COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

594162

~~I~~
We

SHELL OIL COMPANY , of
900 Louisiana,
Houston,
Texas 77001,
United States of America

hereby apply for the grant of a Standard Patent for an invention entitled:

"PROCESS FOR PREPARING OLEFIN POLYMERIZATION CATALYST COMPONENT"

which is described in the accompanying ~~provisional~~ complete specification.

Details of basic application(s):—

Number	Convention Country	Date
875845	United States of America	18th June 1986

APPLICATION ACCEPTED AND AMENDMENTS
ALLOWED 13 . 12 . 89

LODGED AT SUB-OFFICE
15 JUN 1987
Melbourne

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this 15th day of June 1987

To: THE COMMISSIONER OF PATENTS

K. W. Rimington

(a member of the firm of DAVIES & COLLISON for and on behalf of the Applicant).

Davies & Collison, Melbourne and Canberra.

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952–1973

DECLARATION IN SUPPORT OF CONVENTION OR NON–CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

Insert title of invention

In support of the Application made for a patent ~~patent of addition~~ for an invention entitled: "Process for preparing olefin polymerization catalyst component"

Insert full name(s) and address(es) of declarant(s) being the applicant( ) or person(s) authorized to sign on behalf of an applicant company.

I ~~We~~ RAND N. SHULMAN, Assistant General Counsel of: SHELL OIL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America of:900, Louisiana, Houston, Texas 77001, United States of America.

Cross out whichever of paragraphs 1(a) or 1(b) does not apply

1(a) relates to application made by individual(s)

1(b) relates to application made by company; insert name of applicant company.

do solemnly and sincerely declare as follows :–

~~1(a) I am We are the applicant for the patent patent of addition~~

or (b) I am authorized by
SHELL OIL COMPANY,

the applicant............. for the patent ~~patent of addition~~ to make this declaration on its ~~their~~ behalf

Cross out whichever of paragraphs 2(a) or 2(b) does not apply

2(a) relates to application made by inventor(s)

2(b) relates to application made by company(s) or person(s) who are not inventor(s). Insert full name(s) and address(es) of inventors.

~~2(a) I am We are the actual inventor of the invention~~

or (b) ROBERT CHARLES JOB, a citizen of the United States of America of: 12126 Westmere, Houston, Texas 77077, United States of America.

~~is~~ are the actual inventor........... of the invention and the facts upon which the applicant.S........ is ~~are~~ entitled to make the application are as follows :–

State manner in which applicant(s) derive title from inventor(s)

"The Applicant would, if a patent were granted upon an application made by the Inventor , be entitled to have the patent assigned to it"

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications, insert basic country(s) followed by date(s) and basic applicant(s).

3. The basic application............ as defined by Section 141 of the Act was ~~were~~ made

in United States of America U.S.A. No.875,845 on the 18th June, 1986

by ROBERT CHARLES JOB

in .... on the ....

by ....

in .... on the ....

by ....

4. The basic application.......... referred to in paragraph 3 of this Declaration was ~~were~~ the first application.......... made in a Convention country in respect of the invention the subject of the application.

Insert place and date of signature.

Declared at Houston, Texas U.S.A. this 21st day of May, 1987

Signature of declarant(s) (no attestation required)

Rand N. Shulman

Note: Initial all alterations.

DAVIES & COLLISON, MELBOURNE and CANBERRA.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-74220/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 594162

(54) Title
NOVEL MG/TI CATALYST COMPONENT AND CATALYST THEREOF

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(71) Applicant(s)
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(57) Claim

1. A process for preparing a solid magnesium halide/titanium halide catalyst component for use in the polymerization of alpha olefins, which process comprises;

a) contacting a magnesium compound of the formula $[Mg_4(OR)_6(R'OH)_{10}]X$, wherein X is at least one counter ion and has a total charge of -2 and R and R', which may be the same or different, are alkyl groups of 1 to 4 carbon atoms, with a halogen compound of tetravalent titanium in the presence of an electron donor;

b) contacting the resulting halogenated product with a halogen compound of tetravalent titanium;

c) washing the resulting product to remove unreacted titanium compounds; and

d) recovering the solid catalyst component.

13. An olefinic polymerization catalyst composition comprising an organoaluminum compound, a selectivity control agent, and a solid catalyst component as claimed in claim

20 12, wherein the atomic ratio of aluminum to titanium is 30:1 to 100:1.

16. A process for the catalytic polymerization of an alpha olefin by contact with a catalyst comprising a solid component as claimed in claim 12 or with a catalyst composition as claimed in claim 13, 14 or 15.

COMMONWEALTH OF AUSTRALIA

PATENT ACT 1952

COMPLETE SPECIFICATION 594162

(Original)

FOR OFFICE USE

Class Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
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Published:

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Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

Name of Applicant: SHELL OIL COMPANY

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Texas 77001,
United States of America.

Address for Service: DAVIES & COLLISON, Patent Attorneys,
1 Little Collins Street, Melbourne, 3000.

Complete Specification for the invention entitled:

"PROCESS FOR PREPARING OLEFIN POLYMERIZATION CATALYST COMPONENT"

The following statement is a full description of this invention, including the best method of performing it known to us :-

This invention relates to a process for preparing a solid olefin polymerization catalyst component having improved activity and morphological properties, the component being prepared using a magnesium compound of the formula $[Mg_4(OR)_6(R'OH)_{10}]X$.

Numerous proposals have been made to provide olefin polymerization catalysts by combining (i) a solid component comprising at least magnesium, titanium and halogen with (ii) an activating organoaluminum compound. These may be referred to as supported coordination catalysts or catalyst systems. The activity and stereospecific performance of such catalysts is generally improved by incorporating an electron donor (Lewis base) in the solid component (i) and by employing as a third catalyst component (iii) an electron donor which may be complexed in whole or in part with the activating organoaluminum compound (ii).

For convenience of reference, the solid titanium-containing component (i) of such catalysts is referred to herein as "procatalyst", the organoaluminum compound (ii) whether used separately or partially or totally complexed with an electron donor, as "cocatalyst", and the electron donor compound (iii) whether used separately or partially or totally complexed with the organoaluminum compound (ii), as "selectivity control agent" (SCA).

Supported coordination catalysts of this type are disclosed in numerous patents. The catalyst systems of this type which have been disclosed in the prior art generally are able to produce olefin polymers in high yield and, in the case of catalysts for polymerization of propylene or higher alpha-olefins, with high selectivity to stereoregular polymers. However, further improvements in productivity at high stereoregularity are still being sought.

The objective of workers in this art is to provide catalyst systems which exhibit sufficiently high activity to permit the production of olefin polymers in such high yield as to obviate the necessity of extracting residual catalyst components from the polymers in a deashing step. In the case of propylene and higher olefins, an equally important objective is to provide catalyst systems of sufficiently high selectivity toward isotactic or otherwise stereoregular products to obviate the necessity of extracting atactic polymer components from the polymer product.

Although many chemical combinations provide active catalyst systems, practical considerations have led the workers in the art to concentrate on certain preferred components. The procatalysts typically comprise magnesium chloride, titanium chloride, generally in tetravalent form, and as electron donor an aromatic ester such as ethyl benzoate or ethyl p-toluate. The cocatalyst typically is an aluminum trialkyl, such as aluminum triethyl or aluminum tri-isobutyl, often used at least partially complexed with a selectivity control agent. The selectivity control agent typically is an aromatic ester such as ethyl p-methoxybenzoate(ethyl anisate) or methyl p-toluate.

While the selection of cocatalyst and selectivity control agent affects the performance of those catalyst systems, the component which appears to be subject to most significant improvement with respect to activity and productivity of the system is the procatalyst.

Preferred methods of preparing such procatalysts are claimed in U.S. Patent Nos. 4,329,253; 4,393,182; 4,400,302; 4,328,328; 4,478,952 and 4,414,132. The typical manner of preparing such procatalysts involves the reaction of a magnesium compound, titanium tetrachloride and electron donor in the presence of a halohydrocarbon. The resulting solid particles are then contacted with additional quantities of $TiCl_4$, excess $TiCl_4$ is washed off using light hydrocarbons (e.g. isooctane and isopentane), and the particles are dried.

The procatalysts thus prepared have excellent polymerization activity (polymer yield) and stereospecific performance (isotactic content). However, for some applications the polymer morphology is not ideal. In olefin polymerization, polymer morphology is known to be a replica of catalyst morphology. Still further, the procatalyst morphology also depends upon the morphology of the starting magnesium compound. Accordingly, if one desires to have optimal catalyst morphology (e.g. spheroidal particles), then it is desirable to employ starting magnesium compounds of the same morphology.

A number of different approaches to improved morphology are suggested in the patent literature. One approach, disclosed in GB-A-2,101,610 involves reacting a solid particulate material with an organic magnesium compound, treating the supported magnesium composition with oxygen, carbon dioxide or a hydroxyl compound, reacting the treated product with a carbonyl compound and simultaneously or subsequently reacting with a transition metal compound. Another approach, disclosed in US-A-4,465,783, involves the spray drying of a transition metal composition, or a support for a transition metal compound, suspended in a liquid medium. Still another method is disclosed in DE-A-2,839,188, where solid magnesium dialkoxide particles are dispersed in a suitable liquid phase, followed by spray-drying. However, this last process is not attractive as the dispersed solid particles tend to clog the fine orifices of the spray-drying equipment and foul the pumping and metering system. In US-A-4,540,679, use is made of a magnesium hydrocarbyl carbonate support. A suspension of magnesium alcoholate with carbon dioxide is reacted with a transition metal component to precipitate a "magnesium hydrocarbyl carbonate" support. Various techniques, including prepolymerization and the use of triethyl aluminum (TEA), are used to remove ethanol, to improve productivity. However, these techniques are not desirable since, for example, prepolymerization is an additional step and the addition of TEA adds ash to the polymer product.

The above-mentioned approaches to morphology control all depend upon starting from roughly spherical amorphous, non-stoichiometric shapes. A new method to improve morphology is greatly desired.

A new approach has now been found, unique in that the magnesium precursor is a crystalline compound of well defined stoichiometry and shape, which permits the preparation of procatalyst particles having not only excellent productivity and selectivity, but also possessing excellent morphology.

The present invention provides a process for preparing a solid magnesium halide/titanium halide catalyst component for use in the polymerization of alpha olefins, which process comprises;

a) contacting a magnesium compound of the formula $[Mg_4(OR)_6(R'OH)_{10}]X$, wherein X is at least one counter ion and has a total charge of -2 and R and R', which may be the same or different, are alkyl groups of 1 to 4 carbon atoms, with a halogen compound of tetravalent titanium in the presence of an electron donor;

b) contacting the resulting halogenated product with a halogen compound of tetravalent titanium;

c) washing the resulting product to remove unreacted titanium compounds; and

d) recovering the solid catalyst component.

In a preferred embodiment the magnesium compound has the formula $[Mg_4(OCH_3)_6(CH_3OH)_{10}]Cl_2$. This compound has a crystal habit which is an essentially regular rhombic dodecahedron. An advantage of such a structure is that it is esentially tangential to a spherical surface. As shown in the examples which follow, propylene polymers made with catalysts according to the present invention have high bulk densities, up to and greater than 0.4 grams per cubic centimeter.

Also, as shown in the examples, the catalysts of the present invention possess an unexpected balance of excellent catalytic properties, including: high activity, high selectivity to isotactic structures, good resin shape (morphology), low catalytic decay, high bulk density, greater productivity per reactor volume, and narrow range of particle distribution, including low fines. Another advantage is that the alkoxy species in the catalyst appears to be resident on the Mg instead of the Ti as the catalysts of prior art prepared from magnesium ethoxide, which may help to explain the high activity of this catalyst.

There are a number of important aspects to the present invention. One, as mentioned above, relates to the dodecahedron structure. Figure 1 shows the molecular structure of the dication of the preferred magnesium compound, where the blackened circles are Mg, the small open circles are methoxy (OCH_3) and the large open circles are methanol (CH_3OH). Note that two chloride ions serve only to balance the positive charge on the dication but are not essential to the molecular structure.

Another important aspect relates to the method by which the stable magnesium crystal is prepared. Figure 2 shows a ternary phase diagram for the system magnesium methoxide, magnesium chloride, methanol. Until this invention the narrow triangle ABC was the only region which it was thought could be employed to achieve the stable crystal $Mg_4(OMe)_6Cl_2 . 10MeOH$. More about the method to prepare the crystal will be explained below.

Another important aspect of the invention relates to the preparation of the halogenated product from the starting magnesium compound. This halogenation takes place in the presence of a halogen compound of tetravalent titanium (e.g. $TiCl_4$) and an electron donor (e.g. an ester of an aromatic carboxylic acid). As shown in the examples, it is much preferred that the halogenation take place also in the presence of a halohydrocarbon (e.g. chlorobenzene).

The key aspect of the present invention involves the use and preparation of the magnesium compound of the formula $[Mg_4(OR)_6(ROH)_{10}]X$. In a preferred embodiment X is selected from $2Cl^-$, $2I^-$, $2Br^-$, SO_4^{2-} and $C_2O_4^{2-}$, especially $2Cl^-$, while R and R′ are preferably methyl or ethyl, especially methyl.

There are a number of ways to prepare such starting magnesium compounds. One way is disclosed in the article "Alkoxymagnesium Halides" by Turova et al, Journal of Organometallic Chemistry, 42, pages 9-17 (1972). The phase diagram shown in the attached Figure 2 is taken from Figure 1 of the Turova article.

As mentioned above it is much preferred that R and R′ in the crystal structure be a methyl group and the remainder of the disclosure be directed to this embodiment.

The method disclosed in Turova et al involves preparing solutions of $MgCl_2$ in methanol and $Mg(OCH_3)_2$ in methanol, then mixing the controlled solutions in a mole ratio of $MgCl_2$ to $Mg(OCH_3)_2$ of 1:3 and then removing the methanol solvent until the crystals are formed. If desired small amounts of petrolatum ("Vaseline" oil) may be added to improve crystallization.

Another method disclosed herein involves the use of Mg metal, $MgCl_2$ and methanol. In this method three equivalents of the Mg are dissolved in a methanolic solution of $MgCl_2$ to again provide the 3:1 mole ratio of methoxide to chloride.

The extremely narrow stability range required by the ternary phase relationship would tend to make either of the above methods difficult for commercial implementation. As discussed by Turova et al, it requires great care to control solution concentrations and conditions to prepare stable crystal structures. Such care may be possible under laboratory conditions, but such level of care may be very difficult under commercial plant conditions. However, we have discovered a method for preparing such structures by using a "buffer" technique. In this technique advantage is taken of the nearly equivalent lability of the Si-OCH_3 and Si-Cl bonds to use $SiCl_4$ to remove excess methoxide and virtually buffer the methanolic solution over a wide range of effective chloride concentration. This equilibria is shown in the following equation where one or more of the successive K_1, K_2, K_3, K_4 equilibria (eqn 3) is used to buffer the solutions:

Eq. 1 $$8Mg(OMe)_2 + MeOH \rightleftharpoons 2\,[Mg_4(OMe)_6(MeOH)_{10}]^{+2} + 4\,OMe^-$$

$$\downarrow$$

Eq. 2 $$Mg(OMe)_2.MeOH \xrightarrow[K_{1,2,3,4}]{} (Mg(OMe)_2)_n$$

Eq. 3 $$SiCl_4 + 4\,OMe^- \underset{(Buffer)}{\rightleftharpoons} Si(OMe)_4 + 4\,Cl^-$$

In Equation 1, magnesium methoxide and methanol are put in solution. If conditions are not right, then as shown in Equation 2, $Mg(OCH_3)_2$ MeOH precipitate occurs. If concentrations are extremely high, this precipitate occurs as $[Mg(OCH_3)_2]_n$. However, if, as shown in Equation 3, $SiCl_4$ is added to the system, then it is possible to operate effectively in a wide range of concentrations outside the narrow wedge (ABC) described by Turova et al. This is shown in Figure 2 by circle D which represents the effective methoxy/chloro concentrations of Examples 5 and 6 below. This buffering approach effectively opens the wedge by moving the line AC to the right.

Materials other than just $SiCl_4$ can be used to buffer the solution. Anything that can abstract methoxy and does not provide an anion so large as to seriously distort the crystal shape may be used. These compounds include silicon tetrabromide, oxalic acid, acetic acid and formic acid.

In addition to $Mg(OCH_3)_2$, other starting components include halogen-containing magnesium compounds and magnesium dialkoxides. Examples of halogen-containing magnesium compounds that can be used as starting materials for the reaction are alkoxy magnesium halides, such as isobutoxy magnesium chloride, ethoxy magnesium chloride and ethoxy magnesium bromide.

Preferred magnesium compounds are magnesium dialkoxides. In such compounds the alkoxide groups suitably have from 1 to 4 carbon atoms. Examples of these preferred groups of compounds are magnesium di-isopropoxide, magnesium diethoxide, magnesium dibutoxide and ethoxy magnesium isobutoxide. Magnesium dimethoxide is particularly preferred.

Another aspect of the present invention involves removing a portion (or all) of the methanol from the crystal. This may be done by boiling the crystal in an inert liquid hydrocarbon, e.g. isooctane. Any liquid hydrocarbon that forms azeotropes with methanol may be used. The advantage of this approach is to decrease the Ti level by decreasing the amount of sparingly soluble (Cl)(OMe)Ti species.

Once the uniformly optimized particles of the magnesium compound have been obtained, it is then necessary to convert the compounds to magnesium halides in a metathesis reaction (digestion), such as that disclosed in US-A-4,414,132.

In the halogenation with [illegible] compound of tetravalent titanium, the magnesium compounds is preferably reacted to form a magnesium halide in which the atomic ratio of halogen to magnesium is at least 1.2:1. Better results are obtained when the halogenation proceeds more completely, i.e. yielding magnesium halides in which the atomic ratio of halogen to magnesium is at least 1.5:1. The most preferred reactions are those leading [illegible] halogenated reaction products, i.e. magnesi [illegible] h halogenation reactions are suitably effected by employing a molar ratio of magnesium compound to titanium compound of 0.005:1 to 2:1, preferably 0.01:1 to 1:1. These halogenation reactions are conducted in the presence of an electron donor and preferably also a halohydrocarbon. An inert hydrocarbon diluent or solvent may also be present. When using an inert diluent or solvent, this should of course not be used as a complete substitute for the halohydrocarbon, for, as shown in the examples, it is preferable that the halogenation reaction proceeds in the presence of a halohydrocarbon.

Suitable halogen compounds of tetravalent titanium include aryloxy- or alkoxy-di- and trihalides, such as dihexanoxy-titanium dichloride, diethoxy-titanium dibromide, isopropoxy-titanium tri-iodide and phenoxy-titanium trichloride; titanium tetrahalides are preferred; most preferred is titanium tetrachloride.

Suitable halohydrocarbons are compounds having only one halogen such as butyl chloride and amyl chloride but preferred compounds are aliphatic halohydrocarbons hydrocarbons with 1 to 12, particularly less than 9, carbon atoms per molecule, comprising at least two halogen atoms, such as dibromomethane, trichloromethane, 1,2-dichloroethane, dichlorobutane, 1,1,3-trichloroethane, trichlorocyclohexane, dichlorofluoroethane, trichloropropane, trichlorofluorooctane, dibromodifluorodecane, hexachloroethane and tetrachloroisooctane. Carbon tetrachloride and 1,1,3-trichloroethane are preferred aliphatic halohydrocarbons. Aromatic halohydrocarbons may also be employed, e.g. chlorobenzene, bromobenzene, dichlorobenzene, dichlorodibromobenzene, naphthyl chloride, chlorotoluene and dichlorotoluenes; chlorobenzene and dichlorobenzene are preferred aromatic halohydrocarbons.

Suitable electron donors which are used in the preparation of the solid catalyst component are ethers, esters, ketones, phenols, amines, amides, imines, nitriles, phosphines, phosphites, stibines, arsines, phosphoramides and alcoholates. Examples of suitable donors are those referred to in US-A-4,136,243 or its equivalent GB-A-1,486,194 and in GB-A-1,554,340 or its equivalent DE-A-2,729,126. Preferred donors are esters, diesters and diamines, particularly esters and diesters of aromatic carboxylic acids, such as ethyl and methyl benzoate, p-methoxy ethyl benzoate, p-ethoxy methyl or ethyl benzoate, ethyl acrylate, methyl methacrylate, ethyl acetate, dimethyl carbonate, dimethyl adipate, isobutyl phthalate, dihexyl fumarate, dibutyl maleate, ethylisopropyl oxalate, p-chloro ethyl benzoate, p-amino hexyl benzoate, isopropyl naphthenate, n-amyl toluate, ethyl cyclohexanaoate, propyl pivalate, N,N,N',N'-tetramethylethylene diamine, 1,2,4-trimethyl piperazine and 2,2,5,5-tetramethyl piperidine. The electron donors may be used singly or as mixtures. Preferred electron donors for use in preparing the titanium constituent are ethyl benzoate and isobutyl phthalate.

The halogenation normally proceeds with formation of a solid reaction product which may be isolated from the liquid reaction medium by filtration, decantation or another suitable method and may be subsequently washed with an inert hydrocarbon diluent, such as n-hexane, iso-octane or toluene, to remove any unreacted material, including physically absorbed halohydrocarbon.

Subsequent to halogenation, the product is contacted with a halogen compound of tetravalent titanium such as a dialkoxy-titanium dihalide, alkoxy-titanium trihalide, phenoxy-titanium trihalide or titanium tetrahalide. The most preferred titanium compounds are titanium tetrahalides and especially titanium tetrachloride. This treatment increases the content of tetravalent titanium in the solid catalyst component. This increase should preferably be sufficient to achieve a final atomic ratio of tetravalent titanium to magnesium in the solid catalyst component of from 0.005:1 to 3.0:1 particularly of from 0.02:1 to 1:1. To this purpose the contacting with the halogen compound of tetravalent titanium is most suitably carried out at a temperature of from 60° to 136°C for 0.1 to 6 hours, optionally in the presence of an inert hydrocarbon or halohydrocarbon diluent. Particularly preferred contacting temperatures are 70° to 120°C and the most preferred contacting periods are 0.5 to 3.5 hours. The treatment may be carried out in successive contacts of the solid with separate portions of $TiCl_4$, which may contain suitable electron donors chosen from the previous list.

The preferred halogen atom, possibly contained in the magnesium compound to be halogenated, and contained in the titanium which serves as halogenating agent and in the halogen compound of tetravalent titanium with which the halogenated product is contacted, is chlorine.

After the treatment with a halogen compound of tetravalent titanium the catalyst component is suitably isolated from the liquid reaction medium and washed to remove unreacted titanium compound. The titanium content of the final, washed, catalyst constituent is suitably 1.5 to 3.6 percent by weight but can be up to 4.5 percent by weight.

The material used to wash the catalyst component suitably is an inert, light hydrocarbon liquid. Preferred light hydrocarbon liquids are aliphatic, alicyclic and aromatic hydrocarbons. Examples of such liquids include iso-pentane, n-hexane, iso-octane and toluene, with iso-pentane being most preferred.

The amount of light hydrocarbon liquid employed suitably is 5 to 100 cm^3/gm of procatalyst in each of 2 to 6 separate washes, preferably about 25 cm^3 gm.

The resulting solid component is the procatalyst, which is used with cocatalyst and selectivity control agent in the polymerization process.

Suitable electron donors, which are used in combination with or reacted with an organoaluminum compound as selectivity control agents are those described above in connection with the preparation of the solid catalyst component and silanes. Preferred donors are esters and organic silicon compounds. Preferred esters are esters or diesters of aromatic carboxylic acids such as those mentioned above in connection with the preparation of the solid catalyst component. Examples of the organic silicon compounds which may be used include alkoxysilanes and acyloxysilanes of the general formula $R^1{}_nSi(OR^2)_{4-n}$ where n is from 0 to 3, R^1 is a hydrocarbon group or a halogen atom and R^2 is a hydrocarbon group. Specific examples include trimethylmethoxy silane, triphenylethoxy silane, dimethyldimethoxy silane and phenyltrimethoxy silane. The donor used as selectivity control agent in the catalyst may be the same as or different from the donor used for preparing the titanium containing catalyst component. Preferred electron donors for use as selectivity control agent are p-ethoxy ethyl benzoate, phenethyl trimethoxy silane and diphenyldimethoxy silane.

The organoaluminum compound to be employed as cocatalyst may be chosen from any of the known activators in olefin polymerization catalyst systems comprising a titanium halide but is most suitably free of halogens. While trialkylaluminum compounds, dialkylaluminum halides and dialkylaluminum alkoxides may be used, trialkylaluminum compounds are preferred, particularly those wherein each of the alkyl groups has 2 to 6 carbon atoms, e.g. triethylaluminum, tri-n-propylaluminum, triisobutylaluminum, triisopropylaluminum and dibutyl-n-amylaluminum.

Preferred proportions of selectivity control agent, employed separately, in combination with, or reacted with an organoaluminum compound, calculated as mol per mol aluminum compound, are from 0.005 to 1.5, particularly from 0.1 to 0.5. Preferred proportions of selectivity control agent calculated as mol per mol Ti are 0.1 to 50, particularly 0.5 to 20.

Proportions of electron donor contained in the solid catalyst component, calculated as mol per mol of magnesium, are suitably from 0.01 to 10, preferably 0.05 to 5.0 and especially 0.05 to 0.5.

To prepare the final polymerization catalyst composition, procatalyst, cocatalyst and selectivity control agent, if used separately, may be simply mixed, most suitably employing a molar ratio to produce in the final catalyst an atomic ratio of aluminum to titanium of from 1:1 to 150:1 and suitably from 10:1 to 150:1. Preferably the components are injected separately into the reactor. The catalysts of this invention tend to exhibit very good activity at much lower Al:Ti ratios, e.g. below 80:1 and even below 50:1, than prior art catalysts of the same type. It may, however, be advantageous under some conditions to employ them at higher Al:Ti ratios. Increasing the Al:Ti ratio tends to increase catalyst activity at the expense of increased catalyst residue in the unextracted product. These factors, as well as the desired level of isotacticity, will be considred in selecting the Al:Ti ratio for any given process and desired product. In general, Al:Ti ratios of 30:1 to 100:1 and especially of 50:1 to 80:1 will be found advantageous.

The present invention is also concerned with a process for polymerizing an alpha monoolefin such as ethylene or butylene, preferably propylene, employing the novel catalyst components and compositions. The polymerization may be carried out by any of the conventional techniques, such as gas phase polymerization or slurry polymerization using liquid monomer or an inert hydrocarbon diluent as liquid medium. Hydrogen may be used to control the molecular weight of the polymer without detriment to the stereospecific performance of the catalyst compositions. Polymerization may be effected batchwise or continuously with constant or intermittent supply of the catalyst compositions or one or more of the catalyst components to the polymerization reactor. The activity and stereospecificity of the catalyst compositions are so pronounced that there is no need for any catalyst removal or polymer extraction techniques. Total metal residues in the polymer, i.e. the combined aluminum, magnesium and titanium content, can be as low as 150 ppm, even less then 75 ppm.

It is well known that supported coordination procatalysts and catalyst systems of the type used herein are highly sensitive, in varying degrees, to catalyst poisons such as moisture, oxygen, carbon oxides, acetylenic compounds and sulfur compounds. It will be understood that in the practice of this invention, as well as in the following Examples, both the equipment and the reagents and diluents are carefully dried and freed of potential catalyst poisons.

The productivity of the procatalyst is determined as kg polymer/g procatalyst in a standard one or two hour batch reaction; it may also be expressed as kg polymer/g Ti. Catalyst activity is sometimes reported as kg polymer/g procatalyst/hr. If determined in a standard one hour test, activity thus is numerically the same as productivity.

The selectivity to isotactic polypropylene is determined by measuring the amount of xylene soluble polymer (XS), in accordance with regulations of the U.S. Food and Drug Administration (FDA). The XS test is carried out as follows:

The sample is completely dissolved in xylene, which contains oxidation inhibitor, in a stirred flask by heating under reflux at 120°C. The flask is then immersed in a water bath at 25°C without stirring for one hour, during which the insoluble portion precipitates. The precipitate is filtered off and the solubles present in the filtrate are determined by evaporating a 10 cm^3 aliquot of the filtrate, drying the residue under vacuum, and weighing the residue. The xylene-solubles consist of amorphous material with some low molecular weight crystalline material. (FDA regulations 121.2501 and 1.1.2510, 1971).

The numerical value of XS in the case of propylene homopolymer is typically about 2 percent less than the amount of polymers extractable in refluxing n-heptane. Thus the isotacticity index of polypropylene (amount insoluble in refluxing n-heptane) is approximately 100 - (XS+2).

Catalyst productivity at standard conditions exhibits an inverse relationship with stereoselectivity. This relationship is characteristic for any given procatalyst. It is generally possible to control these variables, within limits, by changing the proportion of selectivity control agent (SCA). Increasing the amount of SCA increases selectivity to isotactic or stereoregular polymer but reduces activity, and hence productivity, in a standard one hour test.

The following Examples will serve to illustrate the invention:

Examples 1 to 6

Preparation of magnesium containing precursors:

A. Preparations using exact stoichiometry (i.e. OCH_3/Cl = 3.0/1).

Example 1. (Staying within the metastable wedge.) Anhydrous magnesium chloride was dissolved in methanol and about 1/6 of the solvent distilled away. 3.0 equivalent of magnesium metal was added slowly, to maintain a gentle reflux, then the reaction kept under reflux to finish the magnesium consumption. After standing, a mixture of pumpkin shaped crystals and some grey powder was obtained. The product was slurried in a mixture of methanol/isopropanol and the grey powder decanted. After washing again with the methanol/isopropanol solution, the crystals were dried under moving nitrogen to give a recovery of 65% basis total magnesium. (Analysis: Mg = 15.5%, Cl = 12.2%, Mg/Cl = 1.85 mol/mol). The mother liquor had the approximate composition of 8.5% $Mg(OCH_3)_2$ + 3.0% $MgCl_2$, a stable solution according to the ternary phase diagram.

Example 2. (Control) (Leaving the metastable wedge by dilution.) The preparation was carried out as in Example 1 above except that, at the end of the reflux, an equal volume of isooctane was added to the hot methanol solution together with enough isopropanol to yield a homogeneous solution. Upon cooling, the yield of crystalline product was essentially quantitative, based on total magnesium.

(Analysis: Mg = 14.1%, Cl - 10.4%, Mg/Cl - 2.0 mol/mol). In contrast to 1 above, the product appeared to be a mixture of crystalline forms.

B. Preparations using excess chloride (i.e. $OCH_3/Cl < 3/1$).

Example 3. (Control) (Moving outside the metastable wedge via high Cl concentration.) Commercially available magnesium chloride was dissolved in 8% commercially available methanolic magnesium methoxide (70 g $MgCl_2$ per 0.95 dm^3 (U.S. quart) of solution). After standing overnight the floculant magnesium was filtered away from the solution. 1.5 liter of the clear solution was mixed with 1.5 l of isooctane and 0.8 l of isopropanol was added to ensure homogeneity. The solution was stirred at 230 rpm with a polytetrafluoroethylene paddle stirrer. After a day, the precipitate was collected, washed with isooctane and dried under moving nitrogen. The yield, based on total magnesium, was 42%. (Analysis: Mg = 15.9%, Cl = 22.8%, Mg/Cl = 1.0 mol/mol). The product appeared to be a mixture of well formed crystal in the 5-30 μm range.

Example 4. (Control) Anhydrous magnesium chloride was dissolved in methanol then 1.0 equivalent of magnesium turnings was added to maintain a gentle reflux. Reflux was continued overnight then an equal volume of isooctane was added, to the hot solution, together with sufficient isopropanol to homogenize. The solution was allowed to cool, with vigorous stirring, to give spheroidal amorphous -

product in the size range of 20-80 μm. The yield, based on total magnesium, was 81.5%.

C. Preparation with excess chloride in the presence of $SiCl_x(OCH_3)_y$ buffer.

Example 5. Magnesium (43 g, 1.77 mol) was added, in 5-8 g portions, to 1200 cm^3 of methanol in a 21 Erlenmeyer flask. The solvent was heated gently to initiate the magnesium dissolution. After that, the heat of reaction was sufficient to maintain a gentle reflux. After all of the magnesium had dissolved, silicon tetrachloride (45 g, 264 mmol; 20% excess basis total Cl) was added slowly (since this presents a rather exothermic acid/base reaction). Two of these preparations were combined and sufficient methanol distilled away to bring the total volume to 1.6 to 1.7 1. The hot solution, 'A', was then poured into a 2 1 reaction kettle, equipped with a large bladed paddle stirrer and stainless steel baffles, and stirred at high speed until the solution had cooled and a large mass of small crystals was obtained. The crystals were collected upon a coarse fritted funnel, washed twice with a mixture of 500 g isooctane/150 g isopropanol, washed twice with isooctane and dried under moving nitrogen for about 20 minutes. The yield was 420 g (71%). Visible and scanning electron microscopic examination reveal the product to be of a homogeneous crystal type in the shape of rhombic dodecahedrons.

Example 6. 105 g of the hot solution 'A', from 5 above, was mixed with 6 g of toluene to give a clear solution. Upon stirring overnight 8.1 g of well formed, transparent crystals, in the shaped of rhombic dodecahedrons, were obtained.

In the above, the crystals made in Example 1 demonstrate the preparation according to the invention, and make good catalysts. The procedure in Example 2 is outside the wedge ABC and does not make good catalysts, likewise Examples 3 and 4 are also outside the invention. Examples 5 and 6 describe buffered systems according to the present invention.

Examples 7 to 17

Preparation of Procatalysts

Procatalysts were prepared as follows: Electron donor (type and amount shown in Table 1) were added along with 150 cm^3 of a 1:1 (vol:vol) mixture of titanium tetrachloride and chlorobenzene to 50 mmol of the appropriate magnesium precursor (Table 1) and stirred at room temperature for 15 minutes. The mixture was then stirred for an hour at 110°C and filtered hot. The residual solid was slurried in 150 cm^3 of the 1:1 titanium tetrachloride/chlorobenzene solution, 0.2 to 0.4 ml of phthaloyl chloride was added (US-A-4,535,068), and the slurry stirred for 30-60 minutes at 110°C. After a hot filtration, the solid was slurried in 150 cm^3 of the 1:1 titanium tetrachloride/chlorobenzene solution and stirred at

110°C for 30 minutes and filtered hot. The reaction vessel was cooled to below 40°C and the solid was washed 6 times with 150 cm^3 portions of isopentane then dried for 100 minutes, at 40°C, under moving nitrogen. The titanium content of the various procatalysts is shown in Table 1. Examples 11 to 13 are Controls.

Table 1

Procatalyst Example	Mg Precursor Example	Electron Donor (mmol)	Titanium (% wt)	Comments
7	1	iBP (9.7)	3.44	
8	1	iBP (6.0)	4.63	
9	1	iBP (7.5)	4.06	
10	1	MpT (16.7)	5.30	
11	2	iBP (7.6)	4.10	
12	3	iBP (17.3)	4.98	
13	4	iBP (11.1)	4.81	
14	5	iBP (9.9)	4.67	
15	5	iBP (8.7)	2.00	The magnesium precursor was boiled in isooctane for 1 hr to remove 92% of the bound methanol.
16	5	iBP (8.7)	4.49	
17	6	iBP (8.7)	4.04	

iBP = isobutyl phthalate
MpT = methyl p-toluate

Examples 18 to 33

Liquid Pool (LIPP) and Gas Phase Propylene Polymerizations

LIPP polymerizations were carried out for two hours at 67°C, in a 3.8 dm^3 (1 U.S. gal) autoclave, using 2.7 1 of propylene, 132 mmol of hydrogen, and sufficient catalyst to provide 8 micromoles of titanium.

Triethylaluminum (70 mol/mol Ti) was mixed with 17.5 mmol of SCA (ethyl p-ethoxybenzoate for Example 23, diphenyldimethoxysilane for all others) and either premixed with the procatalyst 5 to 30 minutes before injection or injected directly to the autoclave before procatalyst injection.

Gas phase polymerizations were carried out, for two hours at 67°C, at a pressure of (300 psig) with a 10 g/min propylene flow, in a 15 dm^3 (4 U.S. gal) autoclave equipped with a ribbon stirrer. After gas flow had been established in the autoclave, the SCA was injected (17.5 mol/mol Ti) followed by the triethyl aluminum (70 mol/mol Ti) followed by the procatalyst (sufficient to provide 8 micromoles of titanium).

The results are shown in Table 2. Note that Examples 24 to 26 are Control Examples using catalysts prepared from magnesium chloro methoxides which are not pure $Mg_4(OMe)_6(MeOH)_{10}Cl_2$ and that is why their productivities are so much poorer than those of the other Examples illustrating liquid phase polymerizations.

TABLE 2

Polymerization Example	Catalyst Example	Productivity (Kg PP/g cat)	X.S. (% wt)	Phase (g/1)	Morphology Details
18	7	44.7	6.8	1	
19	7	24.0	4.5	g	0.37 b.d., 84.5% of polymer at 0.25-2.0 mm
20	8	40.6	9.1	1	0.32 b.d., 85.6% of polymer at 0.50-2.0 mm
21	8	20.4	13.8	g	0.35 b.d., 88.6% of polymer at 0.50-2.0 mm
22	9	40.9	6.1	1	0.39 b.d., 87.1% of polymer at 0.25-2.0 mm
23	10	18.8 (1 hr)	7.9	1	
24	11	24.9	6.5	1	
25	12	6.0	8.5	1	
26	13	10.5	9.7	1	
27	14	66.1	7.2	1	0.43 b.d
28	14	15.8	5.4	g	
29	15	34.3	3.4	1	0.37 b.d., 84.3% of polymer at 0.25-2.0 mm
30	15	10.2	2.0	g	
31	16	46.1	6.2	1	0.39 b.d., 80.7% of polymer at 0.5-2.0 mm
32	17	63.9	7.5	1	0.36 b.d.
33	17	20.9	5.4	g	

"g" is gas phase polymerization
"1" is liquid phase polymerization
"b.d." is bulk density

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for preparing a solid magnesium halide/titanium halide catalyst component for use in the polymerization of alpha olefins, which process comprises;

a) contacting a magnesium compound of the formula $[Mg_4(OR)_6(R'OH)_{10}]X$, wherein X is at least one counter ion and has a total charge of -2 and R and R', which may be the same or different, are alkyl groups of 1 to 4 carbon atoms, with a halogen compound of tetravalent titanium in the presence of an electron donor;

b) contacting the resulting halogenated product with a halogen compound of tetravalent titanium;

c) washing the resulting product to remove unreacted titanium compounds; and

d) recovering the solid catalyst component.

2. A process according to claim 1 wherein R and R' are methyl or ethyl and X is $2Cl^-$, $2I^-$, $2Br^-$, SO_4^{2-} or $C_2O_4^{2-}$.

3. A process according to claim 1 or 2 wherein said magnesium compound is contacted with said halogen compound of tetravalent titanium and said electron donor in the presence of a halohydrocarbon.

4. A process according to claim 1, 2 or 3 wherein said halogen compound of tetravalent titanium is $TiCl_4$.

5. A process according to claim 3 wherein said

halogen compound of tetravalent titanium is $TiCl_4$ and said halohydrocarbon is a chlorohydrocarbon.

6. A process according to any one of the preceding claims wherein said magnesium compound is heated in an inert light hydrocarbon so as to remove at least some of the alcohol (R'OH) before contacting with said halogen compound of tetravalent titanium.

7. A process according to claim 6 wherein said inert light hydrocarbon is isooctane.

8. A process according to any one of the preceding claims wherein said electron donor is an ester or diester of an aromatic carboxylic acid.

9. A process according to any one of the preceding claims wherein the magnesium compound has been prepared by contacting $Mg(OR)_2$, MgX and R'OH, wherein R, R' and X are as defined in claim 1, in the presence of a buffer compound.

10. A process according to claim 9 wherein $Mg(OR)_2$ is $Mg(OCH_3)_2$, MgX is $MgCl_2$, R'OH is CH_3OH and said buffer compound is $SiCl_4$.

11. A process according to claim 1 substantially as described herein.

12. A solid catalyst component when prepared by a process as claimed in any one of the preceding claims.

13. An olefinic polymerization catalyst composition comprising an organoaluminum compound, a selectivity control agent, and a solid catalyst component as claimed in claim

20 12, wherein the atomic ratio of aluminum to titanium is 30:1 to 100:1.

14. A catalyst composition according to claim 13 wherein said organoaluminum compound is a trialkylaluminum and said selectivity control agent is selected from esters or diesters of aromatic carboxylic acids and silicon compounds of the general formula $R^1{}_nSi(OR^2)_{4-n}$, where n is from 0 to 3, R^1 is a hydrocarbon group or a halogen atom and R^2 is a hydrocarbon group.

15. A catalyst composition according to claim 12 wherein said trialkylaluminum is triethyl aluminum and said selectivity control agent is selected from ethyl benzoate, diisobutyl phthalate, diphenyl dimethoxy silane and phenethyltrimethoxy silane.

16. A process for the catalytic polymerization of an alpha olefin by contact with a catalyst comprising a solid component as claimed in claim 12 or with a catalyst composition as claimed in claim 13, 14 or 15.

17. An alpha olefin polymer when prepared by a process as claimed in claim 16.

DATED this 8th day of December 1989.

SHELL OIL COMPANY

By Its Patent Attorneys

DAVIES & COLLISON

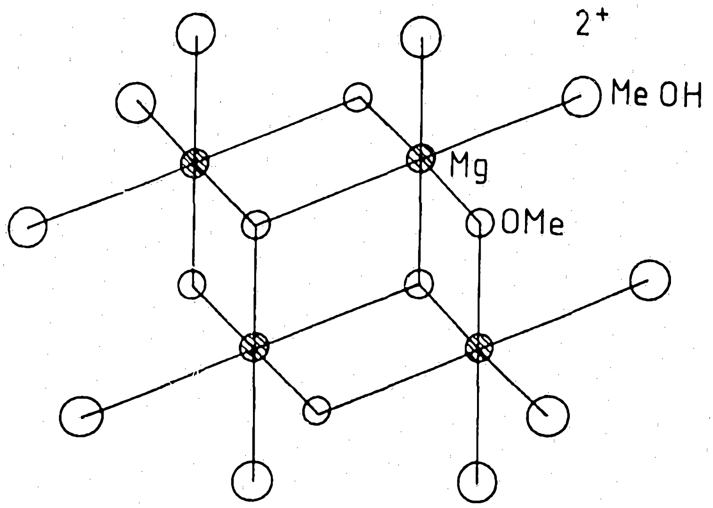
2+
Me OH
Mg
OMe

Fig. 1

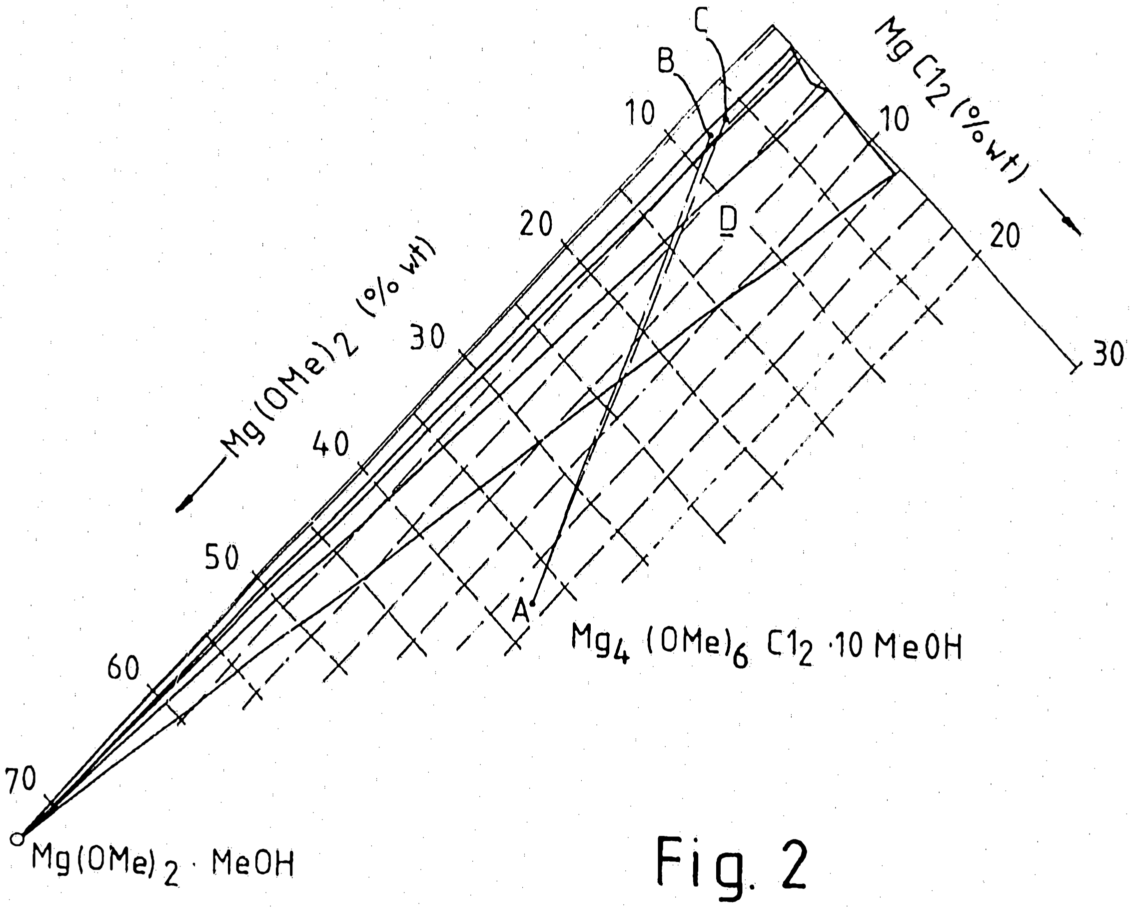
C
B
10
Mg Cl2 (% wt)
10
D
20
20
30
30
Mg(OMe)2 (% wt)
40
50
A
Mg4 (OMe)6 Cl2 ·10 MeOH
60
70
Mg(OMe)2 · MeOH

Fig. 2