

SPECIFICATION

Catalyst and process for the production of polymers of olefins or other ethylenically unsaturated hydrocarbons

The present invention relates to a composition, which can form the basis of a high activity catalyst for use in the homopolymerization or copolymerization of ethylenically unsaturated hydrocarbons, especially olefins. The invention also provides a process for preparing homopolymers or copolymers of ethylenically unsaturated hydrocarbons using such a catalyst. For convenience, the invention is described primarily with reference to the polymerization of olefins to produce olefin homopolymers or copolymers (hereafter "olefin polymers"), however, it will be appreciated that what is said in connection with the polymerization of olefins applied *mutatis mutandis* to the polymerization of other ethylenically unsaturated hydrocarbons.

It is well-known to produce olefin polymers using the so-called Ziegler-Natta catalysts, which comprise a compound of a transition metal from Group IVb to VIb of the Periodic Table of the Elements and an organic compound of a metal from Group I to III of the Periodic Table. In practice, it is generally convenient that any catalyst should be employed on a carrier and it is now well-known that the nature of the carrier can have an important influence on the efficiency of the polymerization process. For example, it has been found that a catalyst comprising a transition metal compound supported on a carrier, particularly an inorganic compound, such as an oxide, hydroxide, chloride or carbonate of a metal or of silicon, is very useful in the polymerization of olefins. Of these inorganic compounds, compounds of magnesium are particularly useful as carriers and, for example, magnesium halides are used as carriers to provide catalysts having a high activity, as disclosed in Japanese Patent Publications No. 12105/64 and 41676/72. Although the activity of these catalysts is relatively high, it is not always satisfactory and, moreover, the catalysts generally have a wide particle size distribution and do not always produce olefin polymers having a narrow particle size distribution.

In any catalytic process for the polymerization of olefins, there is almost inevitably some residual catalyst in the polymer produced. The residual catalyst can cause many problems, for example it can reduce the stability and processability of the polymer and, as a result, it is necessary to provide equipment to remove the catalyst residue and thus stabilize the polymer. This disadvantage can be reduced by increasing the catalyst activity (which is expressed as the yield of olefin polymer per unit weight of catalyst or per unit weight of transition metal in the catalyst) and, provided the activity can be increased sufficiently that the proportion of catalyst residue remaining in the polymer is small enough, it is no longer necessary to remove the catalyst residue from the polymer. This is called the "non-deashing process". Since equipment for removing residual catalyst and the extra manufacturing step of removal are not required in this process, manufacturing costs can be considerably reduced.

Another important factor in the commercial use of the slurry polymerization process for the production of olefin polymers is that bulk density, average particle size of the polymer and particle size distribution of the polymer have a significant effect on productivity. Improvements in these characteristics result in a decrease in the amount of polymer attached to the polymerization vessel and an increase in the efficiency of use of the reactor and the efficiency of transfer, drying and granulation, thus making it possible to raise the productivity and thus reduce manufacturing costs. Furthermore, the powdery olefin polymers thus produced can be used as they are without pelletizing. Generally, however, olefin polymers produced by means of a supported catalyst have such disadvantages as low bulk density, low average particle size and broad particle size distribution. Consequently, there is considerable interest in the development of a supported catalyst having a high activity, high bulk density and narrow particle size distribution but which can produce olefin polymers by the non-deashing process; such a supported catalyst would have a very high value to industry.

In our United Kingdom Patent Specification No. 1,554,460 we describe and claim a catalyst component comprising the solid product produced by reacting a Grignard compound with an aluminium halide and/or a silicon halide and, supported on the solid product, a titanium compound and/or a vanadium compound. When this catalyst component is combined with an organoaluminium compound, the resulting catalyst has outstandingly high activity in olefin polymerization.

We have now discovered a solid carrier useful for the production of supported catalyst which has a very high activity, not only per unit weight of transition metal but also per unit weight of the solid catalyst component. Moreover, the catalyst produced using this solid carrier is able to provide olefin polymers in a good slurry state having a narrow particle size distribution and free from adhesion to the reactor walls; moreover, the catalyst can be used in the non-deashing process.

Thus, the present invention consists in a process for producing a solid composition, in which an organo-magnesium compound is reacted in solution with a hydrocarbyl-oxyaluminium compound of formula

$$R^1_aAl(OR^2)_bX_c$$

[in which R^1 and R^2 are the same or different and each represents an optionally substituted hydrocarbon group having from 1 to 20 carbon atoms, X represents a halogen atom and a , b , and c are numbers such that $0 \leq a < 3$, $0 < b \leq 3$, $0 \leq c < 3$ and $(a+b+c)=3$] and/or a hydrocarbyloxyphosphorus compound of formula



[in which R^3 and R^4 are the same or different and each represents an optionally substituted hydrocarbon group having from 1 to 20 carbon atoms, X represents a halogen atom and d , e and f are numbers such that $0 \leq d < 3$, $0 < e \leq 3$, $0 \leq f < 3$ and $(d+e+f)=3$] to produce a solid product and supporting a titanium compound and/or a vanadium compound on said solid product.

The invention further consists in a solid composition when produced by the process of the invention and in a composition suitable for the catalysis of olefin polymerization and comprising the solid composition of the invention and an organoaluminium compound.

The invention still further consists in a method of preparing a polymer in which an ethylenically unsaturated hydrocarbon is polymerized in the presence of a catalyst system comprising the solid composition of the invention and an organoaluminium compound.

By carrying out the process of the invention as described hereafter, it is possible to produce a solid composition having both high activity and a narrow particle size distribution.

The organomagnesium compound used in the process of the invention may itself be prepared by reaction between an organo-halogen compound and metallic magnesium. For example, preferred organomagnesium compounds are Grignard compounds of formula R^5MgX (in which R^5 represents a hydrocarbon group having from 1 to 20 carbon atoms and X represents a halogen atom) and dialkylmagnesium compounds of formula R^5_2Mg . Examples of groups which may be represented by R^5 include alkyl, aryl, aralkyl and alkenyl groups having from 1 to 20 carbon atoms, for example methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, t-butyl, pentyl, isopentyl, hexyl, octyl, 2-ethylhexyl, phenyl and benzyl groups. The halogen atom represented by X is preferably a chlorine, bromine or iodine atom.

Specific examples of Grignard compounds which may be used in the process of the invention include: ethylmagnesium chloride; ethylmagnesium bromide; ethylmagnesium iodide; propylmagnesium chloride; propylmagnesium bromide; butylmagnesium chloride; butylmagnesium bromide; pentylmagnesium chloride; phenylmagnesium chloride; and phenylmagnesium bromide. Specific examples of dialkylmagnesium compounds which may be used include: diethylmagnesium; dipropylmagnesium; dibutylmagnesium; dipentylmagnesium; and diphenylmagnesium.

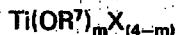
These organomagnesium compounds are normally synthesized in the presence of a solvent, which may be, for example: an ether, e.g. diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, diisobutyl ether, dipentyl ether, diisopentyl ether, dihexyl ether, dioctyl ether, diphenyl ether, dibenzyl ether, phenetole, anisole or tetrahydrofuran; a hydrocarbon, e.g. hexane, heptane, octane, cyclohexane, methylcyclohexane, benzene, toluene or xylene; or a mixture of one or more ethers with one or more hydrocarbons.

We prefer that the organomagnesium compounds should be used in the form of an ether solution or of a complex with an ether for the synthesis of the solid product in the process of the invention. It is particularly preferred to use Grignard compounds of formula R^5MgCl , particularly as ether solutions or as complexes with ether.

This organomagnesium compound is optionally reacted with a hydrocarbyloxyaluminium compound of formula $R^1Al(OR^2)_bX_c$, the better results being obtained as the number of hydrocarbyloxy groups increases. Aluminium trihydrocarbyloxides of formula $Al(OR^2)_3$ are most desirable. Specific examples of such aluminium compounds include: $Al(OCH_3)_3$, $Al(OC_2H_5)_3$, $Al(O-n-C_3H_7)_3$, $Al(O-n-C_4H_9)_3$, $Al(O-sec-C_4H_9)_3$, $Al(O-t-C_4H_9)_3$, $Al(O-iso-C_4H_9)_3$, $Al(OC_6H_5)_3$, $C_2H_5Al(OC_2H_5)_2$, $Al(O-iso-C_3H_7)_3$, $C_2H_5Al(O-iso-C_3H_7)_2$, $(C_2H_5)_2Al(O-iso-C_3H_7)$, $iso-C_3H_7Al(O-n-C_4H_9)_2$, $(iso-C_3H_7)_2Al(OC_2H_5)$, $Al(OC_2H_5)_2Cl$, $Al(O-iso-C_3H_7)Cl_2$, $C_2H_5Al(OC_2H_5)Cl$ and $iso-C_4H_9Al(OC_2H_5)Cl$. These compounds may be prepared by well-known methods, for example, they can be obtained particularly easily by reaction of an organoaluminium compound with an alcohol.

Alternatively, or in addition, the organomagnesium compound may be reacted with a hydrocarbyloxyphosphorus compound of formula $R^3P(OR^4)_eX_f$ and, as with the aluminium compounds, better results are obtained as the number of hydrocarbyloxy groups increases. Examples of suitable hydrocarbyloxyphosphorus compounds include: $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O-iso-C_3H_7)_3$, $P(O-n-C_4H_9)_3$, $P(OCH_2CH=CH_2)_3$, $P(OC_6H_5)_3$, $P(OCH_2CH_2Cl)_3$, $P(OCH_3)_2Cl$, $P(OC_2H_5)_2Cl$, $P(O-n-C_4H_9)_2Cl$, $P(OC_6H_5)_2Cl$, $CH_3P(OCH_3)_2$, $C_2H_5P(OC_2H_5)_2$, $n-C_4H_9P(OC_6H_5)_2$, $(C_2H_5)_2P(OCH_3)$, $(n-C_4H_9)_2P(OC_6H_5)$, $CH_3P(OC_2H_5)Cl$ and $C_2H_5P(OC_6H_5)Cl$. Of these compounds, trialkyl phosphites of formula $P(OR^4)_3$ are most preferred.

Examples of suitable titanium compounds and/or vanadium compounds which are supported on the solid product formed by the reaction between organomagnesium compound and the hydrocarbyloxyaluminium and/or hydrocarbyloxyphosphorus compound include, for example, titanium compounds of formula



(in which R^7 represents a hydrocarbon group having from 1 to 20 carbon atoms, X represents a halogen atom and m is a number such that $0 \leq m \leq 4$), vanadium tetrachloride or vanadium oxytrichloride. Specific examples of suitable titanium compounds include titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, titanium tetraethoxide, titanium tetrapropoxide, titanium tetraisopropoxide, titanium tetrabutoxide, tetrakis(2-ethylhexyl) titanate, tetrastearyl titanate, ethoxytitanium trichloride, diethoxytitanium dichloride, triethoxytitanium chloride, isopropoxytitanium trichloride,

diisopropoxytitanium dichloride, triisopropoxytitanium chloride, butoxytitanium trichloride, dibutoxytitanium dichloride, tributoxytitanium chloride, ethoxytitanium tribromide, diethoxytitanium dibromide, triethoxytitanium bromide, propoxytitanium tribromide, dibutoxytitanium dibromide and tributoxytitanium bromide. Of these compounds, titanium tetrachloride is particularly preferred. These

titanium and vanadium compounds may be used singly or in any combination. The preparation of the solid composition of the present invention is highly preferably carried out in an atmosphere of an inert gas, such as nitrogen or argon. The reaction between the organomagnesium compound and the hydrocarbyloxy compound is preferably carried out at a temperature of from -30°C to $+150^{\circ}\text{C}$, more preferably from -10°C to $+100^{\circ}\text{C}$, and must be carried out in the presence of a solvent. When carrying out this reaction, the hydrocarbyloxy compound may be added as such or in solution or suspension in a suitable liquid to a solution of the organomagnesium compound; alternatively, the organomagnesium compound may be added to the hydrocarbyloxy compound in the presence of a solvent. There is no particular limitation upon the reaction time, provided that sufficient time is allowed to complete the reaction, but normally the reaction will require at least 10 minutes and more commonly from 30 minutes to 5 hours.

The preferred molar ratio of organomagnesium compound to hydrocarbyloxy compound is from 1:10 to 10:1, more preferably from 1:3 to 3:1. The solvent employed for this reaction may be, for example: an aliphatic hydrocarbon, e.g. pentane, hexane, heptane or octane; an aromatic hydrocarbon, e.g. benzene, toluene or xylene; an alicyclic hydrocarbon, e.g. cyclohexane or cyclopentane; or an ether compound of formula $\text{R}^8-\text{O}-\text{R}^9$ (in which R^8 and R^9 are the same or different and each represents a hydrocarbon group having from 1 to 20 carbon atoms or, together with the oxygen atom to which they are attached, they form a heterocyclic ring). Specific examples of such ethers include: diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, di-sec-butyl ether, dipentyl ether, diisopentyl ether, dihexyl ether, dioctyl ether, diphenyl ether, dibenzyl ether, anisole, phenetole, methyl benzyl ether and tetrahydrofuran. A single one of these solvents or a mixture of any two or more thereof may be used.

The solid product obtained by reaction of the organomagnesium compound with the hydrocarbyloxy compound is then isolated and used as a solid carrier in the next stage of the process of the invention. For example, the solid product may be isolated by filtration and then used directly in the next stage or, before its use in the next stage, it may be washed with an inert hydrocarbon solvent (e.g. hexane, heptane, octane, benzene, toluene, xylene or cyclohexane) or it may be dried. A particularly preferred product for use as the solid carrier is a complex having a coordinated ether compound, which can be produced by carrying out this reaction using the ether compound as a solvent or simply in the presence of the ether compound. The amount of coordinated ether can be adjusted by varying the reaction conditions, the nature of the ether and the washing and drying conditions, we generally prefer that the amount should be adjusted to from 0.1 to 100% by weight, more preferably from 0.5 to 50% by weight, based on the weight of the solid product excluding the ether.

The product thus obtained has good particle size distribution and, in general, has physical properties indicating that it will function as a superior catalyst carrier. Generally, the solid product is amorphous or very weakly crystalline and the X-ray diffraction pattern of the product shows hardly any peak or, if a peak is there, it is very broad and weak at 51 to 52° (2θ).

The resulting solid product is then used as a carrier for a titanium compound and/or vanadium compound. The titanium compound and/or vanadium compound may be applied to the carrier by any of the well-known methods such as impregnation or kneading. For example, the titanium compound and/or vanadium compound and the solid carrier may be contacted with each other either in the absence of a solvent or in the presence of a suitable inert solvent, which is preferably a hydrocarbon. This reaction is preferably carried out at a temperature from room temperature to 150°C . The reaction product may then be filtered, washed with inert hydrocarbon solvent (e.g. one of those described above in relation to the washing of the solid product) and used as it is or after drying.

The reaction conditions and reaction time are preferably so chosen as to adjust the amount of titanium compound and/or vanadium compound supported on the carrier so that the content of titanium atoms and/or vanadium atoms is from 0.01 to 30% by weight, more preferably from 0.1 to 15% by weight, based on the weight of the resulting solid composition. This solid composition has good particle shape and a narrow particle size distribution, like the solid product, and has very good properties for use as a catalyst.

The organoaluminium compound which, together with the solid composition of the invention, forms a catalyst system for olefin polymerization is preferably a compound of formula:



[in which R^{10} and R^{11} are the same or different and each represents a hydrocarbon group having from 1 to 20 carbon atoms, Y represents a hydrogen atom or a halogen atom and p and q are numbers such that $0 \leq p < 3$, $0 \leq q < 3$, and $0 \leq (p+q) < 3$]. Specific examples of such aluminium compounds include: trialkylaluminiums, e.g., triethylaluminium, tripropylaluminium, triisobutylaluminium or trihexylaluminium; dialkylaluminium monohalides, e.g. diethylaluminium monochloride, dipropylaluminium monochloride, diisobutylaluminium monochloride or dihexylaluminium

monochloride; alkylaluminium dihalides, e.g. ethylaluminium dichloride, propylaluminium dichloride, isobutylaluminium dichloride or hexylaluminium dichloride; alkylaluminium sesquihalides, e.g. ethylaluminium sesquichloride, propylaluminium sesquichloride, isobutylaluminium sesquichloride or hexylaluminium sesquichloride; alkylaluminium hydrides, e.g. diethylaluminium hydride or diisobutylaluminium hydride; and alkylaluminium hydrocarbyloxides, e.g. diethylaluminium methoxide, diethylaluminium ethoxide, diisobutylaluminium ethoxide, diethylaluminium propoxide, diisobutylaluminium butoxide, diethylaluminium phenoxide, ethylaluminium diethoxide or isobutylaluminium dibutoxide. One of these organoaluminium compounds may be used alone or a mixture of any two or more may be used.

The molar ratio of titanium and/or vanadium atoms in the solid composition of the invention to organoaluminium compound can vary over a very wide range, e.g. from 10:1 to 1:500, but a range from 2:1 to 1:200 is particularly preferred.

The molecular weight distribution of the olefin polymer produced using this composition as catalyst can easily be controlled by varying the type of organoaluminium compound.

The ethylenically unsaturated compound polymerized in the method of the present invention is preferably an olefin and preferably has from 2 to 15 carbon atoms. Examples of suitable ethylenically unsaturated compounds include ethylene, propylene, butene-1, butadiene, 4-methylpentene-1, pentene-1, hexene-1, vinylcyclohexene, styrene and divinylbenzene.

The stereoregularity of polymers of α -ethylenically unsaturated compounds (especially α -olefins such as propylene or butene-1) can be improved by carrying out the polymerization in the additional presence of an electron donor. Suitable electron donors include, for example: oxygen-containing organic compounds, e.g. alcohols, ethers, ketones or esters; nitrogen-containing organic compounds, e.g. amines or amides; and phosphorus-containing organic compounds, e.g. phosphines or phosphates. Specific examples of suitable electron donors include: ethyl alcohol, butyl alcohol, isopentyl alcohol, diethyl ether, dibutyl ether, diisopentyl ether, diphenyl ether, tetrahydrofuran, dioxan, acetone, acetophenone, benzophenone, acetylacetone, ethyl acetate, ethyl benzoate, ethyl *p*-anisate, pyridine, triethylamine, triphenylphosphine, triphenyl phosphite, triphenylphosphine oxide and hexamethylphosphoric triamide.

Although the present invention is useful in the production of homopolymers and copolymers of the ethylenically unsaturated compounds previously described, its effect is particularly remarkable in the production of ethylene homopolymers and copolymers of ethylene with other ethylenically unsaturated compounds, especially olefins such as propylene, butene-1, 4-methylpentene-1, pentene-1, hexene-1 and butadiene.

The polymerization method of the present invention may be carried out using conventional procedures, for example the slurry polymerization process, the gas-phase polymerization process or the solution polymerization process. One desirable procedure for carrying out the polymerization method is to mix the solid composition and the organoaluminium compound in an inert hydrocarbon solvent and then continuously supply the olefin or other ethylenically unsaturated compound to the mixture at a reaction temperature between room temperature and 200°C and at a reaction pressure between atmospheric pressure and about 100 atmospheres. However, it should be understood that the reaction temperature and pressure are not limited to the ranges suggested above and may be outside these ranges, especially both may be higher. Also, for example, hydrogen could be added as a molecular weight regulator. The polymerization may be carried out either continuously or batchwise.

Examples of suitable inert hydrocarbon solvents which may be used as the polymerization medium include: aliphatic hydrocarbons, such as propane, butane, pentane, hexane, heptane or octane; alicyclic hydrocarbons, such as cyclohexane or cycloheptane, and aromatic hydrocarbons, such as benzene, toluene or xylene. A single one of these solvents or a mixture of two or more thereof may be employed. Also, the spent BB fraction may be used as a polymerization solvent.

The invention is further illustrated by the following Examples, in which the properties of the polymers produced were measured by the following methods:

Melt index (MI): Measured at 190°C using a weight of 2.16 kg, according to the method of ASTM D—1238, and expressed in g/10 minutes.

Density: Measured according to Japanese Industrial Standard (JIS) K—6760.

Bulk density: Measured according to JIS K—6721.

EXAMPLE 1

(i) Synthesis of organomagnesium compound

32.0 g of magnesium chips of a quality suitable for the preparation of Grignard reagents were charged into a 1 litre, four-necked flask equipped with a stirrer, a reflux condenser and a dropping funnel; air and moisture in the flask were then completely removed and replaced by nitrogen. A mixture of 120 g of butyl chloride and 500 ml of diethyl ether was placed in the dropping funnel and about 30 ml of the mixture was dropped onto the magnesium to allow the reaction to start. If, at this stage, the reaction does not begin, it can be started by slightly heating the flask. Addition was continued after the reaction had commenced, the mixture being added dropwise at such a rate as to allow the reaction to proceed smoothly. When the addition was complete, the reaction was allowed to continue under reflux.

for about one more hour. The reaction solution was then cooled to room temperature and unreacted magnesium was filtered off using a glass filter.

- 5 The content of Grignard compound in diethyl ether was determined by hydrolyzing the compound with 1N sulphuric acid, followed by back titration with 1N sodium hydroxide using phenolphthalein as indicator. It was found that the content was 2.00 mole/litre. 5

(iii) Synthesis of solid catalytic composition

The air and moisture in a 100 ml four-necked flask equipped with a stirrer, a dropping funnel and a thermometer were thoroughly removed and replaced by nitrogen.

- 10 10.2 g of aluminium triisopropoxide were dissolved in 30 ml of diethyl ether in the flask. To this solution were gradually added dropwise through the dropping funnel and with ice-cooling 25 ml of the diethyl ether solution of butylmagnesium chloride synthesized in step (i) and containing 50.0 mmole of butylmagnesium chloride. A white precipitate was formed. The reaction was allowed to continue for 1 hour with ice-cooling and then at the boiling point of diethyl ether for a further 1 hour. After the reaction, the precipitate was separated by filtration, washed with 50 ml of purified heptane and then again filtered. This washing/filtration cycle was repeated five times, after which the precipitate was 15 dried under reduced pressure at room temperature to give 5.2 g of a white solid. It was found by analysis that the contents of magnesium, aluminium, chloride and diethyl ether in the white solid were 20.5%, 1.3%, 28.8% and 8.7% by weight, respectively. 15

- 20 3.0 g of this white solid were dipped into 30 ml of titanium tetrachloride in a 100 ml four-necked flask and allowed to react at 130°C for 1 hour. After the reaction had finished, the solid product was repeatedly washed with heptane, until titanium tetrachloride could no longer be detected in the washings. The resulting solid catalyst composition was dried and analyzed and it was found that it contained 53 mg of titanium per gram of solid composition. 20

(iii) Polymerization

- 25 The atmosphere in a 1 litre stainless steel autoclave equipped with a magnetic stirrer was completely replaced by nitrogen and then the autoclave was heated to 90°C. 500 ml of heptane completely free from moisture and oxygen, 2.5 mmole of triethylaluminium and 4.2 mg of the solid catalytic composition produced in step (ii) were then added to the autoclave, with stirring. Hydrogen gas corresponding to a partial pressure of 2 kg/cm² gauge and then ethylene to a total pressure of 12 kg/cm² gauge were charged into the autoclave to start the polymerization. The polymerization was 30 continued at 90°C for 1 hour whilst keeping the total pressure at 12 kg/cm² by supplying ethylene. When the polymerization was complete the resulting polymer was filtered off, washed with heptane and dried at 60°C under reduced pressure to give 72 g of polyethylene. The polyethylene had a melt index of 0.26 g/10 minutes and a bulk density of 0.31 g/cm³. In this case, the catalytic activity was 17,000 g (polyethylene)/g(solid catalyst composition).hour or, put another way, 323,000 g(polyethylene)/gTi.hour. 35

EXAMPLE 2

(i) Synthesis of organomagnesium compound

- 35.0 g of magnesium chips of a quality suitable for the preparation of Grignard reagents were charged into a 1 litre four-necked flask equipped with a stirrer, a reflux condenser and a dropping funnel; 40 the air and moisture in the flask were completely removed and replaced by nitrogen. A mixture of 125 g of butyl chloride and 500 ml of dibutyl ether was placed in the dropping funnel and about 30 ml of this mixture was dropped onto the magnesium chips in the flask to allow the reaction to start. After the reaction had commenced, the dropwise addition of the mixture was continued at such a rate as to allow the reaction to proceed smoothly. After all of the mixture has been added, the reaction was allowed to 45 continue at 60—70°C for about 1 more hour. The reaction solution was then cooled to room temperature and unreacted magnesium was filtered off using a glass filter. 45

The content of the Grignard compound in the dibutyl ether solution was determined by hydrolyzing the compound with 1N sulphuric acid, following by back titration with 1N sodium hydroxide, using phenolphthalein as indicator, and it was found to be 2.10 moles/litre.

50 *(ii) Synthesis of solid catalyst composition* 50

The air and moisture in a 100 ml four-necked flask equipped with a stirrer, a dropping funnel and a thermometer were thoroughly removed and replaced by nitrogen.

- 23.8 ml of the dibutyl ether solution prepared in step (i) and containing 50 mmole of butylmagnesium chloride was placed in the flask and stirred. 4.2 g of triethyl phosphite were then 55 gradually added dropwise to the solution, with ice-cooling. A white precipitate formed. The reaction was carried out for about 1 hour with ice-cooling and then for a further 1 hour at 60°C. After completion of the reaction, the precipitate was separated by filtration and washed with 50 ml of purified heptane and filtered. This washing/filtration cycle was repeated five times, and then the precipitate was dried at room temperature under reduced pressure to give 8.4 g of a white solid. On analysis, it was found that 60 the contents of magnesium, phosphorus, chlorine and dibutyl ether were 20.0%, 0.3%, 25.8% and 16.8% by weight, respectively. 60

3.5 g of this white solid was dripped into 30 ml of titanium tetrachloride in a 100 ml four-necked flask and allowed to react at 130°C for 1 hour. After the reaction had finished, the solid product was repeatedly washed with heptane until titanium tetrachloride could no longer be detected in the washings. 3.3 g of a solid catalytic composition was obtained. This composition was dried and analyzed and it was found that the amount of titanium supported was 47 mg/g of solid catalytic composition.

(iii) Polymerization

Polymerization was carried out in the same way as in step (iii) of Example 1, except that 5.1 mg of the solid catalytic composition obtained in step (ii) of this Example was used. 105 g of polyethylene were obtained. This polyethylene had a melt index of 0.64 g/10 minutes and a bulk density of 0.32 g/cm³. The catalytic activity was 20,600 g(polyethylene)/g(solid catalyst composition).hour or 438,000 g(polyethylene)/g Ti.hour.

EXAMPLE 3

A solid catalyst composition was prepared and ethylene was polymerized following the procedures described in Example 1, except that 2.5 mmoles of triisobutylaluminium was used in place of the triethylaluminium and that 3.2 mg of the solid catalyst composition was used. 60.0 g of polyethylene were obtained, the polyethylene having a melt index of 0.20 g/10 minutes and a bulk density of 0.30 g/cm³. The catalytic activity was 18,800 g(polyethylene)/g(solid catalyst composition).hour or 345,000 g(polyethylene)/g Ti.hour.

EXAMPLE 4

A solid catalyst composition was prepared and the ethylene was polymerized following the procedures described in Example 2, except that 2.5 mmoles of diisobutylaluminium hydride was used in place of the triethylaluminium and that 3.5 mg of the solid catalyst composition were employed. 81.0 g of polyethylene were obtained, this polyethylene having a melt index of 0.35 g/10 minutes and a bulk density of 0.31 g/cm³. The catalytic activity was 23,100 g(polyethylene)/g(solid catalyst composition).hour or 491,000 g(polyethylene)/g Ti.hour.

EXAMPLE 5

A solid catalyst composition was prepared and ethylene was polymerized following the procedures described in Example 2, except that 2.5 mmoles of diethylaluminium chloride were used in place of the triethylaluminium, 15.5 mg of the solid catalyst composition were used, the hydrogen pressure was 10 kg/cm² and the total pressure was 20 kg/cm². 74.0 g of polyethylene were obtained, this polyethylene having a melt index of 0.23 g/10 minutes and a bulk density of 0.34 g/cm³. The catalytic activity was 4,770 g(polyethylene)/g(solid catalyst component).hour or 101,000 g(polyethylene)/g Ti.hour.

EXAMPLE 6

A solid catalyst composition was synthesized as described in step (ii) of Example 2, except that 50 mmoles of ethylaluminium diisobutoxide (produced by reaction between triethylaluminium and isobutyl alcohol) was used in place of the triethyl phosphite and that 30 ml of heptane was used as solvent. 4.2 g of a white solid were obtained; this white solid contained 15.8% of dibutyl ether. 3.0 g of this white solid were reacted with titanium tetrachloride as described in step (ii) of Example 1 to give a solid catalyst composition, which was found to contain 51 mg of titanium per 1 g of solid catalyst composition.

Ethylene was then polymerized as described in step (iii) of Example 1, except that 4.0 mg of the solid catalyst composition obtained as described above were used and that 2.5 mmoles of triisobutylaluminium were used in place of the triethylaluminium. 93.5 g of polyethylene were obtained; this polyethylene has a melt index of 0.67 g/10 minutes and a bulk density of 0.32 g/cm³. the catalytic activity was 23,400 g(polyethylene)/g(solid catalyst composition).hour or 459,000 g(polyethylene)/g Ti.hour.

EXAMPLES 7 to 13

Following the procedure described in Example 1, solid catalyst compositions were prepared and used for the polymerization of ethylene, but using the various compounds and polymerization conditions shown in Table 1. The results are also shown in Table 1. In Table 1 and subsequent Tables, the following abbreviations are used:

Et	=	ethyl;
i-Pr	=	isopropyl;
n-Bu	=	n-butyl;
i-Bu	=	isobutyl;
5 Ph	=	phenyl;
THF	=	tetrahydrofuran;
PE	=	polyethylene;
PP	=	polypropylene.

5

Table 1

Ex. No.	Preparation of solid catalyst component			
	Organo-magnesium compound (ether)	$R^1_a A1(OR^2)_b X_c$	$\frac{Mg}{A1}$ (atomic ratio)	Reaction solvent
7	n-BuMgCl (Et ₂ O)	A1(O-i-Pr) ₃	$\frac{1.0}{0.5}$	Diethyl ether
8	n-BuMgCl (Et ₂ O)	A1(O-i-Pr) ₃	$\frac{1.0}{0.3}$	Diethyl ether
9	n-BuMgCl (THF)	A1(O-i-Pr) ₃	$\frac{1.0}{1.0}$	Toluene
10	EtMgCl [(n-Bu) ₂ O]	A1(O-n-Bu) ₃	$\frac{1.0}{1.0}$	Heptane
11	i-PrMgCl [(n-Bu) ₂ O]	A1(OEt) ₃	$\frac{1.0}{1.0}$	Diisopentyl ether
12	n-BuMgCl [(n-Bu) ₂ O]	A1(OC ₆ H ₅) ₃	$\frac{1.0}{1.0}$	Dibutyl ether
13	n-BuMgCl [(n-Bu) ₂ O]	A1(O-i-Pr) ₃	$\frac{1.0}{1.0}$	Dibutyl ether

Table 1 (continued)

Ex. No.	Amount of ether co-ordinated (wt %)	Ti/V compound (amount supported, wt %)	Polymerization conditions		Yield (g)
			Solid catalyst component (mg)	Organo-aluminium compound	
7	6.3	TiCl ₄ (4.3)	4.5	Et ₃ Al	71.0
8	5.5	TiCl ₄ (4.8)	4.0	Et ₃ Al	55.7
9	38.7	TiCl ₄ (5.8)	3.2	(i-Bu) ₃ Al	65.8
10	16.2	TiCl ₄ (3.5)	4.1	(i-Bu) ₃ Al	70.5
11	23.4	Ti(OEt) ₂ Cl ₂ (4.7)	5.5	Et ₃ Al	77.6
12	20.3	TiCl ₄ (5.6)	3.1	Et ₃ Al	80.0
13	18.7	VOCl ₃ (6.4)	5.1	Et ₃ Al	37.0

Table 1 (continued)

Ex. No.	Catalytic activity		Bulk density (g/cm ³)	Melt index (MI) (g/10 min.)
	g (PE)/g(solid catalyst component). hr	g(PE)/g Ti.hr		
7	15,800	367,000	0.31	0.30
8	13,900	290,000	0.30	0.35
9	20,600	355,000	0.28	0.25
10	17,200	491,000	0.32	0.23
11	14,100	300,000	0.27	0.08
12	25,800	461,000	0.31	0.48
13	7,250	113,000	0.28	0.17

EXAMPLES 14 to 20

Following the procedure described in Example 2, solid catalyst compositions were prepared and used to polymerize ethylene using the compounds and polymerization conditions shown in Table 2. The results are also shown in Table 2.

Table 2

Ex. No.	Preparation of solid catalyst component		
	Organo- magnesium compound (ether)	$R^3_dP(OR^4)_eX_f$	$\frac{Mg}{P}$ (atomic ratio)
14	n-BuMgCl (Et ₂ O)	P(OEt) ₃	$\frac{1.0}{3.0}$
15	n-BuMgCl [(n-Bu) ₂ O]	P(O-n-Bu) ₃	$\frac{1.0}{1.0}$
16	n-BuMgCl [(n-Bu) ₂ O]	P(OPh) ₃	$\frac{1.0}{0.5}$
17	EtMgCl (THF)	P(OPh) ₃	$\frac{1.0}{0.5}$
18	n-BuMgCl [(n-Bu) ₂ O]	P(OCH ₂ CH ₂ C1) ₃	$\frac{1.0}{1.0}$
19	n-BuMgCl [(n-Bu) ₂ O]	n-BuP(O-i-Pr) ₂	$\frac{1.0}{1.0}$
20	n-BuMgCl [(n-Bu) ₂ O]	P(OEt) ₂ C1	$\frac{1.0}{1.0}$

Table 2 (continued)

Ex. No.	Amount of ether coordinated (wt %)	Ti/V compound (amount supported wt %)	Polymerization conditions		Yield (g)
			Solid catalyst component (mg)	Organo-aluminium compound	
14	5.8	TiCl ₄ (5.3)	3.6	Et ₃ Al	80.6
15	16.3	TiCl ₄ (6.2)	3.0	(i-Bu) ₃ Al	75.6
16	20.5	TiCl ₄ (2.8)	4.1	Et ₃ Al	88.2
17	42.0	TiCl ₄ (6.5)	3.3	(i-Bu) ₂ AlH	77.0
18	15.4	TiCl ₄ (4.8)	4.8	Et ₃ Al	88.8
19	16.0	VOCl ₃ (5.0)	5.6	Et ₃ Al	47.2
20	20.5	Ti(O-n-Bu) ₂ -C ₁₂ (3.7)	4.5	(i-Bu) ₃ Al	77.4

Table 2 (continued)

Ex. No.	Catalytic activity		Bulk density (g/cm ³)	Melt index (g/10 min)
	g(PE)/g(solid catalyst component).hr	g(PE)/g Ti.hr or g(PE)/g V.hr		
14	22,400	423,000	0.31	0.57
15	25,200	406,000	0.32	0.48
16	21,500	768,000	0.30	0.60
17	23,300	358,000	0.28	0.45
18	18,500	385,000	0.32	0.38
19	8,430	169,000	0.30	0.35
20	17,200	465,000	0.29	0.14

EXAMPLE 21

5 90.0 g of an ethylene/propylene copolymer were prepared using the same polymerization procedure described in Example 1, except that 3.1 mg of the solid catalyst composition of Example 1 was used, 10 g of propylene were added and the polymerization was carried out at 70°C for 30 minutes. This copolymer contained 15.0 methyl groups/1000 carbon atoms. The physical properties of the copolymer were as follows:

Density, 0.40 g/cm³;

Melt Index, 0.18 g/10 minutes;

Bulk density, 0.30 g/cm³.

The catalytic activity was 58,100 g(polymer)/g(solid catalyst composition).hour or 1,520,000 g(polymer)/g Ti.hour.

EXAMPLE 22

75.5 g of an ethylene/butene-1 copolymer were obtained using the same polymerization procedure described in Example 1, except that 3.0 mg of the solid catalyst composition of Example 2 were used, 10 g of butene-1 were added and the polymerization was carried out at 70°C for 30 minutes. This copolymer contained 5.0 ethyl groups/1000 carbon atoms. The physical properties of the copolymer were as follows:

Density, 0.942 g/cm³;

Melt Index, 0.38/10 minutes;

Bulk density, 0.40 g/cm³.

The catalytic activity was 50,300 g(polymer)/g(solid catalyst composition).hour or 1,070,000 g(polymer)/g Ti.hour.

EXAMPLE 23

94.6 g of an ethylene/butene-1 copolymer were obtained following the procedure described in Example 1, except that 3.1 mg of the solid catalyst composition of Example 2 were used, 250 g of butene-1 were used in place of the 500 ml of heptane, the polymerization temperature was 50°C, and the hydrogen pressure, ethylene pressure and total pressure were 2.5 kg/cm², 18 kg/cm² and 27 kg/cm², respectively (the partial pressure of butene-1 at 50°C was 6.5 kg/cm²). This copolymer contained 18.5 ethyl groups/1000 carbon atoms. The physical properties of the copolymer were as follows:

Density, 0.924 g/cm³;

Melt Index, 0.35 g/10 minutes;

Bulk density, 0.42 g/cm³.

The catalytic activity was 30,500 g(polymer)/g(solid catalyst composition).hour or 649,000 g(polymer)/g Ti. hour.

EXAMPLE 24

The air in a 1 litre stainless steel autoclave equipped with a magnetic stirrer was completely replaced by nitrogen and then 10.5 mg of the solid catalyst composition prepared in step (ii) of Example 1, 2.5 mmoles of triethylaluminium and 300 g of liquid propylene were charged into the autoclave. Polymerization was then carried out at 60°C for 1 hour, after which the propylene was purged and the product was removed and dried at 60°C under reduced pressure to give 92.0 g of polypropylene. The boiling heptane-insoluble portion of this polypropylene was 38.5% by weight. The catalytic activity was 8,760 g (polypropylene)/g(solid catalyst composition).hour or 165,000 g(polypropylene)/gTi.hour.

EXAMPLES 25 to 27

Propylene was polymerized following the same procedure as was used in Example 24, except that the solid catalyst composition and its amount were varied as shown in Table 3 and that an electron donor of the type and in the amount shown in Table 3 was added as a third catalyst component. The results are shown in Table 3.

Table 3

Ex. No.	Polymerization conditions			
	Solid catalyst component of Ex. No. (mg)	Organo-aluminium compound	Third component	Amount of third component (mole)
25	Example 2 25.0	(C ₂ H ₅) ₃ Al	Ethyl p-anisate	1.0
26	Example 1 18.5	(C ₂ H ₅) ₃ Al	Acetone	2.5
27	Example 1 25.0	(C ₂ H ₅) ₃ Al	Hexamethyl-phosphoric triamide	0.5

Table 3 (continued)

Ex. No.	Yield (g)	Catalytic activity		Boiling n-heptane-insoluble portion (%)
		g(PP)/g (solid catalyst component) . hr	g(PP)/g Ti, hr	
25	30.0	1,200	25,500	91.0
26	55.2	2,980	56,300	68.5
27	87.5	3,500	66,000	75.0

CLAIMS

1. A process for producing a solid composition in which an organomagnesium compound is reacted in solution with a hydrocarbyoxyaluminium compound of formula:



[in which R¹ and R² are the same or different and each represents an optionally substituted hydrocarbon group having from 1 to 20 carbon atoms, X represents a halogen atom and a, b and c are numbers such that 0 ≤ a < 3, 0 ≤ b ≤ 3, 0 ≤ c < 3 and (a + b + c) = 3] and/or a hydrocarbyoxyphosphorus compound of formula:



[in which R³ and R⁴ are the same or different and each represents an optionally substituted hydrocarbon group having from 1 to 20 carbon atoms, X represents a halogen atom and d, e and f are numbers such that 0 ≤ d < 3, 0 ≤ e ≤ 3, 0 ≤ f < 3 and (d + e + f) = 3] to produce a solid product and supporting a titanium compound and/or a vanadium compound on said solid product.

2. A process according to Claim 1, in which the solvent for said solution is an aliphatic hydrocarbon, aromatic hydrocarbon, alicyclic hydrocarbon or ether.

3. A process according to Claim 1, in which said solid product is produced in the presence of an ether and is isolated from the reaction mixture.

4. A process according to any one of the preceding Claims, in which said solid product is isolated from the reaction mixture in the form of a complex with a co-ordinated ether.



Table 3

Ex. No.	Polymerization conditions			
	Solid catalyst component of Ex. No. (mg)	Organo-aluminium compound	Third component	Amount of third component (mole)
25	Example 2 25.0	(C ₂ H ₅) ₃ Al	Ethyl p-anisate	1.0
26	Example 1 18.5	(C ₂ H ₅) ₃ Al	Acetone	2.5
27	Example 1 25.0	(C ₂ H ₅) ₃ Al	Hexamethylphosphoric triamide	0.5

Table 3 (continued)

Ex. No.	Yield (g)	Catalytic activity		Boiling n-heptane-insoluble portion (%)
		g(PP)/g (solid catalyst component) . hr	g(PP)/g Ti, hr	
25	30.0	1,200	25,500	91.0
26	55.2	2,980	56,300	68.5
27	87.5	3,500	66,000	75.0

CLAIMS

1. A process for producing a solid composition in which an organomagnesium compound is reacted in solution with a hydrocarbyloxyaluminium compound of formula:



[in which R¹ and R² are the same or different and each represents an optionally substituted hydrocarbon group having from 1 to 20 carbon atoms, X represents a halogen atom and a, b and c are numbers such that 0 ≤ a < 3, 0 < b ≤ 3, 0 ≤ c < 3 and (a + b + c) = 3] and/or a hydrocarbyloxyphosphorus compound of formula:



[in which R³ and R⁴ are the same or different and each represents an optionally substituted hydrocarbon group having from 1 to 20 carbon atoms, X represents a halogen atom and d, e and f are numbers such that 0 ≤ d < 3, 0 < e ≤ 3, 0 ≤ f < 3 and (d + e + f) = 3] to produce a solid product and supporting a titanium compound and/or a vanadium compound on said solid product.

2. A process according to Claim 1, in which the solvent for said solution is an aliphatic hydrocarbon, aromatic hydrocarbon, alicyclic hydrocarbon or ether.

3. A process according to Claim 1, in which said solid product is produced in the presence of an ether and is isolated from the reaction mixture.

4. A process according to any one of the preceding Claims, in which said solid product is isolated from the reaction mixture in the form of a complex with a co-ordinated ether.



5. A process according to Claim 4, in which the solid product contains from 0.1 to 100% by weight of said ether, based on the weight of the solid product excluding the ether.
6. A process according to Claim 5, in which the amount of ether is from 0.5 to 50% by weight.
7. A process according to any one of Claims 2 to 6, in which said ether is a compound of formula
- 5 R^8-O-R^9 , in which R^8 and R^9 are the same or different and each represents a hydrocarbon group having from 1 to 20 carbon atoms or R^8 and R^9 , together with the oxygen atom to which they are attached, form an oxygen-containing heterocyclic ring. 5
8. A process according to Claim 6, in which said ether is diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, di-sec-butyl ether, dipentyl ether, diisopentyl ether, dihexyl ether, dioctyl ether,
- 10 diphenyl ether, dibenzyl ether, anisole, phenetole, methyl benzyl ether or tetrahydrofuran. 10
9. A process according to any one of the preceding Claims, in which said organomagnesium compound is a compound of formula R^5MgX or R^5_2Mg , in which R^5 represents a hydrocarbon group having from 1 to 20 carbon atoms and X represents a halogen atom.
10. A process according to Claim 9, in which R^5 represents an alkyl, aryl, aralkyl or alkenyl group
- 15 having from 1 to 20 carbon atoms and X represents a chlorine, bromine or iodine atom. 15
11. A process according to any one of the preceding Claims, in which the molar ratio of said organomagnesium compound to said hydrocarbyloxyaluminium compound and/or said hydrocarbyloxy-phosphorus compound is from 1:10 to 10:1.
12. A process according to Claim 11, in which said molar ratio is from 1:3 to 3:1.
- 20 13. A process according to any one of the preceding Claims, in which the reaction between said organomagnesium compound and said hydrocarbyloxyaluminium compound and/or said hydrocarbyloxyphosphorus compound is effected at a temperature from -30°C to $+150^\circ\text{C}$. 20
14. A process according to Claim 13, in which said temperature is from -10°C to $+100^\circ\text{C}$.
15. A process according to any one of the preceding Claims, in which said hydrocarbyloxy-aluminium compound is a compound of formula $Al(OR^2)_3$, in which R^2 is as defined in Claim 1.
- 25 16. A process according to any one of the preceding Claims, in which said hydrocarbyloxy-phosphorus compound is a compound of formula $P(OR^4)_3$, in which R^4 is as defined in Claim 1. 25
17. A process according to any one of the preceding Claims, in which said titanium compound is a compound of formula:
- 30 $Ti(OR^7)_mX_{(4-m)}$ 30
- in which R^7 represents a hydrocarbon group having from 1 to 20 carbon atoms, X represents a halogen atom and m is a number such that $0 \leq m \leq 4$.
18. A process according to Claim 17, in which said titanium compound is titanium tetrachloride.
19. A process according to any one of the preceding Claims, in which said vanadium compound is
- 35 vanadium tetrachloride or vanadium oxytrichloride. 35
20. A process according to any one of the preceding Claims, in which the content of titanium atoms and/or vanadium atoms in said solid composition is from 0.01 to 30% by weight.
21. A process according to Claim 20, in which the content of titanium atoms and/or vanadium atoms in said solid composition is from 0.1 to 15% by weight.
- 40 22. A process according to any one of the preceding Claims, substantially as hereinbefore described with reference to any one of the foregoing Examples. 40
23. A solid composition when produced by a process according to any one of the preceding Claims:
24. A composition suitable for the catalyst of olefin polymerization and comprising a solid
- 45 composition according to Claim 23 and an organoaluminium compound of formula: 45
- $R^{10}_{[p+q]}Al(OR^{11})_pY_q$
- in which R^{10} and R^{11} are the same or different and each represents a hydrocarbon group having from 1 to 20 carbon atoms, Y represents a hydrogen atom or a halogen atom and p and q are numbers such that:
- 50 $0 \leq p < 3$, $0 \leq q < 3$ and $0 \leq (p + q) < 3$. 50
25. A composition according to Claim 24, in which said organoaluminium compound is a trialkylaluminium, a dialkylaluminium monohalide, an alkylaluminium dihalide, an alkylaluminium sesquihalide, an alkylaluminium hydride or an alkylaluminium alkoxide.
26. A composition according to Claim 24, substantially as hereinbefore described with reference
- 55 to any one of the foregoing Examples. 55
27. A method of preparing a polymer in which an ethylenically unsaturated hydrocarbon is polymerized in the presence of a catalyst system comprising a solid composition according to Claim 23 and an organoaluminium compound.
28. A method according to Claim 27, in which said organoaluminium compound is a compound of
- 60 formula: 60
- $R^{10}_{[3-(p+q)]}Al(OR^{11})_pY_q$



in which R^{10} , R^{11} , Y, p and q are as defined in Claim 24.

29. A method according to Claim 28, in which said organoaluminium compound is a trialkylaluminium, a dialkylaluminium monohalide, an alkylaluminium dihalide, an alkylaluminium sesquihalide, an alkylaluminium hydride or an alkylaluminium alkoxide.

5 30. A method according to any one of Claims 27 to 29, in which said ethylenically unsaturated hydrocarbon is an olefin. 5

31. A method according to any of Claims 27 to 30, in which said ethylenically unsaturated hydrocarbon has from 2 to 15 carbon atoms.

10 32. A method according to Claim 31, in which said ethylenically unsaturated hydrocarbon is ethylene, propylene, butene-1, butadiene, 4-methylpentene-1, pentene-1, hexene-1, vinylcyclohexane, styrene or divinylbenzene. 10

33. A method according to any one of Claims 27 to 32, applied to the preparation of a homopolymer.

15 34. A method according to any one of Claims 27 to 32, applied to the preparation of a copolymer of two or more of said ethylenically unsaturated hydrocarbons. 15

35. A method according to any one of Claims 27 to 34, effected in the presence of an electron donor.

36. A method according to Claim 27 substantially as hereinbefore described with reference to any one of the foregoing Examples.

20 37. A polymer when produced by a process according to any one of Claims 27 to 36. 20