the same manner as in Example 1 (E). PP/cat = 22,100; CXS = 1.5; BD = 0.44.

Comparative Example 1

(A) Synthesis of solid catalyst

25 A solid catalyst was synthesized in the same manner as in Example 2, except that, at the time of synthesizing solid catalyst, activating treatment was



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- 1 carried out with a mixture of butyl ether and titanium
tetrachloride without using diisobutyl phthalate.

The solid catalyst thus obtained contained 2.2%
by weight of titanium atom, 20.4% by weight of magnesium
5 atom and 7.4% by weight of phthalic ester.

(B) Polymerization of propylene

Propylene was polymerized in the same manner as
in Example 1 (E)

- PP/cat = 18,200; CXS = 2.4; BD = 0.42. Since
10 activating treatment was carried out with a mixture of
butyl ether and titanium tetrachloride without using
diisobutyl phthalate in this comparative example, the
polymer obtained in this comparative example was inferior
in stereospecificity to the polymers obtained in Examples
15 1 and 2.

Comparative Example 2

(A) Synthesis of solid catalyst

- A solid catalyst was synthesized in the same
manner as in Example 2, except that the ester-treatment
20 preceding the synthesis of solid catalyst was omitted and
the amount of titanium tetrachloride used in the
activating treatment was decreased to 13.5 mmoles per one
gram of solid product. The solid catalyst thus obtained
contained 6.5% by weight of titanium atom, 19.8% by weight
25 of magnesium atom and 10.0% by weight of phthalic ester.

(B) Polymerization of propylene

Propylene was polymerized in the same manner as



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1 in Example 1 (E). PP/cat = 14,000; CXS = 10; BD = 0.16.

Since the ester-treatment preceding the activating treatment was omitted in this comparative example, the polymer obtained herein was much inferior to
5 the polymers obtained in Examples 1 and 2 in stereospecificity and bulk density.

Example 3 to 5

A solid catalyst was synthesized in the same manner as in Example 2, except that the amounts of
10 chemicals used in the ester-treatment and activating treatment were varied as shown in Table 1. Then, propylene was polymerized in the same manner as in Example 1 (E). Conditions of the synthesis and the results are summarized in Table 1.

Table 1

	Catalyst synthesis						
	Ester treatment	Activating treatment			Analyses		
	Amount of DBP (mmole/g)	Amount of DBP (mmole/g)	Amount of Bu ₂ O (mmole/g)	Amount of TiCl ₄ (mmole/g)	Ti (% by wt.)	Mg (% by wt.)	Phthalic ester (% by wt.)
Example 1	2.5	0.2	0	13.5	2.1	20.2	17.3
" 2	"	"	2.0	53.2	2.1	19.9	12.7
Comparative Example 1	"	0	"	"	2.2	20.4	7.4
" 2	0	0.2	"	13.5	6.5	19.8	10.0
Example 3	2.5	0.4	"	53.2	2.1	20.1	17.9
" 4	"	0.1	"	13.5	1.7	20.2	12.3
" 5	1.0	0.2	"	"	2.2	20.1	15.6

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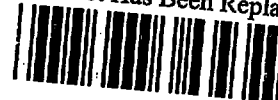


Table 1 (cont'd)

Results of polymerization		
PP/cat	CXS	BD
(g/g)	(% by wt.)	(g/ml)
16,300	1.3	0.42
22,100	1.5	0.44
18,200	2.4	0.42
14,000	10	0.16
24,300	1.1	0.43
18,900	1.1	0.42
30,700	1.1	0.42

The amounts of reagents are expressed by millimoles reagent/one gram solid product.





1 Example 6

(A) Synthesis of solid product

After replacing inner atmosphere of a 300 ml flask equipped with a stirrer and a dropping funnel with
5 argon gas, 18.6 g of a styrene-divinylbenzene copolymer which had been dried under reduced pressure at 100°C for 3 hours (mean particle diameter was 40 microns; pore volume in pore radius range of 200 to 2,000 angstroms was 0.99 ml/g as measured by means of porosimeter), 93 ml of
10 heptane, 1.29 g (3.8 mmoles) of tetrabutoxytitanium and 13.3 g (63.8 mmoles) of tetraethoxysilane were charged into the flask and stirred at 30°C for 30 minutes. Then, 33.8 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped thereinto from the dropping
15 funnel over a period of 45 minutes, while keeping the inner temperature of the flask at 5°C. After dropping it, the mixture was stirred at 30°C for 45 minutes, twice washed with each 95 ml portions of heptane, and dried under reduced pressure to obtain 29.5 g of a brown colored
20 solid product.

The solid product thus obtained contained 0.5% by weight of titanium atom.

(B) Synthesis of ester-treated solid

After replacing inner atmosphere of a 100 ml
25 flask with argon gas, 4.3 g of the solid product synthesized in the reduction step of (A), 14.3 ml of toluene and 0.77 ml (2.3 mmoles) of diisobutyl phthalate were charged and reacted at 95°C for 30 minutes. After



1 the reaction, solid material was separated from liquid,
and it was twice washed with each 14.3 ml portions of
toluene.

(C) Synthesis of solid catalyst (activating treatment)

5 After completing the washing step of (B), 14.3
ml of toluene, 0.066 ml (0.24 mmole) of diisobutyl
phthalate, 0.57 ml (3.4 mmoles) of butyl ether and 8.6 ml
(78 mmoles) of titanium tetrachloride were charged and
reacted at 95°C for 3 hours. After the reaction, solid
10 material was separated at 95°C from liquid and twice
washed with each 14.5 ml portions of toluene at the same
temperature. The above-mentioned treatment using a
mixture of diisobutyl phthalate, butyl ether and titanium
tetrachloride was repeated once more over a period of one
15 hour, and the solid was twice washed with each 14.5 ml
portions of heptane and then dried under reduced pressure
to obtain 3.9 g of a brown colored solid product.

The solid catalyst thus obtained contained 0.5%
by weight of titanium atom, 4.5% by weight of magnesium
20 atom and 3.8% by weight of phthalic ester.

(C) Polymerization of propylene

Propylene was polymerized in the same manner as
in Example 1 (E). PP/cat = 3,240; CXS = 1.4; BD = 0.45.

Example 7

25 (A) Synthesis of pre-polymerization catalyst

After replacing inner atmosphere of a 300 ml
flaks equipped with a stirrer with argon gas, 7.6 ml of a



1 product prepared by contacting 8.7 mmoles of 2,2,6,6-
tetramethylpiperidine with 100 ml of a 0.29 mole/liter
solution of triethylaluminum in heptane at 60°C for 3
hours, 250 ml of heptane and 1.25 g of the solid catalyst
5 synthesized in Example 5 were charged into the flask and
kept at 30°C. Then, propylene was introduced into the
flask at atmospheric pressure and polymerized for 20
minutes. A part of the resulting slurry was sampled out
and the quantity of polymerization was determined. PP/cat
10 was 4.7.

(B) Polymerization of propylene

After replacing inner atmosphere of an 8 liter
agitation type autoclave made of stainless steel with
argon gas, 9.0 ml of the solution prepared in (A) by
15 contacting 2,2,6,6-tetramethylpiperidine with triethyl-
aluminum and 1 ml of the pre-polymerization catalyst
slurry synthesized in (A) were charged, and then hydrogen
was fed until its partial pressure reached 0.33 kg/cm^2 .
Then, 780 g of liquefied propylene was charged and
20 temperature of the autoclave was elevated to 80°C, after
which polymerization was continued at 80°C for 2 hours.
After the polymerization, the unreacted monomer was
purged, and the formed polymer was dried under reduced
pressure at 60°C for 2 hours to obtain 255 g of powdery
25 polypropylene.

The polymer thus obtained contained 4.0 ppm by
weight of magnesium atom. CXS = 3.6; BD = 0.40.

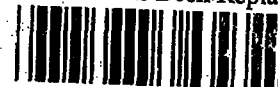


1 product prepared by contacting 8.7 mmoles of 2,2,6,6-
tetramethylpiperidine with 100 ml of a 0.29 mole/liter
solution of triethylaluminum in heptane at 60°C for 3
hours, 250 ml of heptane and 1.25 g of the solid catalyst
5 synthesized in Example 5 were charged into the flask and
kept at 30°C. Then, propylene was introduced into the
flask at atmospheric pressure and polymerized for 20
minutes. A part of the resulting slurry was sampled out
and the quantity of polymerization was determined. PP/cat
10 was 4.7.

(B) Polymerization of propylene

After replacing inner atmosphere of an 8 liter
agitation type autoclave made of stainless steel with
argon gas, 9.0 ml of the solution prepared in (A) by
15 contacting 2,2,6,6-tetramethylpiperidine with triethyl-
aluminum and 1 ml of the pre-polymerization catalyst
slurry synthesized in (A) were charged, and then hydrogen
was fed until its partial pressure reached 0.33 kg/cm^2 .
Then, 780 g of liquefied propylene was charged and
20 temperature of the autoclave was elevated to 80°C, after
which polymerization was continued at 80°C for 2 hours.
After the polymerization, the unreacted monomer was
purged, and the formed polymer was dried under reduced
pressure at 60°C for 2 hours to obtain 255 g of powdery
25 polypropylene.

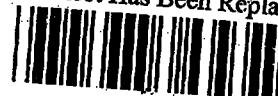
The polymer thus obtained contained 4.0 ppm by
weight of magnesium atom. CXS = 3.6; BD = 0.40.



1 The polymer thus obtained contained 5.5 ppm by
weight of magnesium atom. CXS = 1.6; BD = 0.40.

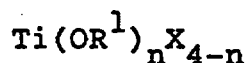
Example 9: Copolymerization of ethylene and butene-1

After sufficiently replacing inner atmosphere of
5 a 0.4 liter autoclave equipped with electromagnetic
stirrer with argon gas, 90 g of butane, 1.0 mmole of
triethylaluminum and 10 g of butene-1 were charged. After
elevating the temperature to 60°C, hydrogen was fed until
the total pressure reached 9 kg/cm² and thereafter
10 ethylene was fed until the total pressure reached 15
kg/cm². Then, 2.1 mg of the solid catalyst synthesized
in Example 5 was added to start a polymerization
reaction. Thereafter, copolymerization of ethylene and
butene-1 was continued for one hour at 60°C, while
15 maintaining the total pressure constant by feeding
ethylene continuously. After completion of the
polymerization, the formed polymer was collected by
filtration and dried under reduced pressure at 60°C.
Yield of the polymer was 29 g. In this experiment,
20 catalyst activity was 630,000 g polymer/g titanium, the
copolymer had 16 ethyl groups per 1,000 carbon atoms.



CLAIMS:

1. A process for producing a trivalent titanium compound-containing solid catalyst for use in the polymerization of olefins which comprises treating, with an ester compound, a solid product obtained by reducing a titanium compound represented by the following general formula:

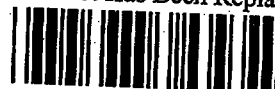


(R^1 represents hydrocarbon group having 1 to 20 carbon atoms, X represents halogen atom, and n represents a number satisfying $0 < n \leq 4$) with an organomagnesium compound in the presence of an organic silicon compound having Si-O bond(s), and thereafter treating the ester-treated solid product with a mixture of an ester compound and titanium tetrachloride.

2. A process according to claim 1, wherein after treating the solid product with an ester compound, the ester-treated solid product is treated with a mixture of an ester compound, an ether compound and titanium tetrachloride.

3. A process according to claim 1, wherein R^1 in the titanium compound represented by the general formula $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$ is alkyl groups having 2 to 18 carbon atoms and aryl groups having 6 to 18 carbon atoms.

4. A process according to claim 3, wherein R^1 in the titanium compound represented by the general formula



$\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$ is straight chain alkyl groups having 2 to 18 carbon atoms.

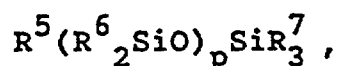
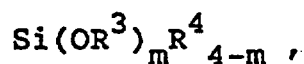
5. A process according to claim 1, wherein the value of n in the titanium compound represented by general formula $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$ is $2 \leq n \leq 4$.

6. A process according to claim 5, wherein the value of n is 4.

7. A process according to claim 1, wherein the organomagnesium compound is one having magnesium-carbon bond.

8. A process according to claim 7, wherein the organomagnesium compound is Grignard compounds represented by general formula R^9MgX (R^9 represents hydrocarbon group having 1 to 20 carbon atoms and X represents halogen atom), dialkylmagnesium compounds or diarylmagnesium compounds represented by general formula $\text{R}^{10}\text{R}^{11}\text{Mg}$ (R^{10} and R^{11} each represents hydrocarbon group having 1 to 20 carbon atoms), among which R^9 , R^{10} and R^{11} are identical or different from one another.

9. A process according to claim 1, wherein the organic silicone compound having Si-O bond(s) is a compound represented by the general formula





wherein R^3 represents hydrocarbon group having 1 to 20 carbon atoms; R^4 , R^5 , R^6 , R^7 and R^8 each represents hydrocarbon group having 1 to 20 carbon atoms or hydrogen atom; m represents a number satisfying $0 < m \leq 4$; p represents an integer of 1 to 1,000; and q represents an integer of 2 to 1,000.

10. A process according to claim 9, wherein the organic silicone compound is an alkoxyasilane compound represented by the general formula $Si(OR^3)_m R^4_{4-m}$ wherein m satisfies $1 \leq m \leq 4$.

11. A process according to claim 10, wherein the alkoxyasilane compound is a tetraalkoxyasilane compound satisfying $m = 4$.

12. A process according to claim 1, wherein the ester compound is mono- or poly-valent carboxylic ester including aliphatic carboxylic esters, olefinic carboxylic esters, alicyclic carboxylic esters and aromatic carboxylic esters.

13. A process according to claim 1, wherein the ether compound is diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, diamyl ether, diisoamyl ether, dineopentyl ether, dihexyl ether, dioctyl ether, methyl butyl ether, methyl isoamyl ether, or ethyl isobutyl ether.

14. A process according to claim 13, wherein the ether compound is dibutyl ether or diisoamyl ether.

15. A process according to claim 1, wherein the organomagnesium compound is added to a mixture of titanium



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compound and an organic silicone compound.

16. A process according to claim 15, wherein the titanium compound and organic silicone compound are used after dissolving or diluting them with an appropriate solvent.

17. A process according to claim 16, wherein the solvent is aliphatic hydrocarbons, aromatic hydrocarbons, alicyclic hydrocarbons, or ether compounds.

18. A process according to claim 1, wherein the reduction is carried out at a temperature ranging from -50 to 70°C.

19. A process according to claim 1, wherein the reduction is carried out in the presence of a porous material having a pore volume of 0.3 ml/g or more as measured at a pore radius of 200 to 2,000 angstroms and having a mean particle diameter of 5 to 300 microns.

20. A process according to claim 19, wherein the porous material is inorganic oxide or organic polymer.

21. A process according to claim 20, wherein the porous inorganic oxide is SiO_2 , Al_2O_3 , MgO , TiO_2 , ZrO_2 , $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$, $\text{MgO} \cdot \text{Al}_2\text{O}_3$ or $\text{MgO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3$.

22. A process according to claim 20, wherein the porous organic polymer is polystyrene type, polyacrylic ester type, polymethacrylic ester type, polyacrylonitrile type, polyvinyl chloride type or polyolefin type polymers.

23. A process according to claim 1, wherein the amount of organic silicon compound is in the range of 1 to 50 as expressed in terms of atomic ratio of silicon atom to titanium atom (Si/Ti) in titanium compound.



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24. A process according to claim 1, wherein the amount of the organomagnesium compound is in the range of 0.1 to 10 as expressed in terms of atomic ratio of the sum of titanium atom and silicon atom to magnesium atom (Ti+Si/Mg).

25. A process according to claim 1, wherein the amount of ester compound for treating the solid product is 0.1 to 50 moles per one mole of titanium atom in the solid product.

26. A process according to claim 1, wherein the amount of ester compound for treating the solid product is used in an amount of 0.01 to 1.0 mole per one mole of magnesium atom in the solid product.

27. A process according to claim 1, wherein the solid product is treated with the ester compound in the presence of a diluent.

28. A process according to claim 27, wherein the diluent is aliphatic hydrocarbons, aromatic hydrocarbons, alicyclic hydrocarbons or halogenated hydrocarbons.

29. A process according to claim 27, wherein the amount of diluent is 0.1-1000 ml per one gram of the solid product.

30. A process according to claim 1, wherein the solid product is treated with the ester compound at -50 to 150°C for 10 minutes or more.

31. A process according to claim 30, wherein the solid product is treated with the ester compound at 0-120°C for 30 minutes to 3 hours.



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32. A process according to claim 1, wherein the ester-treated solid product is treated with a mixture of an ester compound and titanium tetrachloride in a slurry state.

33. A process according to claim 32, wherein a solvent used for slurry is aliphatic hydrocarbons, aromatic hydrocarbons, alicyclic hydrocarbons or halogenated hydrocarbons.

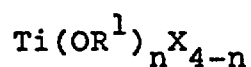
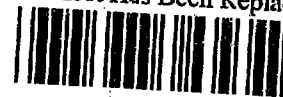
34. A process according to claim 32, wherein a concentration of slurry is 0.05-0.7 g·solid per ml of solvent.

35. A process according to claim 32, wherein the treatment is carried out at a temperature of 30-150°C for 30 minutes to 6 hours.

36. A process according to claim 1, the amount of the ester compound in the mixture for treating the ester-treated solid product is 0.02 to 30 moles per one mole of titanium atom in the ester-treated solid product.

37. A process according to claim 1, wherein the amount of titanium tetrachloride in the mixture for treating the ester-treated solid product is 1 to 1,000 moles per one mole of titanium atom in the ester-treated solid product.

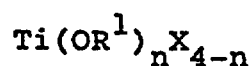
38. A trivalent titanium compound-containing solid catalyst for use in the polymerization of olefins which is produced by treating, with an ester compound, a solid product obtained by reducing a titanium compound represented by the following general formula:



wherein R^1 represents hydrocarbon group having 1 to 20 carbon atoms, X represents halogen atom and n represents a number satisfying $0 < n \leq 4$, with an organomagnesium compound in the presence of an organic silicon compound having Si-O bond(s) and thereafter treating the ester-treated solid product with a mixture of an ester compound and titanium tetrachloride.

39. A trivalent titanium compound-containing solid catalyst according to claim 38, wherein after treating the solid product with an ester compound, the ester-treated solid product is treated with a mixture of an ester compound, an ether compound and titanium tetrachloride.

40. A process for polymerizing olefins which comprises polymerizing olefins by using a trivalent titanium compound-containing solid catalyst produced by treating, with an ester compound, a solid product obtained by reducing a titanium compound represented by the following general formula:

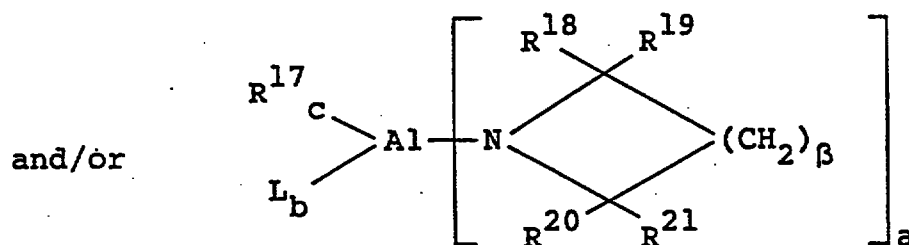
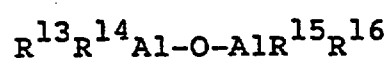


(R^1 represents hydrocarbon group having 1 to 20 carbon atoms, X represents halogen atom, and n represents a number satisfying $0 < n \leq 4$) with an organomagnesium compound in the presence of an organic silicon compound having Si-O bond(s), and thereafter treating the ester-



treated solid product with a mixture of an ester compound and titanium tetrachloride, and an organoaluminum compound.

41. A process for polymerizing olefins according to claim 40, wherein the organoaluminum compound has the general formula



wherein R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} and R^{21} each represents hydrocarbon group having 1 to 20 carbon atoms; Y and L each represents halogen atom, hydrogen atom or alkoxy group; γ represents a number satisfying $2 \leq \gamma \leq 3$; β represents a number of 2 or 3; a represents a number satisfying $0 < a < 1$; b represents a number satisfying $0 \leq b < 3$; and c represents a number satisfying $1 \leq c < 3$; provided that $(a+b+c)$ is equal to 3.

42. A process for polymerizing olefins according to claim 40, wherein an electron donor selected from organic silicon compounds having Si-OR²bond(s) (R² is hydrocarbon group having 1 to 20 carbon atoms) or Si-N-C bond(s), aromatic carboxylic ester compounds and sterically

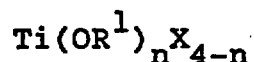


hindered amines are added at the time of polymerization.

43. A process for polymerizing olefins according to claim 40, wherein the olefin is at least one member selected from the group consisting of ethylene, propylene, butene-1, pentene-1, hexene-1, 3-methylpentene-1, 4-methylpentene-1, octene-1, decene-1, and dodecene-1.

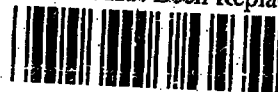
44. A process for polymerizing olefins according to claim 40, wherein the polymerization is carried out at a temperature of -30°C to 300°C under a pressure of about 3 to 2,000 atmospheres.

45. A process for polymerizing olefins which comprises polymerizing olefins by using a trivalent titanium compound-containing solid catalyst produced by treating, with an ester compound, a solid product obtained by reducing a titanium compound represented by the following general formula:

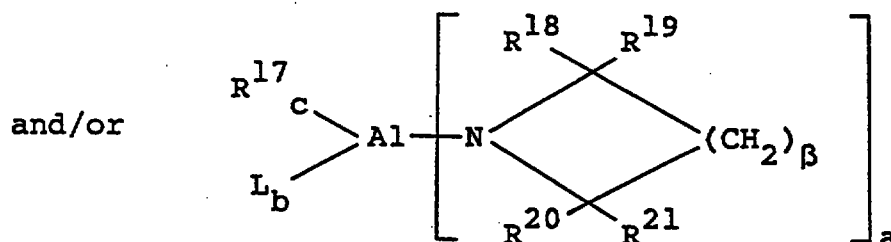
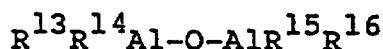
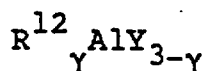


(R^1 represents hydrocarbon group having 1 to 20 carbon atoms, X represents halogen atom, and n represents a number satisfying $0 < n \leq 4$) with an organomagnesium compound in the presence of an organic silicon compound having Si-O bond(s), and thereafter treating the ester-treated solid product with a mixture of an ester compound, an ether compound and titanium tetrachloride, and an organoaluminum compound.

46. A process for polymerizing olefins according to



claim 45, wherein the organoaluminum compound is represented by the general formula



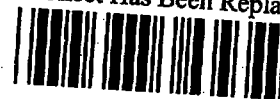
wherein R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} and R^{21} each represents hydrocarbon group having 1 to 20 carbon atoms; Y and L each represents halogen atom, hydrogen atom or alkoxy group; γ represents a number satisfying $2 \leq \gamma \leq 3$; β represents a number of 2 or 3; a represents a number satisfying $0 < a < 1$; b represents a number satisfying $0 \leq b < 3$; and c represents a number satisfying $1 \leq c < 3$; provided that $(a+b+c)$ is equal to 3.

47. A process for polymerizing olefins according to claim 45, wherein an electron donor selected from organic silicon compounds having Si-OR² bond(s) (R² is hydrocarbon group having 1 to 20 carbon atoms) or Si-N-C bond(s), aromatic carboxylic ester compounds and sterically hindered amines are added at the time of polymerization.

48. A process for polymerizing olefins according to claim 45, wherein the olefin is at least one member



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selected from the group consisting of ethylene, propylene, butene-1, pentene-1, hexene-1, 3-methylpentene-1, 4-methylpentene-1, octene-1, decene-1, and dodecene-1.

49. A process for polymerizing olefins according to claim 45, wherein the polymerization is carried out at a temperature of -30°C to 300°C under a pressure of about 3 to 2,000 atmospheres.