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OLEFIN POLYMERIZATION CATALYST AND PROCESS
FOR PRODUCING ETHYLENE COPOLYMERS ✓

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This invention relates to a catalyst for olefin polymerization and a process for producing ethylene copolymers. More particularly, this invention relates to an olefin polymerization catalyst comprising a solid catalyst component exhibiting a very high activity per transition metal in gas phase polymerization process and slurry polymerization process, as well as to a process for producing ethylene copolymers having a narrow molecular weight distribution and a small content of low molecular weight component by the use of said catalyst. Further, this invention relates also to a process for producing ethylene copolymers having a high bulk density, a low fine powder content and a good flow property while controlling the particle shape of solid catalyst component quite excellently.

It is needless to say that a high catalyst activity (quantity of polymerization per unit quantity of catalyst), particularly a high activity per transition metal, is quite valuable industrially because it makes unnecessary the removal of catalyst residue from the polymer after polymerization and thereby simplifies the production process of polymer.

1 On the other hand, it is desirable to minimize
the adhesion of polymer to/^{the}polymerization reactor as much as
possible because the adherent polymer makes various
troubles on the operations and thereby lowers the
5 efficiency of work. Thus, a high bulk density, a narrow
particle size distribution and a good flow property of the
polymer powder are desirable from the viewpoint of
stability and efficiency of operation. Further, molecular
weight distribution and existence (or nonexistence) of low
10 molecular weight component are factors governing trans-
parency, impact resistance and blocking property of
processed articles, and a process capable of producing an
ethylene copolymer having a narrow molecular weight
distribution and a small content of low molecular weight
15 component is desirable.

 In the recent years, catalyst made of a transi-
tion metal compound supported on a carrier such as
titanium tetrachloride and the like were developed
20 (Belgian Patent Application No. 759,601, Japanese Patent
Kokoku (Post-Exam Publn) No. Sho 47-46269, Japanese Patent
Kokoku No. Sho 47-26,383, etc.). Although this type of
catalysts are higher in polymerizing activity than prior
catalysts, they are yet insufficient in the point of
25 catalyst activity per transition metal.

 On the other hand, as a catalyst system made
from a solid product prepared by reducing a titanium
compound with organomagnesium, the solid catalyst

1 component composed of Grignard reagent and titanium
tetrachloride or alkoxy-containing titanium halide
(Japanese Patent Kokai (Laid-Open) No. Sho 46-4,391,
Japanese Patent Kokoku No. Sho 47-40,959, Japanese Patent
5 Kokoku No. Sho 50-30,102, etc.) and the solid catalyst
component prepared by reacting Grignard reagent and
alkoxy-containing titanium halide and treating the
reaction product with titanium tetrachloride (Japanese
Patent Kokoku No. Sho 57-24,361, Japanese Patent Kokai No.
10 Sho 56-115,302, etc.) have been reported. However, these
catalysts are yet insufficient in catalyst activity per
transition metal and particle characteristics of solid
catalyst component.

On the other hand, there have been disclosed a
15 few catalyst components supported on porous inorganic
carriers (Japanese Patent Kokai No. Sho 54-148,093,
56-24,409, 58-179,207, etc.). However, they are yet
insufficient in the point of catalyst activity and
adhesion to polymerization reactor.

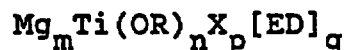
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In view of the above-mentioned state of the art,
the problem to be solved by this invention
consists in providing a solid catalyst
component having so high a catalyst activity per transi-
25 tion metal as to make the removal of catalyst residue
unnecessary and a process for producing an ethylene
copolymer having a narrow molecular weight distribution, a

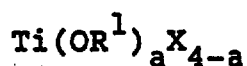
- 1 small content of low molecular weight component, a high bulk density, a small content of fine powder and a good flow property by the use of said catalyst.

This invention provides an olefin polymerization catalyst comprising:

(A) a solid catalyst component containing a tri-valent titanium, which is represented by the composition formula



(wherein R is a hydrocarbon group having 1 to 20 carbon atoms, X is halogen, ED is an electron donative compound, and m, n, p and q are each a number satisfying $1 \leq m \leq 51$, $0 < n \leq 5$, $5 \leq p \leq 106$ and $0.2 \leq q \leq 2$), obtained by reducing a titanium compound represented by the general formula



- 15 (wherein R^1 is a hydrocarbon group having 1 to 20 carbon atoms, X is a halogen atom and a is a number satisfying $0 < a \leq 4$), with an organomagnesium compound in the presence of an organic silicon compound having at least one Si-O bond and an organic porous polymer, treating the resulting solid product with an ester compound and then reacting it with titanium tetrachloride or a mixture of titanium tetrachloride and an electron donative compound, and

1 (B) an organoaluminum compound,
as well as a process for producing an ethylene copolymer
comprising copolymerizing ethylene and at least one
alpha-olefin having 3 or more carbon atoms by the use of
5 said polymerization catalyst.

According to the process of this invention for
producing ethylene copolymer, the quantity of residual
catalyst in the formed polymer is so small that the step
for removal of catalyst can be omitted, owing to the high
10 catalyst activity per transition metal. Further, adhesion
of polymer to ^{the} polymerization reactor is small at the time
of polymerization, and the resulting polymer has a narrow
particle size distribution, a nearly spherical or drawn
spherical shape, a high bulk density and a good flow
15 property, so that the step for pelletization can be
omitted. Thus, the process of this invention is quite
excellent in efficiency of polymerization and work-
ability. Further, it enables to produce a copolymer
having a narrow molecular weight distribution and having a
20 small content of low molecular weight component.

Figure 1 is a flow chart diagram facilitating
understanding of this invention. This flow chart is a
mere typical example of embodiment of this invention and
25 by no means limits this invention.

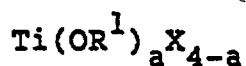
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Next, this invention will be illustrated below concretely.

(a) Titanium compound

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The titanium compound used in this invention is represented by the following general formula:



wherein R^1 represents a hydrocarbon group having 1 to 20 carbon atoms, X represents a halogen atom, and a represents a number satisfying $0 < a \leq 4$.

10

Concrete examples of R^1 include alkyl groups such as methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl, amyl, iso-amyl, hexyl, heptyl, octyl, decyl, and dodecyl; aryl groups such as phenyl, cresyl, xylyl, and naphthyl; cycloalkyl groups such as cyclohexyl and cyclopentyl; allyl groups such as propenyl; and aralkyl groups such as benzyl.

15

Among the above-mentioned groups, alkyl groups having 2 to 18 carbon atoms and aryl groups having 6 to 18 carbon atoms are preferred, and straight chain alkyl groups having 2 to 18 carbon atoms are particularly preferred. It is also possible to use titanium compounds having two or more different OR^1 groups.

Examples of the halogen atom represented by X

- 1 include chlorine, bromine and iodine, among
which chlorine gives a particularly good result.

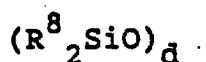
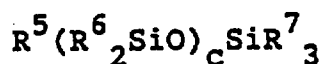
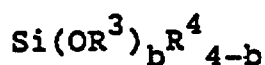
In the titanium compound represented by
 $\text{Ti}(\text{OR}^1)_a\text{X}_{4-a}$, the value of a satisfies $0 < a \leq 4$,

- 5 preferably $2 \leq a \leq 4$, and particularly $a = 4$.

As the method for synthesizing the compound
represented by $\text{Ti}(\text{OR}^1)_a\text{X}_{4-a}$ ($0 < a \leq 4$), any known method
can be employed. For example, a method of reacting
 $\text{Ti}(\text{OR}^1)_4$ and TiX_4 at a necessary ratio, or a method of
10 reacting TiX_4 and a corresponding alcohol at a necessary
ratio can be adopted.

(b) Organic silicon compound having at least one Si-O bond
at least one

The organic silicon compounds having Si-O bond
used in this invention are those represented by the
15 following general formulae:



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

1 1,000.

Concrete examples of the organic silicon compound include the following :

tetramethoxysilane, dimethyldimethoxysilane,
5 tetraethoxysilane, triethoxyethylsilane, diethoxydiethylsilane, ethoxytriethylsilane, tetra-iso-propoxysilane, di-iso-propoxy-di-iso-propylsilane, tetrapropoxysilane, dipropoxydipropylsilane, tetrabutoxysilane, dibutoxydibutylsilane, dicyclopentoxydiethylsilane, diethoxy-
10 diphenylsilane, cyclohexyloxytrimethylsilane, phenoxytrimethylsilane, tetraphenoxysilane, triethoxyphenylsilane, hexamethyldisiloxane, hexaethyldisiloxane, hexapropyldisiloxane, octaethyltrisiloxane, dimethylpolysiloxane, diphenylpolysiloxane, methylhydropolysiloxane, and
15 phenylhydropolysiloxane.

Among these organic silicon compounds, the alkoxy-
silane compounds represented by/general formula $\text{Si}(\text{OR}^3)_b\text{R}^4_{4-b}$ are preferred, and those wherein $1 \leq b \leq 4$ are more preferred, and tetraalkoxy-
silane compounds wherein $b = 4$ are particularly preferred.
20

(c) Organomagnesium compounds

Next, as the organomagnesium compound, any form of organomagnesium compounds having/magnesium-carbon bond at least one
can be used. Particularly, Grignard compounds represented
25 by/general formula R^9MgX wherein R^9 represents a hydrocarbon group having 1 to 20 carbon atoms and X represents a halogen, and dialkylmagnesium compounds or diaryl-

the
1 magnesium compounds represented by/general formula
 $R^{10}R^{11}Mg$ wherein R^{10} and R^{11} each represents a hydrocarbon
group having 1 to 20 carbon atoms are preferably usable.
Here, R^9 and R^{10} may be identical or different, and they
5 represent alkyl, aryl, aralkyl or alkenyl group having 1
to 20 carbon atoms such as methyl, ethyl, propyl, iso-
propyl, butyl, sec-butyl, tert-butyl, amyl, iso-amyl,
hexyl, octyl, 2-ethylhexyl, phenyl and benzyl.

Concrete examples of said Grignard compound
10 include methylmagnesium chloride, ethylmagnesium chloride,
ethylmagnesium bromide, ethylmagnesium iodide,
propylmagnesium chloride, propylmagnesium bromide,
butylmagnesium chloride, butylmagnesium bromide, sec-
butylmagnesium chloride, sec-butylmagnesium bromide,
15 tert-butylmagnesium chloride, tert-butylmagnesium bromide,
amylmagnesium chloride, iso-amylmagnesium chloride,
phenylmagnesium chloride, and phenylmagnesium bromide.

Concrete examples of the compound represented by
 $R^{10}R^{11}Mg$ include diethylmagnesium, dipropylmagnesium,
20 diisopropylmagnesium, dibutylmagnesium, di-sec-butyl-
magnesium, di-tert-butylmagnesium, butyl-sec-butyl-
magnesium, diamylmagnesium, ^{and} diphenylmagnesium.

In the synthesis of the above-mentioned
25 organomagnesium compounds, ethereal solvents can be used,
such as diethyl ether, dipropyl ether, di-iso-propyl
ether, dibutyl ether, di-iso-butyl ether, diamyl ether,
di-iso-amyl ether, dihexyl ether, dioctyl ether, diphenyl

- 1 ether, dibenzyl ether, phenetole, anisole, tetrahydro-
furan and tetrahydropyran; and hydrocarbon
solvents such as hexane, heptane, octane, cyclohexane,
methylcyclohexane, benzene, toluene and xylene;
5 and solvent mixtures consisting of these ethereal solvents
and hydrocarbon solvents are also usable. The organo-
magnesium compound is preferably used in a state of an
ethereal solution. For this purpose, ether compounds
having 6 or more carbon atoms in their molecule or ether
10 compounds having a cyclic structure are used.

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

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

(d) Organic porous polymers

- 20 As examples of the organic porous polymer
carrier used in this invention, porous polymer beads made
a polymer of the
of/polystyrene type, polyacrylic ester type, polymetha-
crylic ester type, polyacrylonitrile type, polyvinyl
chloride type and polyolefin type can be
25 referred to. Concrete examples of said polymer include
polystyrene, styrene-divinylbenzene copolymer, styrene-
N,N'-alkylene dimethacrylamide copolymer, styrene-ethylene

- 1 glycol-di(methyl methacrylate) copolymer, polymethyl
acrylate, polyethyl acrylate, methyl acrylate-divinyl-
benzene copolymer, ethyl acrylate-divinylbenzene
copolymer, polymethyl methacrylate, methyl methacrylate-
5 divinylbenzene copolymer, polyethylene glycol-di(methyl
methacrylate), polyacrylonitrile, acrylonitrile-
divinylbenzene copolymer, polyvinyl chloride,
polyvinylpyrrolidone, polyvinylpyridine, ethylvinyl-
benzene-divinylbenzene copolymer, polyethylene, ethylene-
10 methacrylate copolymer and polypropylene.

Among these organic porous polymer carriers,
porous polymer beads of polystyrene type, polyvinyl
chloride type, polyolefin type and polyacrylonitrile type
are preferred, and polystyrene, styrene-divinylbenzene
15 copolymer and polyvinyl chloride are more preferred.

The mean particle diameter of the organic porous
polymer carrier is 5 to 1,000 μm , preferably 10 to
500 μm , and particularly 15 to 200 μm . Its pore
10 to 500 nm
volume in the pore radius range of (100 to 5,000 angstroms)
20 is 0.1 cm^3/g or above, preferably 0.2 cm^3/g or above, and
particularly 0.3 cm^3/g or above. If ^{the}pore volume of the
organic porous polymer carrier is too small, catalyst
component cannot be impregnated therein effectively.
Even if ^{the}pore volume of the organic porous polymer carrier
25 is 0.1 cm^3/g or above, ^{the}catalyst component cannot be
impregnated effectively if said pore radius is out of the
10 to 500
range of (100 to 5,000 angstroms).

1 (e) Ester compound

As the ester compound used in this invention,
esters of mono- and poly-basic carboxylic acids including
aliphatic carboxylic esters, olefinic carboxylic esters,
5 alicyclic carboxylic esters and aromatic carboxylic esters
are used. Concrete examples of the ester compound include
methyl acetate, ethyl acetate, phenyl acetate, methyl
propionate, ethyl propionate, ethyl butyrate, ethyl
valerate, methyl acrylate, ethyl acrylate, methyl
10 methacrylate, ethyl benzoate, butyl benzoate, methyl
toluate, ethyl toluate, ethyl anisate, diethyl succinate,
dibutyl succinate, diethyl malonate, dibutyl malonate,
dimethyl maleate, dibutyl maleate, diethyl itaconate,
dibutyl itaconate, monoethyl phthalate, dimethyl
15 phthalate, methyl ethyl phthalate, diethyl phthalate,
dipropyl phthalate, diisopropyl phthalate, dibutyl
phthalate, diisobutyl phthalate, diheptyl phthalate,
and
dioctyl phthalate, /diphenyl phthalate.

Among these ester compounds, olefinic carboxylic
20 esters such as methacrylic esters and maleic ester and
phthalic esters are preferred, and phthalic diesters are
particularly preferred.

(f) Electron donative compound

As the electron donative compound of this
e.g.
25 invention, /ester compounds, ether compounds, ^{or}ketone
compounds can be used.

As the ester compound, esters of mono- and

1 poly-basic carboxylic acids including aliphatic carboxylic
esters, olefinic carboxylic esters, alicyclic carboxylic
esters and aromatic carboxylic esters are usable. Concrete
examples of the ester compound include methyl acetate,
5 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, dibutyl succinate,
10 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 phthalate, diisobutyl
15 phthalate, diheptyl phthalate, dioctyl phthalate, ^{and} diphenyl
phthalate .

Among these ester compounds, olefinic carboxylic
esters such as methacrylic esters and maleic ester and
phthalic esters are preferred, and phthalic diesters are
20 particularly preferred.

As the ether compound, dialkyl ethers such as
diethyl ether, dipropyl ether, diisopropyl ether, dibutyl
ether, diamyl ether, di-iso-amyl ether, dineopentyl ether,
dihexyl ether, dioctyl ether, methyl butyl ether, methyl
25 iso-amyl ether, and ethyl iso-butyl ether are preferred.

Among them, dibutyl ether and di-iso-amyl ether
are particularly preferred.

1 As the ketone compound, acetone, methyl ethyl
ketone, diethyl ketone, acetophenone, propiophenone,
and
benzophenone, cyclohexanone, 2,4-pentadione, / 1-phenyl-1,3-
butanedione can be referred to.

5 These electron donative compounds may be used
either alone or in the form of a mixture with one or
more compounds.

(g) Synthesis of titanium catalyst component

 The titanium catalyst component of this
10 invention is synthesized by reducing a titanium compound
represented by ^{the} general formula $Ti(OR^1)_aX_{4-a}$ with an
organomagnesium compound in the presence of an organic
silicon compound having ^{at least one} Si-O bond and an organic porous
polymer to obtain a solid product, and thereafter treating
15 the resulting solid product with an ester compound and
then with titanium tetrachloride or a mixture of titanium
chloride and ^{at least one} electron donative compound. At this time, it
is preferable that, upon the reduction, a solid is
deposited on the particles of ^{the} organic porous polymer and
20 the solid product retains the shape of ^{the} organic porous
polymer without formation of ^a fine powder.

 As the method for reducing a titanium compound
with an organomagnesium compound, addition of an
organomagnesium compound to a mixture of a titanium
25 compound, an organic silicon compound and an organic
porous polymer can be referred to.

1 Preferably, the titanium compound, organic silicon compound and organic porous polymer are dissolved or diluted with an appropriate solvent and then put to use.

As said solvent, aliphatic hydrocarbons such as
5 hexane, heptane, octane and decane, aromatic
hydrocarbons such as toluene and xylene,
alicyclic hydrocarbons such as cyclohexane, methylcyclo-
hexane and decalin, and ethers such as diethyl
ether, dibutyl ether, diisoamyl ether and tetrahydrofuran
10 can be used.

The temperature of the reduction is in the range of -50°C to 70°C , preferably -30°C to 50°C , and particularly -25°C to 35°C .

the
Although/period of the dropping is not critical,
15 it is usually about 30 minutes to 6 hours. After
completion of the reduction, a post reaction may be
effected additionally at a temperature of 20°C to 120°C.

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

The organomagnesium compound is used in an amount of 0.1 to 10, preferably 0.2 to 5.0, and particularly 0.5 to 2.0, as expressed in terms of the ratio of the sum of the titanium atoms and the silicon atoms to the magnesium atoms ((Ti+Si)/Mg). That is, the quantities of the titanium compound, the organic silicon compound and the organo-magnesium compound may be decided so that the value of m

1 expressing the molar ratio of Mg to Ti in the composition formula
Mg_mTi(OR)_nX_p(ED)_q of the titanium catalyst component comes
to 1 to 51, preferably 2 to 31 and particularly 4 to 26.

The amount of the organic porous polymer is 20
5 to 90% by weight, preferably 30 to 80% by weight, as
expressed in terms of its proportion in^{the}/solid product.

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

10

The solid product thus obtained contains
trivalent titanium, magnesium and hydrocarbyloxy group and
generally shows an amorphous or very weak crystalline
character. ^{An}/amorphous structure is particularly preferable
15 from the viewpoint of catalyst performances.

Next, the solid catalyst obtained above is
treated with an ester compound.

The ester compound is used in an amount of 0.1
to 50 moles, preferably 0.3 to 20 moles, and particularly
20 0.5 to 10 moles, per one mole of titanium atoms in the
solid product. In other words, the amount of^{the}/ester
compound may be decided so that the value of q in the
composition formula Mg_mTi(OR)_nX_p(ED)_q of^{the}/titanium catalyst
component expressing the molar ratio of the electron
25 donative compound to Ti comes to 0.2 to 2.

^{the}
The amount of/ester compound per one mole of
magnesium atoms in the solid product is 0.01 to 1.0 mole,
and preferably 0.03 to 0.5 mole.

1 the
The treatment of the solid product with/ ester
compound can be performed by any method capable of
contacting both materials, such as^a/slurry method and a
mechanical pulverization using a ball mill. However,
5 mechanical pulverization forms a large amount of fine
powder in the solid catalyst component and thereby
broadens the particle size distribution. Therefore, it is
undesirable from the industrial point of view. Prefer-
ably, both materials should be contacted in the
10 presence of a diluent.

As the diluent, aliphatic hydrocarbons such as
pentane, hexane, heptane, and octane, aromatic
hydrocarbons such as benzene, toluene and xylene,
alicyclic hydrocarbons such as cyclohexane and
15 cyclopentane , and halogenated hydrocarbons
such as 1,2-dichloroethane and monochlorobenzene
can be used.

The diluent is used in an amount of 0.1 ml to
1,000 ml, preferably 1 ml to 100 ml, per 1 g of the solid
20 product. /temperature of the treatment is -50°C to 150°C,
and preferably 0°C to 120°C./^{The} period of the treatment is
10 minutes or longer, and preferably 30 minutes to 3
hours. After completion of the treatment, the mixture is
allowed to stand to separate the solid from liquid, after
25 which the solid is washed several times with an inert
hydrocarbon solvent to obtain an ester-treated solid.

The solid product obtained in the above-
mentioned manner is then treated with titanium

1 tetrachloride. This treatment may be carried out in the
presence of an electron donative compound, if desired.
For example, the treatment may be carried out with a
mixture of an ether compound and titanium tetrachloride or
5 with a mixture of an ether compound, an ester compound and
titanium tetrachloride.

the
The treatment of/solid product using titanium
tetrachloride is preferably carried out in the state of a
slurry. As the solvent used for formation of/slurry,
10 aliphatic hydrocarbons such as pentane, hexane, heptane,
octane and decane, aromatic hydrocarbons such as
toluene and xylene, alicyclic hydrocarbons such
as decalin, cyclohexane and methylcyclohexane,
and halogenated hydrocarbons such as dichloroethane,
15 trichloroethane, trichloroethylene, monochlorobenzene,
dichlorobenzene and trichlorobenzene can be
referred to.

The concentration of the slurry is 0.05 to 0.5 g
solid/ml solvent, and particularly 0.1 to 0.3 g solid/ml
20 solvent.

The temperature of the reaction is 30°C to 150°C,
preferably 45°C to 120°C, and particularly 60°C to 100°C.

the
Though/period of the reaction is not critical,
it is usually 30 minutes to 6 hours.

25 The method for combining/solid product and titanium
tetrachloride may be any of the methods of adding titanium
tetrachloride to/solid product and the methods of adding a
solid product into a solution of titanium tetrachloride.

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1 The trivalent titanium-containing solid catalyst
component obtained by the above-mentioned method is
separated from the liquid, washed several times with an inert
hydrocarbon solvent such as hexane and heptane and
5 then put to use in the polymerization.

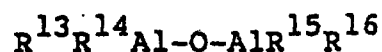
According to another allowable embodiment, the
trivalent titanium-containing solid catalyst component is
separated from ^{the}liquid, washed at least once with a large
quantity of ^a/halogenated hydrocarbon solvent such as
10 monochlorobenzene or an aromatic hydrocarbon
solvent such as toluene or xylene at a tempera-
ture of 50°C to 120°C, and then washed several times with
an aliphatic hydrocarbon solvent such as hexane,
after which it is put to use in ^{the}polymerization.

15 The solid obtained in the above-mentioned manner
is used as a titanium catalyst component.

(h) Organoaluminum compound

The organoaluminum compound used in this
invention in combination with the above mentioned titanium
20 catalyst component has at least one Al-carbon bond in its
molecule.

Typical examples are as follows:



1 wherein R^{12} , R^{13} , R^{14} , R^{15} and R^{16} each represents a hydrocarbon group having 1 to 8 carbon atoms, Y represents halogen, hydrogen or alkoxy group, and γ represents a number satisfying $2 \leq \gamma \leq 3$.

5 Concrete examples of the organoaluminum compound include trialkylaluminums such as triethylaluminum, triisobutylaluminum and trihexylaluminum, dialkylaluminum hydrides such as diethylaluminum hydride, and diisobutylaluminum hydride, dialkylaluminum
10 halide such as diethylaluminum chloride, a mixture of trialkylaluminum and dialkylaluminum halide, and alkylalumoxanes such as tetraethyldialumoxane, and tetrabutylalumoxane.

Among these organoaluminum compounds, trialkyl-
15 aluminum, mixtures of trialkylaluminum and dialkylaluminum halide and alkylalumoxanes are preferred, and triethylaluminum, triisobutylaluminum, ^amixture of triethylaluminum and diethylaluminum chloride, and tetraethyldialumoxane are particularly preferred.

20 The amount of the organoaluminum compound may be appropriately selected in a wide range. For example, it can be selected from a range of 1 to 1,000 moles and preferably 5 to 600 moles, per one mole of titanium atoms in the solid catalyst.

25 (i) Preliminary polymerization

Prior to the copolymerization of ethylene, the titanium catalyst component of this invention may be

1 subjected to a preliminary polymerization. The
preliminary polymerization is carried out by contacting it
with the above-mentioned organoaluminum compound and an
olefin. As the olefin, ethylene, propylene, butene-1 and
5 the like can be used. The preliminary polymerization may
be any of homopolymerization and copolymerization.

The preliminary polymerization may be carried
out in the presence of an electron donative compound,
hydrogen and the like in order to obtain a highly
10 crystalline prepolymer. As the electron donative compound
used for this purpose, organic compounds having ^{at least one} Si-OR
bond, wherein R represents a hydrocarbon group having 1 to
20 carbon atoms, are preferred.

Preferably, the titanium catalyst component of
15 this invention is subjected to ^a preliminary polymerization
in the state of a slurry. As the solvent used for forming
the slurry, aliphatic hydrocarbons such as butane,
pentane, hexane and heptane, and aromatic
hydrocarbons such as toluene and xylene can be
20 referred to.

The concentration of the slurry is preferably 0.001
to 0.5 g solid/ml solvent, and particularly 0.01 to 0.3 g
solid/ml solvent. Preferably, an organoaluminum compound
is used at this time in such an amount as to give an Al/Ti
25 molar ratio of 0.1 to 100, and particularly 0.1 to 10.

The temperature of the preliminary polymerization is
preferably -30°C to 80°C, and particularly -10°C to 50°C.

Preferably, the preliminary polymerization is

1 carried out so as to form 0.1 to 100 g of polymer,
particularly 0.5 to 50 g of polymer, per one gram of^{the} solid
catalyst component.

(j) Production of ethylene copolymer

5 This invention provides a process for copoly-
merizing ethylene and at least one alpha-olefin by the
use of an organoaluminum compound and the above-mentioned
titanium catalyst component or the titanium catalyst
component having been subjected to preliminary polymeri-
10 zation.

Now, the embodiment of the polymerization will
be mentioned below more concretely.

The method for feeding^{the} titanium catalyst
component and^{the} organoaluminum compound into^{the} polymerization
15 reactor is not critical, so far as it is carried out in a
moisture-free state in the presence of an inert gas such
as nitrogen or argon gas or in the presence of e.g.
hydrogen, ethylene or propylene.

The titanium catalyst component and the
20 organoaluminum compound may be fed either separately or
after a previous mutual contact.

The polymerization reaction may be carried out
according to known processes such as ^ausual gas phase
or a
polymerization, /slurry polymerization.

25 The conditions of the polymerization are as
follows. The polymerization is preferably carried
out at a temperature not higher than the temperature at

1 which the polymer melts, preferably 20°C to 100°C and
particularly 40°C to 90°C, under a pressure ranging from
ordinary pressure to ^{39.2 bar} (40 kg/cm²). Further, in the
copolymerization process, hydrogen may be added to the
5 polymerization system for the purpose of regulating the
melt flow property of the final product. The polymeri-
zation process may be carried out according to any of a
continuous system and/^abatch system.

This invention can be applied to alpha-olefins
10 having 3 or more carbon atoms. More concretely speaking,
the alpha-olefins to which this invention is applicable
include propylene, butene-1, pentene-1, hexene-1,
3-methyl-pentene-1 and 4-methylpentene-1, though
this invention is by no means limited to these olefins.
15 According to the polymerization process of this invention,
an ethylene copolymer can be produced by contacting a
mixture of ethylene and at least one alpha-olefin with the
catalyst.

20 Next, the process of this invention will be
illustrated below in more detail with reference to the
following examples. This invention is by no means limited
by these examples.

In the examples, ^{the} properties of ^{the} polymer were
25 measured by the following methods.

The density was determined according to JIS K-6760.

The melt index was measured at 190°C according to

1 JIS K-6760.

The bulk density was measured according to JIS
K-6721.

The melt flow rate (MFR) was adopted as the measure
5 of ^{the}/melt flow property. Herein, MFR is expressed by the
ratio of ^{the}/melt flow at a load of 21.60 kg to ^{the}/melt flow at a
load of 2.160 kg, both measured according to ASTM 1238-57T
(measurement of melt index MI):

$$\text{MFR} = \frac{\text{Melt flow at a load of 21.60 kg}}{\text{Melt flow at a load of 2.160 kg}}$$

It is known that a broader molecular weight
10 distribution generally gives a greater value of MFR.

Example 1

(A) ^{the}Synthesis of/organomagnesium compound

^{the}After replacing/inner atmosphere of a flask
being
having a capacity of one liter and/equipped with a
15 stirrer, a reflux condenser, a dropping funnel and a
thermometer with argon gas, 32.0 g of sliced metallic
magnesium for Grignard reaction was thrown into the flask.

After charging 120 g of butyl chloride and 500
ml of dibutyl ether into the dropping funnel, about 30 ml
20 of their mixture was dropped onto the magnesium in the
flask to start ^{the}/ reaction. After start of the reaction,
the dropping was continued at 50°C over a period of 4
hours. After completing the dropping, the reaction was

1 continued for an additional hour at 60°C. Then, the
the
reaction mixture was cooled to room temperature and/ solid
matter was filtered off.

The butylmagnesium chloride dissolved in the
5 dibutyl ether was hydrolyzed with 1 N sulfuric acid and
back titrated with 1 N aqueous solution of sodium
hydroxide to determine its concentration, by using
phenolphthalein as indicator. As the result, its
concentration was 2.0 moles/liter.

the
10 (B) Synthesis of/ solid product

After replacing^{the} inner atmosphere of a flask
having a capacity of 1,000 ml and^{being} equipped with a stirrer
and a dropping funnel with argon gas, 51.0 g of a
styrene-divinylbenzene copolymer (its mean particle
15 diameter was 50 microns, and its pore volume (cm^3/g) in the
10 to 500 nm
pore radius range of/ 100 to 5,000 angstroms ; hereinafter,
referred to as dVp) was 1.05 cm^3/g as measured with a
porosimeter) which had been dried at 80°C for 5 hours
under reduced pressure, 250 ml of heptane, 4.5 g (13.2
20 millimoles) of tetrabutoxytitanium and 47.5 g (228
millimoles) of tetraethoxysilane were charged into the
flask and stirred at 30°C for 45 minutes.

Then, 120 ml of the organomagnesium compound
synthesized in (A) was dropped from the dropping funnel
25 over a period of 45 minutes, while maintaining the inner
temperature of the flask at 5°C. After dropping it, the
resulting mixture was stirred at 5°C for 45 minutes and

1 then at 30°C for 45 minutes, and then it was washed twice
with 300 ml portions of hexane and dried under reduced
pressure to obtain 85.2 g of a brown colored solid product.

the
(C) Synthesis of/solid catalyst component
the

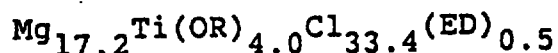
5 After replacing/inner atmosphere of a flask
having a capacity of 500 ml with argon gas, 57.3 g of the
solid product synthesized in the reduction (B), 191 ml of
toluene and 16.0 ml (60 millimoles) of diisobutyl
phthalate were charged into the flask and reacted at 95°C
10 for 30 minutes.

the
After the reaction,/solid matter was separated
the
from/liquid and washed twice with 200 ml portions of
toluene.

After washing it, 191 ml of toluene, 1.2 ml (7
15 millimoles) of butyl ether and 17.2 ml (156 millimoles) of
titanium tetrachloride were added to the flask and reacted
at 95°C for 3 hours. After the reaction,^{the} solid matter was
separated from^{the} liquid at 95°C and washed twice with
200 ml portions of toluene at that temperature.

20 After additionally washing it with a 200 ml
portion of hexane, it was dried under reduced pressure to
obtain 52.8 g of a brown colored solid catalyst component.

The composition of the catalyst component contained
in the organic porous polymer carrier was as follows:



1 (D) Polymerization

After thoroughly replacing^{the} inner atmosphere of an autoclave having a capacity of 5 liters and^{being} equipped with a stirrer with argon gas, 200 g of a sufficiently dried high density polyethylene was fed as a dispersant. After reducing the inner pressure, 22 g of butene-1 was fed and heated to 80°C. Then, hydrogen was fed until the total pressure reached^{2.25 bar} (2.3 kg/cm^2), and then ethylene was fed until^{the} total pressure reached^{8.62 bar} (8.8 kg/cm^2). Then, 12.1 mg of the catalyst component obtained in (C), 2.5 millimoles of triethylaluminum and 15 ml of hexane were fed under a pressure of argon to start^{the} polymerization. Thereafter, a gas phase polymerization was continued at 80°C for 2 hours at a constant total pressure while continuously feeding an ethylene/butene-1 gas mixture (ethylene content 92% by weight).

After completion of the polymerization, the unreacted monomers were purged and the high density polyethylene used as dispersant was removed to obtain 102.1 g of a polymer which was free from fine powder and coarse particles and had good powder characteristics. No adhesion of polymer was observed at all on the inner wall of the autoclave and the stirrer.

The formation (grams) of polymer per 1 gram of titanium atoms, i.e.^{the} catalyst activity, was 1,690,000 g^{of} polymer/g/titanium atoms. The density of this polymer was 0.921 g/cm^3 , its MI was 0.98 g/10 minutes, its MFR was 27.5, and its bulk density was 0.46 g/cm^3 . The proportion of the cold

- 1 xylene-soluble fraction in the total polymer yield
(hereinafter referred to as CXS) was 6.4%. The polymer
powder had a nearly spherical shape, a narrow particle
size distribution and a good flow property. No fine
5 polymer with particles having a size of 125 μm or below was
formed at all.

Comparative Example 1

- A polymerization was carried out in the same
manner as in Example 1 (D), except that 350 mg of the
10 solid product obtained in Example 1 (B) (composition
formula $\text{Mg}_{17.9}\text{Ti}(\text{OR})_{20.9}\text{Cl}_{17.9}(\text{ED})_{0.4}$) was used as
catalyst component.

As the result, only a small quantity of polymer
was obtained.

15 Comparative Example 2

- (A) Synthesis of ^{the}solid product
the

- After replacing/inner atmosphere of a flask
having a capacity of 300 ml and/equipped with a stirrer
and a dropping funnel with argon gas, 20.1 g of the same
20 styrene-divinylbenzene copolymer as in Example 1 (B) which
had been dried at 80°C for one hour under reduced
pressure, 100 ml of heptane and 7.2 g (21.2 millimoles) of
tetrabutoxytitanium were charged into the flask and
stirred at 30°C for 45 minutes.

- 25 Then, 10.6 ml of the organomagnesium compound
synthesized in Example 1 (A) was dropped from the dropping

1 funnel over a period of 20 minutes, while maintaining the
inner temperature of the flask at 5°C. After dropping it,
the resulting mixture was stirred at 5°C for 45 minutes
and then at 30°C for 45 minutes, after which the solid
5 matter was washed thrice with 100 ml portions of
heptane and dried under reduced pressure to obtain 29.8 g
of a brown colored solid product.

the
(B) Synthesis of/solid catalyst component

After replacing^{the} inner atmosphere of a flask
10 having a capacity of 100 ml with argon gas, 9.0 g of the
solid product synthesized in the reduction (A), 45.0 ml of
toluene and 2.5 ml (9.5 millimoles) of diisobutyl
phthalate were charged into the flask and reacted at 95°C
for 30 minutes.

15 After the reaction,^{the}/solid matter was separated
from^{the}/liquid and washed twice with 30 ml portions of
toluene.

After washing it, 30.0 ml of toluene, 0.19 ml
(0.64 millimole) of butyl ether and 2.7 ml (25 millimoles)
20 of titanium tetrachloride were added and reacted at 95°C
for 3 hours. After the reaction,^{the}/solid matter was
separated from^{the}/liquid at 95°C, washed twice at that tempera-
ture with 30 ml portions of toluene, further washed twice
with 30 ml portions of heptane, and dried under
25 reduced pressure to obtain 28.1 g of a red-brown colored
solid.

- 1 The composition of the catalyst component contained
in the organic porous polymer carrier was as follows:



(C) Polymerization

A polymerization was carried out in the same
5 manner as in Example 1 (D), except that 4.2 mg of the
above-mentioned solid catalyst was used as ^{the} catalyst
component.

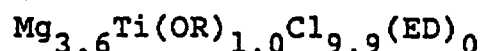
As the result, 64.0 g of a polymer were
^{The} obtained. / catalyst activity was 270,000 g polymer/g of
10 titanium atoms which was much lower than that in Example 1.

Comparative Example 3

(A) ^{the} Synthesis of / solid catalyst component

After replacing ^{the} / inner atmosphere of a flask
having a capacity of 100 ml with argon gas, 8.3 g of the
15 solid product obtained in Example 1 (B), 45 ml of toluene,
0.2 ml (1.2 millimoles) of butyl ether and 2.5 ml (22.7
millimoles) of titanium tetrachloride were charged into
the flask and reacted at 95°C for 3 hours. After the
reaction, ^{the} / solid matter was separated from ^{the} / liquid at 95°C,
20 washed twice at that temperature with 50 ml portions
of toluene, further washed twice with 50 ml portions
of hexane, and dried under reduced pressure to obtain 8.5
g of a brown colored solid catalyst component.

- 1 The composition of the catalyst component contained
in the organic porous polymer carrier was as follows:



(B) Polymerization

- A polymerization was carried out in the same
5 manner as in Example 1 (D), except that 5.7 mg of the
above-mentioned solid catalyst was used as/catalyst
component. As the result, 103 g of a polymer were obtained.
There was found an adhesion of/polymer onto the
inner wall and/stirrer of the autoclave. The catalyst
10 activity was 450,000 g polymer/g/titanium atoms. The density
of this polymer was 0.918/ g/cm³, its MI was 1.72 g/10 minutes,
its MFR was 33.1, and its bulk density was 0.41 g/cm³.
Its CXS was 15.9%.

- As compared with the polymer obtained in Example
15 1, this polymer was broader in molecular weight distri-
bution and larger in the quantity of low molecular weight
product.

Comparative Example 4

(A) Synthesis of/solid product

- 20 After replacing/inner atmosphere of a flask
having a capacity of 300 ml and/equipped with a stirrer
and a dropping funnel with argon gas, 200 ml of heptane,
2.5 g (7.4 millimoles) of tetrabutoxytitanium and 26.0 g

1 (125 millimoles) of tetraethoxysilane were charged into
the flask. A homogenous solution was prepared and
stirred at room temperature for 30 minutes. Then, 66.7 ml
of the organomagnesium compound synthesized in Example 1
5 (A) was slowly dropped from the dropping funnel over a
period of one hour, while maintaining the inner
temperature of the flask at 5°C. After dropping it, the
resulting mixture was stirred at room temperature for one
hour. The solid matter was separated from the liquid,
10 washed thrice with 200 ml portions of heptane and dried under
reduced pressure to obtain 21.5 g of a brown colored solid
product.

the

(B) Synthesis of/solid catalyst component

the

After replacing/inner atmosphere of a flask
15 having a capacity of 200 ml with argon gas, 13.8 g of the
solid product synthesized in the reduction (A), 69 ml of
toluene and 10.1 ml (37.7 millimoles) of diisobutyl
phthalate were charged into the flask and reacted at 95°C
for one hour.

the

20 After the reaction,/solid matter was separated
from the liquid, and washed twice with 69 ml portions of
toluene.

After washing it, 69 ml of toluene, 1.0 ml (6
millimoles) of butyl ether and 13.6 ml (124 millimoles) of
25 titanium tetrachloride were added and reacted at 95°C for
3 hours. After the reaction, the solid matter was
separated from the liquid at 95°C, washed twice at that

1 temperature with 69 ml portions of toluene and further
washed twice with 69 ml portions of n-heptane, and
dried under reduced pressure to obtain 10.4 g of a brown
colored solid catalyst component.

5 (C) Polymerization

Using the above-mentioned solid catalyst, a
polymerization was carried out in the same manner as in
Example 1 (D).

Since in this run the solid catalyst component
10 was not impregnated into ^a porous polymer carrier, ^{the} particle
characteristics of ^{the} product were not good. When the
autoclave was opened and its inside was examined, a part
of ^{the} polymer particles was adherent to the stirrer, etc.
Further, the product contained 1.5% by weight of fine
15 polymer with particles having a particle size of 125 μm or
below.

Example 2

(A) Preliminary polymerization of solid catalyst component

After replacing ^{the} inner atmosphere of a flask
having a capacity of one liter and ^{being} equipped with a stirrer
20 with argon gas, 3.8 g of the solid catalyst component
obtained in Example 1 (C), 500 ml of butane and 2.5
millimoles of triethylaluminum were charged into the
flask. Then, hydrogen gas was introduced until the
pressure reached ^{1.96 bar} (1 kg/cm² gage). Then, while feeding
25 ethylene at a rate of 6 g/g solid catalyst ^{per} hour, the
reaction was continued for a period of 3 hours. After the

1 reaction, the butane was purged, and there were obtained
72.2 g of a preliminary polymerization catalyst. This
catalyst contained 270 ppm of titanium atoms.

(B) Polymerization

5 Using the solid catalyst component prepared
above in a fluidized bed type gas phase polymerization
reactor, a random copolymerization of ethylene and
butene-1 was carried out.

After heating the polymerization reactor to
10 85°C, 300 g of a high density polyethylene powder which
had previously been dried under reduced pressure were added
as a dispersant, and thereafter 5.34 g of triethylaluminum
and 0.22 g of the solid catalyst component prepared above
were charged into the reactor while applying a pressure of
15 a small quantity of hexane. A gaseous mixture consisting
of ethylene, butene-1 and hydrogen which had been prepared
so as to have an ethylene/butene-1/hydrogen molar ratio of
69/24/7 was circulated at a flow rate of 0.3 m/second as
measured in the polymerization reactor at a pressure of 9.8 to 10.29 bar
20 (9 to 9.5 kg/cm² G). When the ethylene/butene-1/hydrogen ratio
deviated from the predetermined value, the necessary
component was additionally added to adjust the molar
ratio. Under such a condition, a fluidized bed gas phase
copolymerization was carried out for 2 hours so that the
25 ratio (L/d) of the polymer height to the reactor diameter in
polymerization reactor retained a value of 2-4. After the

1 polymerization, a quantity, comparable to the amount of the
resulting polymer, of polymer was withdrawn from the
reactor, and the polymer remaining in the reactor was used
as a dispersant for the next run. By repeating the
5 above-mentioned procedure six times, the proportion of the
initially fed high density polyethylene powder in the
polymer became negligible small.

After the polymerization, the polymer was
recovered, and the catalyst activity thereof was determined.

10 As the result, the catalyst activity was 1,540,000 g
polymer/g of titanium atoms. The density of this polymer was
0.921^{g/cm³}, its MI was 1.15 g/10 minutes, its MFR was 27.0, its
bulk density was 0.46 g/cm³, and its CXS was 6.2%.

Similarly to Example 1, the formed polymer had good
15 particle characteristics, and adhesion to ^{the} reactor wall was
hardly observed.

Example 3

(A) ^{the}Synthesis of/solid catalyst component

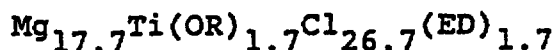
After replacing ^{the}inner atmosphere of a flask
20 having a capacity of 100 ml with argon gas, 8.2 g of the
solid product synthesized in reduction of Example 1 (B),
27.3 ml of toluene and 1.2 ml (4.3 millimoles) of
diisobutyl phthalate were charged into the flask and
reacted at 95°C for 30 minutes.

25 After the reaction, ^{the}/solid matter was separated
from the liquid and washed twice with 40 ml portions of
toluene.

1 After washing the solid matter, 40 ml of toluene, 0.1 ml (0.4 millimole) of diisobutyl phthalate, 0.3 ml (1.8 millimoles) of butyl ether and 4.9 ml (45 millimoles) of titanium tetrachloride were added to the flask and reacted at 95°C for 3 hours. After the reaction, the solid matter was separated from ^{the} liquid at 95°C, and washed twice with 50 ml portions of toluene at that temperature.

Further, it was washed twice with 50 ml portions of hexane and dried under reduced pressure to obtain 8.0 g of a brown colored solid catalyst component.

The composition of the catalyst component contained in the organic porous polymer carrier was as follows:



(B) Preliminary polymerization of ^{the} solid catalyst component

After replacing ^{the} inner atmosphere of a flask having a capacity of one liter and ^{being} equipped with a stirrer with argon gas, 3.8 g of the solid catalyst component obtained in (A), 500 ml of butane, 2.5 millimoles of triethylaluminum and 0.38 millimole of iso-butyltriethoxysilane were charged. While continuously feeding propylene at a rate of 6 g/g solid catalyst ^{per} hour, ^{the} reaction was continued for 4 hours. After the reaction, the butane was purged and there were obtained 72.3 g of a preliminary polymerization catalyst. It contained 262 ppm of titanium atoms.

1 (C) Polymerization

Using the solid catalyst component prepared above a polymerization was carried out in the same manner as in Example 2 (B), except that the ethylene/butene-1/hydrogen
5 molar ratio was altered to 65/23/12.

The catalyst activity was 720,000 g polymer/g of titanium atoms. The density of this polymer was 0.920 g/cm³, its MI was 0.71 g/10 minutes, its MFR was 26.8, its bulk density was 0.45 g/cm³, and its CXS was 8.1%.

10 Similarly to Example 1, the formed polymer had good particle characteristics, and adhesion to^{the} reactor wall was hardly observable.

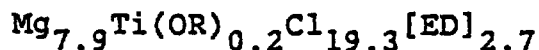
Comparative Example 5

(A) Synthesis of^{the} solid catalyst component

15 After replacing^{the} inner atmosphere of a flask having a capacity of 100 ml with argon gas, 6.1 g of the solid product synthesized in the reduction of Example 1 (B), 30 ml of toluene, 0.7 ml (2.5 millimoles) of diisobutyl phthalate, 2.6 ml (15.4 millimoles) of butyl
20 ether and 36.6 ml (333 millimoles) of titanium tetrachloride were charged into the flask and reacted at 95°C for 3 hours. After the reaction,^{the} solid matter was separated from^{the} liquid at 95°C and washed twice with 50 ml portions of toluene at that temperature.

25 Further, it was washed twice with 50 ml portions of hexane and dried under reduced pressure to obtain 6.2 g of a brown colored solid catalyst component.

- 1 The composition of the catalyst component contained
in the organic porous polymer carrier was as follows:



- (B) Preliminary polymerization of ^{the}solid catalyst component

5 A preliminary polymerization of propylene was
carried out in the same manner as in Example 3 (B), except
that 3.2 g of the catalyst obtained in (A) was used. As
the result, 57.6 g of a preliminary polymerization
catalyst were obtained. It contained 830 ppm of titanium
atoms.

10 (C) Polymerization

A polymerization was carried out in the same
manner as in Example 3 (C), except that the solid catalyst
component prepared above was used.

15 The catalyst activity was 230,000 g polymer/g of
titanium atoms. The density of this polymer was 0.920 g/cm³, its MI
was 0.77 g/10 minutes, its MFR was 30, its bulk density
was 0.43 g/cm³, and its CXS was 9.1%.

This catalyst was lower than that of Example 3
in catalyst activity.

20 Example 4

A polymerization was carried out in the same
manner as in Example 2 (B), except that the composition

1 (molar ratio of ethylene/butene-1/hydrogen) of the gas mixture,
was 75/18/7.

The catalyst activity was 780,000 g polymer/g of
titanium atoms. The density of this polymer was 0.927 g/cm³, its MI
5 was 2.21 g/10 minutes, its MFR was 27.1, its bulk density
was 0.45 g/cm³, and its CXS was 3.7%.

The polymer thus obtained had good particle
characteristics, a narrow molecular weight distribution
and a small content of^a low molecular weight component.

10 Example 5

A polymerization was carried out in the same
manner as in Example 2 (B), except that the gaseous
mixture had a composition (molar ratio ethylene/butene-1/
hydrogen) of 60/34/6.

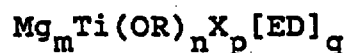
15 The catalyst activity was 620,000 g polymer/g of
titanium atoms. The density of this polymer was 0.911 g/cm³, its MI
was 1.20 g/10 minutes, its MFR was 27.5, and its bulk
density was 0.42 g/cm³.

Although it was an ultra-low density polymer,
20 its particle characteristics were good, and its molecular
weight distribution was narrow.



CLAIMS

1. An olefin polymerization catalyst comprising:
(A) a solid catalyst component containing a tri-valent titanium, which is represented by the composition formula



(wherein R is a hydrocarbon group having 1 to 20 carbon atoms, X is a halogen, ED is an electron donative compound, and m, n, p and q are each a number satisfying $1 \leq m \leq 51$, $0 < n \leq 5$, $5 \leq p \leq 106$ and $0.2 \leq q \leq 2$) obtained by reducing a titanium compound represented by the general formula $\text{Ti}(\text{OR}^1)_a \text{X}_{4-a}$ (wherein R^1 is a hydrocarbon group having 1 to 20 carbon atoms, X is a halogen atom and a is a number satisfying $0 < a \leq 4$) with an organomagnesium compound in the presence of an organic silicon compound at least one having/Si-O bond and an organic porous polymer, treating the resulting solid product with an ester compound and then reacting it with titanium tetrachloride or a mixture of titanium tetrachloride and an electron donative compound, and

(B) an organoaluminum compound.

2. A solid catalyst component according to Claim 1, wherein the R^1 of the titanium compound represented by the general formula $\text{Ti}(\text{OR}^1)_a \text{X}_{4-a}$ is a linear alkyl group having 2 to 18 carbon atoms.



3. A solid catalyst component according to Claim 1, wherein the a of the titanium compound represented by the general formula $\text{Ti}(\text{OR}^1)_a\text{X}_{4-a}$ is a number satisfying $2 \leq a \leq 4$.

4. A solid catalyst component according to Claim 1, wherein the X of the titanium compound represented by the general formula $\text{Ti}(\text{OR}^1)_a\text{X}_{4-a}$ is chlorine.

5. A solid catalyst component according to Claim 1, wherein the organic silicon compound having ^{at least one} Si-O bond is an organic silicon compound represented by the general formula $\text{Si}(\text{OR}^3)_b\text{R}^4_{4-b}$, $\text{R}^5(\text{R}^6_2\text{SiO})_c\text{SiR}^7$ or $(\text{R}^8_2\text{SiO})_d$ (wherein R^3 is a hydrocarbon group having 1 to 20 carbon atoms, R^4 , R^5 , R^6 , R^7 and R^8 are each a hydrocarbon group having 1 to 20 carbon atoms or/hydrogen atom, b is a number satisfying $0 \leq b \leq 4$, c is an integer of 1 to 1000 and d is an integer of 2 to 1000).

6. A solid catalyst component according to Claim 5, wherein b of the organic silicon compound represented by the general formula $\text{Si}(\text{OR}^3)_b\text{R}^4_{4-b}$ is a number satisfying $1 < b \leq 4$.

7. A solid catalyst component according to Claim 1, wherein the organomagnesium compound is a Grignard compound represented by the general formula R^9MgX (wherein R^9 is a hydrocarbon group having 1 to 20 carbon atoms and X is a halogen atom), or/dialkylmagnesium compound or a diarylmagnesium compound represented by the general formula $\text{R}^{10}\text{R}^{11}\text{Mg}$ (wherein R^{10} and R^{11} are each a hydrocarbon group having 1 to 20 carbon atoms).



8. A solid catalyst component according to Claim 1, wherein the organic porous polymer is polystyrene, styrene-divinylbenzene copolymer or polyvinyl chloride.
9. A solid catalyst component according to claim 8, wherein the particles of the organic porous polymer have a mean particle diameter of 5 to 1,000 μm and a pore volume of 0.1 cm^3/g or above at a pore radius of 10 to 500 nm (100 to 5,000 angstroms).
10. A solid catalyst component according to Claim 1, wherein the ester compound is an aliphatic carboxylic acid ester, an olefinic carboxylic acid ester, an alicyclic carboxylic acid ester or an aromatic carboxylic acid ester.
11. A solid catalyst component according to Claim 1, wherein the electron donative compound is an ester compound, an ether compound or a ketone compound.
12. A solid catalyst component according to Claim 11, wherein the ester compound is an aliphatic carboxylic acid ester, an olefinic carboxylic acid ester, an alicyclic carboxylic acid ester or an aromatic carboxylic acid ester.
13. A solid catalyst component according to Claim 1, wherein the organic silicon compound is used in an amount of 1 to 50 in terms of the atomic ratio of the silicon atoms to the titanium atoms (Si/Ti).
14. A solid catalyst component according to Claim 1, wherein the organomagnesium compound is used in an amount of 0.1 to 10 in terms of the atomic ratio of the sum of the titanium atoms and the silicon atoms to the magnesium atoms (Si+Ti/Mg).



15. A solid catalyst component according to Claim 1, wherein the reduction is conducted at a temperature of -50 to 70°C.

16. A solid catalyst component according to Claim 1, wherein the organic porous polymer is used in an amount of 20 to 90% by weight in terms of the proportion in the solid product.

17. A solid catalyst component according to Claim 1, wherein the ester compound is used in an amount of 0.1 to 50 moles per 1 mol of the titanium atoms in the solid product and in an amount of 0.01 to 1.0 mole per 1 mol of ^{the} /magnesium atoms in the solid product.

18. A solid catalyst component according to Claim 1, wherein titanium tetrachloride is used in an amount of 1 to 1000 moles per 1 mol of the titanium atoms in the solid product.

19. An olefin polymerization catalyst according to Claim 1, wherein the organoaluminum compound is a compound having at least one Al-C bond within the molecule and is represented by the general formula $R^{12}AlY_{3-\gamma}$ or $R^{13}R^{14}Al-O-AlR^{15}R^{16}$ (wherein R^{12} , R^{13} , R^{14} , R^{15} and R^{16} are each a hydrocarbon group having 1 to 8 carbon atoms, Y is halogen atom, hydrogen atom or alkoxy group and γ is a number satisfying $2 \leq \gamma \leq 3$).

20. An olefin polymerization catalyst according to Claim 19, wherein the organoaluminum compound is a trialkylaluminum, a mixture of a trialkylaluminum and a dialkylaluminum halide, ^{an} or alkylalumoxane.

21. An olefin polymerization catalyst according to



Claim 1, wherein the organoaluminum compound is used in an amount of 1 to 1000 moles per 1 mol of the titanium atoms in the solid product.

22. A process for producing an ethylene copolymer comprising copolymerizing ethylene and at least one alpha-olefin having 3 or more carbon atoms by the use of the ethylene polymerization catalyst according to Claim 1.

23. A process for producing an ethylene copolymer according to Claim 22, wherein the process is carried out at a temperature not higher than the temperature at which the polymer melts.

24. A process for producing an ethylene copolymer according to Claim 22, wherein the process is carried out at a temperature of 20 to 100°C and under a pressure ranging from ordinary pressure to 39.2 bar (40 kg/cm²).

25. A process for producing an ethylene copolymer according to Claim 22, wherein the alpha-olefin having 3 or more carbon atoms is propylene, butene-1, pentene-1, hexene-1, 3-methyl-pentene-1 or 4-methylpentene-1.