

PATENT SPECIFICATION

(11) 1 394 378



- (21) Application No. 56719/72 (22) Filed 8 Dec. 1972
 (31) Convention Application No. 64420 (32) Filed 8 Dec. 1971
 (31) Convention Application No. 65445 (32) Filed 1 June 1972 in
 (33) Luxembourg (LU)
 (44) Complete Specification published 14 May 1975
 (51) INT CL² C08F 10/00, 4/44

(52) Index at acceptance

C3P 13D1A 13D1B 13D1X 13D2A 13D2B 13D2C 13D2X
 13D8A 13D8B 13G4B 13G7B1 13G7C 13G7X
 13G7Y 13G8A 13G8X 13G8Y 13H3 13K2A 13N2
 13N4 13R2A 13R3A D4
 B1E 302 322 32Y 341 342 34Y 360 36Y 370 371 37Y 383
 38Y 400 40Y 420 42Y 461 49Y 542 578 580
 584 652 693 754 755 75Y 760

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(54) PROCESS FOR THE POLYMERISATION OF OLEFINS SOLID CATALYTIC COMPLEXES THEREFOR, AND PROCESS FOR THE PREPARATION OF THESE COMPLEXES

(71) We, SOLVAY & CIE, a body corporate organised under the laws of Belgium, of 33, Rue Prince Albert, Brussels 5, Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the polymerisation of alpha-olefins whose molecule contains from 2 to 20 carbon atoms, and in particular to the low-pressure polymerisation of these alpha-olefins. It also relates to solid catalytic complexes (being complexes insoluble in alkanes and cycloalkanes) which can be used for the polymerisation of these alpha-olefins, a process for preparing these complexes, and the polymers obtained by means of the process of the invention.

It is known that, in the low-pressure polymerisation of olefins, catalytic systems containing a transition metal compound and an organo-metallic compound can be used.

It is also known, from our Belgian Patent Specification No. 705220 of the 17th October 1967, that the transition metal compound of the catalytic systems mentioned above can be a solid obtained by reacting a halogen-containing compound of a transition metal with an oxygen-containing compound of a divalent metal, e.g. magnesium. The catalytic systems thus obtained are very active in comparison with those in which a halogen-containing compound of a transition metal is used *per se*.

In our Belgian Patent Specification No. 767586 of the 25th May 1971, catalytic systems are described, one of the components of which is prepared by reacting an oxygen-

containing organic compound of a divalent metal with an alkylaluminium halide, separating the product of this reaction, and subsequently reacting it with a halogen-containing compound of a transition metal. These catalytic systems are also characterised by a high activity.

However, the known catalytic systems with a high activity, do lead to polymers which have a serious defect. Thus, although their physical properties and more particularly their mechanical properties are mostly quite satisfactory, their impact resistance is sometimes inadequate. Impact resistance is of course an important property in polyolefins inasmuch as they are used in large quantities for manufacturing products in the nature of containers or handling aids (crates, tanks, and pallets), and packaging products (bottles and films), these products being frequently subjected to impacts or shocks when in use.

We have now found that the use of a certain new type of catalytic complex for the low-pressure polymerisation of the above-mentioned alpha-olefins makes it possible to manufacture, with very high catalyst activities, polyolefins with very good impact resistance.

According to present invention, therefore, we provide a process for the polymerisation of alpha-olefins whose molecule contains from 2 to 20 carbon atoms, in which the polymerisation is carried out in the presence of a catalytic system comprising: an organometallic compound of a metal (as herein defined) of group Ia, IIa, IIb, IIIb or IVb of the Periodic Table and a solid catalytic complex (being a complex insoluble in alkanes and cycloalkanes) prepared by reacting

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(1) an oxygen-containing organic compound (M) of a metal (as herein defined) (Me) of group Ia, IIa, IIIb, IVb, VIIa or VIII of the Periodic Table comprising only sequences of metal-oxygen-organic radical bonds with

(2) a non-halogenated oxygen-containing organic compound (T) of a metal (Tr) of group IVa, Va or VIa of the Periodic Table in which an organic radical is attached to the metal (Tr) via oxygen; and with

(3) a halide of aluminium (A) (as herein defined).

In the oxygen-containing organic compounds (M) from which the catalytic complexes used in the present invention are derived, the metals (as herein defined) (Me) of Groups Ia, IIa, IIIb, IVb, VIIa and VIII of the Periodic Table (the version referred to herein is that adopted in 1959 by the Société Chimique de France) may for example be: lithium, sodium, potassium (Group Ia); magnesium, calcium (Group IIa); boron, aluminium (Group IIIb); silicon, tin (Group IVb); manganese (Group VIIa); iron, cobalt, nickel (Group VIII). By a "metal" we mean herein a true metal, or boron, or silicon. We prefer to use oxygen-containing organic compounds of divalent metals (Me) (magnesium, calcium, manganese, iron, nickel, cobalt, tin). Good results are also obtainable with oxygen-containing organic compounds of aluminium and silicon. The best results have been obtained with oxygen-containing organic compounds of magnesium. The oxygen-containing organic compound (M) is any organic compound of a metal (Me) comprising only sequences of metal-oxygen-organic radical bonds.

The organic radicals attached to the metal via oxygen can be of any type. They are preferably radicals containing 1 to 20 carbon atoms, and more particularly 1 to 6 carbon atoms. These radicals may be saturated or unsaturated, with branched chains, unbranched chains or cyclic structures; they may also be substituted and/or contain hetero-atoms (e.g. O, S, N or P) in their chain. They may in particular be of any of the following kinds: alkyl, alkenyl, aryl, cycloalkyl, arylalkyl, alkyl-aryl, acyl and aroyl radicals, and their substitution derivatives.

Among the oxygen-containing organic compounds (M) which can be used within the scope of the invention, the following may be mentioned; alkoxides, e.g. methylates, ethylates, isopropylates, *n*-butylates, isobutylates, methoxyethylates and hydroxymethylates; phenates, e.g. salts of monohydroxybenzene, naphthenates, anthracenates, phenanthrenates and cresolates; salts of carboxylic acids, e.g. acetates, butanoates, laurates, pivalates, crotonates, phenylacetates, benzoates, malonates, adipates, sebacates, phthalates, mellitates, acrylates, oleates and maleates; chelates (that is to say oxygen-containing organic compounds

in which the metal (Me) has at least one sequence of normal bonds of the metal-oxygen-organic radical type, and at least one co-ordination bond, so as to form a heterocycle in which the metal (Me) is included), e.g. enolates and in particular acetyl-acetonates, as well as complexes obtained from phenol derivatives possessing an electron donor group in the ortho position with respect to the hydroxyl group, and in particular complexes of 8-hydroxyquinolin; nitrogen and oxygen-containing organic compounds (that is to say compounds containing sequences of metal-oxygen-nitrogen-organic radical bonds), e.g. oximates and in particular butyloximates, dimethylglyoximates and cyclohexyloximates, salts of hydroxamic acids and salts of hydroxylamines, and in particular derivatives of N-nitroso-N-phenylhydroxylamine.

However, it is preferable to use alkoxides and phenates and more particularly those derived from divalent metals (preferably magnesium) which only possess sequences of divalent metal-oxygen-organic radical bonds.

The use of the oxygen-containing organic compounds (M) containing several different organic radicals also falls within the scope of the invention, as also does the use of a number of different oxygen-containing compounds of one and the same metal.

Again, use may be made of a number of oxygen-containing organic compounds of different metals. In this case, these compounds may be used in the form of mixed complex compounds, or again separately. A particularly advantageous procedure in accordance with the invention consists in using jointly an oxygen-containing organic compound of a metal of Group IIa (preferably magnesium) and an oxygen-containing organic compound of a metal of group IIIb or IVb (preferably silicon or, and more particularly, aluminium).

In order to prepare the catalytic complexes used in accordance with the invention use is also made of non-halogenated oxygen-containing organic compounds (T) of metals (Tr) of groups IVa, Va and VIa of the Periodic Table in which an organic radical is attached to the metal (Tr) via oxygen. Among these metals we prefer to use titanium, zirconium and vanadium. The best results have been obtained with titanium.

Compounds containing metal-oxygen bonds and condensed compounds containing sequences of metal-oxygen-metal bonds may be used as the compounds (T), provided they have at least one sequence of metal-oxygen-organic radical bonds per molecule.

The organic radicals attached to the metal (Tr) via oxygen may be of any kind. They may generally comprise from 1 to 20 carbon atoms, and preferably have 1 to 10 carbon atoms. The best results have been obtained when they contain 1 to 6 carbon atoms. The organic radicals are preferably hydrocarbon

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radicals, and more particularly they are preferably alkyl radicals (unbranched or branched), cycloalkyl radicals, arylalkyl radicals, aryl radicals or alkylaryl radicals.

- 5 The non-halogenated oxygen-containing organic compounds (T) may be represented by the general formula $[\text{Tr O}_x(\text{OR})_y]_m$ in which Tr is a metal of group IVa, Va, or VIa of the Periodic Table, in which R is an organic radical as defined above, in which x and y are any numbers such that $x \geq 0$ and $y > 0$, and are compatible with the valency of the metal Tr, and in which m is an integer. It is preferable to use oxygen-containing organic compounds (T) in which x is such that $0 \leq x \leq 1$ and m is such that $1 \leq m \leq 6$.

- 10 Among the non-halogenated oxygen-containing organic compounds (T) which can be used within the scope of the present invention, we may mention:

- alkoxides, e.g. $\text{Ti}(\text{O}i\text{C}_3\text{H}_7)_4$, $\text{Ti}(\text{O}i\text{C}_4\text{H}_9)_4$,
 $\text{V}(\text{O}i\text{C}_3\text{H}_7)_3$, and $\text{Zr}(\text{O}i\text{C}_3\text{H}_7)_4$;
 phenates, e.g. $\text{Ti}(\text{OC}_6\text{H}_5)_3$;
 oxyalkoxides, e.g. $\text{VO}(\text{O}i\text{C}_3\text{H}_7)_3$;
 condensed alkoxides, e.g. $\text{Ti}_2\text{O}(\text{O}i\text{C}_3\text{H}_7)_6$;
 and
 enolates, e.g. titanium acetylacetonate.

- 15 The use of non-halogenated oxygen-containing organic compounds (T) containing several different organic radicals also falls within the scope of the present invention, as also do the use of several different oxygen-containing organic compounds of one and the same metal, and the use of a number of oxygen-containing organic compounds of different metals.

- 20 The third reagent used for preparing the catalytic complexes is an aluminium halide (A); this is defined as an aluminium halide of the general formula $\text{AlR}'_n\text{X}_{3-n}$ in which R' is a hydrocarbon radical containing 1 to 20 carbon atoms and preferably 1 to 6 carbon atoms, X is halogen, and may be F, Cl, Br or I, and n is any number such that $0 \leq n \leq 3$. Preferably R' is an alkyl (unbranched or branched), cycloalkyl, arylalkyl, aryl or alkyl-aryl radical. The best results have been obtained when X represents chlorine and n is such that $0 \leq n \leq 2$ and preferably such that $1 \leq n \leq 2$.

- 25 As examples of the aluminium halides which can be used in accordance with the invention we may mention:

- 55 AlCl_3 , $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, $\text{Al}_2(\text{C}_2\text{H}_5)_5\text{Cl}_3$ and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$.

It is also possible to use a number of different aluminium halides.

- 60 In the preparation of the catalytic complex, the oxygen-containing organic compound (M), the non-halogenated oxygen-containing organic compound (T) and the aluminium halide (A) may be used:

in the solid state, for example in suspension

in an inert diluent or in the form of dry particles;

in the liquid state, when the conditions of operation permit it;

in the form of a solution; or

in the form of a vapour or gas.

70 It is preferable to prepare the solid catalytic complex in a liquid medium, if desired in the presence of a diluent, which is preferably a diluent in which at least one of the reactants is soluble. Virtually all the solvents commonly used in preparative organic chemistry may be employed. However, it is preferable to use alkanes and cycloalkanes whose molecule contains from 4 to 20 carbon atoms, e.g. isobutane, normal pentane, normal hexane, cyclohexane, methylcyclohexane or the dodecanes. Use may also be made of alcohols whose molecule contains 1 to 12 carbon atoms per hydroxyl group, e.g. ethanol, butanol or cyclohexanol. When a diluent is used it is preferable for the total concentration of the dissolved reactant(s) to be greater than 5% by weight and preferably greater than 20 per cent by weight, reckoned on the diluent.

80 It is also possible to prepare the catalytic complex in a liquid medium in the absence of diluent, however, and this is a preferred procedure in accordance with the invention; in this case the temperature and pressure have to be such that at least one of the reactants is in the liquid state. Preferably the conditions are such that the non-halogenated oxygen-containing organic compound (T) is liquid. In practice, it frequently happens that this non-halogenated oxygen-containing organic compound (T) when maintained in the liquid state is capable of dissolving the oxygen-containing organic compound (M). It is also possible to use a second oxygen-containing organic compound (M) which is liquid and which is capable of dissolving the first one.

85 The temperature at which the reaction is carried out is not critical. It may generally be such that at least one of the reactants is liquid or is in solution. For reasons of convenience, it is preferable to operate at between 20 and 300° C and more particularly between 50 and 200° C. The pressure is also not critical; generally it is satisfactory to operate in the vicinity of atmospheric pressure. So as to promote the homogenisation of the reaction medium, it may generally be agitated during the period of the reaction.

90 The order of addition of the reactants may be as desired. However, it is preferable to operate by one of the following methods;

- 1) The oxygen-containing organic compound (M) is brought into contact with the non-halogenated oxygen-containing organic compound (T) by adding one to the other or by mixing them gradually; in practice it frequently happens that a complex is

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formed which is liquid or soluble in the diluent; the aluminium halide (A) is then gradually added.

2) The non-halogenated oxygen-containing organic compound (T) and the aluminium halide (A) are mixed together, preferably rapidly, and then the oxygen-containing organic compound (M) is added.

3) The three reactants are mixed together simultaneously and gradually.

The rate of addition of the reactants is also not critical. It is advisable that it should not be such as to bring about an abrupt heating of the reaction medium due to an excessively rapid reaction. The reaction may be carried out continuously or non-continuously.

The quantities of oxygen-containing organic compound (M), non-halogenated oxygen-containing organic compound (T) and aluminium halide (A) which are preferably used will now be indicated.

The quantity of the compound or compounds (T) which is preferably used is defined in relation to the total quantity of the compound or compounds (M) used. It may vary within wide limits. Generally speaking it may be between 0.01 and 10 gram atoms of metal (Tr) present in the compound (T) per gram atom of metal (Me) present in the compound (M). It has been observed that the productivity of the catalytic complexes of the invention, that is to say the quantity of polymer produced in relation to the quantity of catalytic complex used, is at a maximum with a ratio of between 0.05 and 5 gram atoms of metal (Tr) per gram atom of metal (Me). The best results have been obtained when this ratio is between 0.10 and 2 gram atoms per gram atom. However, when the ratio is between 0.025 and 0.10 gram atoms per gram atom the specific activity, that is to say the quantity of polymer produced in relation to the quantity of metal (Tr) used, is extremely high; on the other hand, the productivity is lower.

The quantity of aluminium halide (A) which is preferably used, reckoned in relation to the total quantity of the compound or compounds (M) and of the compound or compounds (T) used, may also vary within wide limits. Generally speaking it may be between 0.10 and 10 moles of aluminium halide (A) per gram equivalent of metal (Me) and metal (Tr) present altogether in the compounds (M) and (T) used. By "gram equivalent" we mean the weight in grams of these metals which is capable of reacting with or replacing one gram atom of hydrogen. Preferably this quantity is between 0.50 and 5 moles per gram equivalent. The best results have been obtained when it is between 0.75 and 2 moles per gram equivalent.

When use is made of a compound (M) of

a metal (Me)₁ of Group IIa and a second compound (M) of a metal (Me)₂ of Group IIb or IVb, the quantities of these compounds to be used are preferably such that the ratio between the quantity of metal (Me)₁ and that of the Metal (Me)₂ is between 0.01 and 100 gram atoms per gram atom. Preferably this ratio is between 0.1 and 10 gram atoms per gram atom. The best results have been obtained when it is between 0.5 and 1.5 gram atoms per gram atom.

The catalytic complexes prepared in accordance with the invention are solid. As already specified, they are insoluble in alkanes and cycloalkanes, which can be used as diluents. They may be used in polymerisation in the form in which they are obtained, without being separated from the reaction medium. However, it is preferable to separate them from this reaction medium by any applicable means. When the reaction medium is liquid, it is possible to resort to filtration, decantation or centrifuging, for example.

After separation, the catalytic complexes may be washed so as to eliminate excess reactants which may still be adhering to them. For this washing any inert diluent may be used, for example any of those which can be used as constituents of the reaction medium, e.g. alkanes and cycloalkanes. After washing, the catalytic complexes may be dried, for example by passing a stream of dry nitrogen over them, or *in vacuo*.

The mechanism of the formation of the catalytic complexes of the invention is not fully understood. The elementary analysis of the catalytic complexes after separation and washing shows that they are chemically combined complexes, i.e. products of chemical reactions, and not the result of mere mixing or adsorption phenomena. In point of fact it is impossible to dissociate one or other of the constituents of these complexes using purely physical means of separation.

The catalytic complexes of the invention, the exact nature of which is also not fully understood, contain metal (Me), metal (Tr), aluminium and halogen in variable quantities. More often than not they contain, per kg., between 10 and 150 g of metal (Me), between 20 and 250 g of metal (Tr), more than 10 g of aluminium, and between 200 and 700 g of halogen. They are characterised by a high specific surface area, which is more often than not greater than 50 sq.m. per gram and which may be as high as 300 to 400 sq.m. per gram.

The catalytic systems according to the invention also comprise an organometallic compound which serves as an activator, namely an organometallic compound of a metal (as herein defined) of Group Ia, IIa, IIb, IIIb or IVb of the Periodic Table, e.g. an organometallic compound of lithium, magnesium,

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zinc, aluminium or tin. The best results have been obtained with the organometallic compounds of aluminium.

It is possible to use completely alkylated compounds whose alkyl chain contains from 1 to 20 carbon atoms and is unbranched or branched, for example n-butyl lithium, diethyl magnesium, diethyl zinc, trimethyl aluminium, triethyl aluminium, triisobutyl aluminium, tri-n-butyl aluminium, tri-n-decyl aluminium, tetraethyl tin or tetrabutyl tin. However, it is preferable to use trialkyl aluminium whose alkyl chains contain from 1 to 10 carbon atoms and are either unbranched or branched.

It is also possible to use the alkyl metal hydrides in which the alkyl radicals also contain from 1 to 20 carbon atoms, e.g. diisobutyl aluminium hydride or trimethyl tin hydride; and alkyl metal halides in which the alkyl radicals again contain from 1 to 20 carbon atoms, e.g. ethyl aluminium sesquichloride, diethyl aluminium chloride or diisobutyl aluminium chloride.

Finally it is also possible to use organo-aluminium compounds obtained by reacting trialkyl aluminium or dialkyl aluminium hydrides whose radicals contain from 1 to 20 carbon atoms with diolefins containing 4 to 20 carbon atoms, and more particularly the compounds known as isoprenyl aluminiums.

The process of the invention can be applied to the polymerisation of olefins with a terminal unsaturation whose molecule contains from 2 to 20, and preferably 2 to 6 carbon atoms, e.g. ethylene, propylene, butene-1, 4-methylpentene-1 or hexene-1. It is also applicable to the co-polymerisation of these olefins with one another, as well as with diolefins, preferably containing 4 to 20 carbon atoms. These diolefins may be non-conjugated aliphatic diolefins, e.g. hexadiene-1,4; monocyclic diolefins, e.g. 4-vinylcyclohexene, 1,3-divinylcyclohexane, cyclopentadiene or cyclooctadiene-1,5; alicyclic diolefins having an endocyclic bridge, e.g. dicyclopentadiene or norbornadiene; or conjugated aliphatic diolefins, e.g. butadiene or isoprene.

The process of the invention can be applied particularly well to the production of homopolymers of ethylene and co-polymers containing at least 90 moles % and preferably 95 moles % of ethylene.

The polymerisation may be carried out by any applicable process; more particularly it may be carried out in solution or in suspension, in a solvent or hydrocarbon diluent, or again in the gaseous phase. For processes carried out in solution or in suspension, use may be made of solvents or diluents similar to those which may be used for the preparation of the catalytic complex; these are preferably alkanes or cycloalkanes e.g. butane, pentane, hexane, heptane, cyclohexane, methylcyclohexane or mixtures thereof. It is also possible to carry out the polymerisation in the

monomer or one of the monomers if this is maintained in the liquid state.

The polymerisation pressure may generally be between atmospheric pressure and 100 kg/cm², and is preferably 50 kg/cm². The temperature may generally be between 20 and 200° C, and is preferably between 60 and 120° C. The polymerisation may be carried out continuously or non-continuously.

The organo-metallic compound and the catalytic complex may be added to the polymerisation medium separately. Instead, however, they may if desired be brought into contact, at a temperature between -40 and 80° C, for a period of up to 2 hours before they are introduced into the polymerisation reactor. It is also possible to bring them into contact with one another in a number of stages, or again one part of the organometallic compound may be added before the introduction into the reactor, or again use may be made of a number of different organometallic compounds.

The total quantity of organometallic compound used is not critical; it may generally be between 0.02 and 50 millimoles per dm³ of solvent, diluent or reactor volume, and is preferably between 0.2 and 5 millimoles per dm³.

The quantity of catalytic complex used may suitably be determined according to the transition metal (Tr) content of the catalytic complex. It may generally be such that the concentration is between 0.001 and 2.5, and preferably between 0.01 and 0.25, milligram atoms of metal per dm³ of solvent, diluent or reactor volume.

The ratio of the quantities of organometallic compound and catalytic complex is also not critical. It may generally be such that the ratio of organometallic compound to transition metal expressed in mole/gram-atom is greater than 1, and preferably greater than 10.

The average molecular weight as indicated by the melt index of the polymers produced by a process according to the invention may be regulated by the addition to the polymerisation medium of one or more molecular weight modifiers, e.g. hydrogen, diethyl zinc or diethyl cadmium, an alcohol or carbon dioxide.

The specific gravity of the homopolymers produced by a process according to the invention can also be regulated, by the addition to the polymerisation medium of an alkoxide of a metal of groups IVa or Va of the Periodic Table. Thus it is possible to produce polyethylenes with a specific gravity intermediate between that of the polyethylenes manufactured by a high-pressure process and that of the classic high-density polyethylenes.

Of the alkoxides which are suitable for this specific gravity regulation, those of titanium and vanadium whose alkoxy radicals contain 1 to 20 carbon atoms each may be mentioned as being particularly effective. These alk-

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oxides include $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$, $Ti[OCH_2CH(CH_3)_2]_4$, $Ti(OC_4H_9)_4$ and $Ti(OC_{10}H_{21})_4$.

5 The process of the invention makes it possible to produce polyolefins with remarkably high productivities. Thus in the homopolymerisation of ethylene, the productivity expressed in grams of polyethylene per gram of catalytic complex used usually exceeds 10,000
10 and in many cases 20,000. The activity reckoned on the quantity of transition metal present in the catalytic complex is also very high. In the homopolymerisation of ethylene again, the activity expressed in grams of polyethylene per gram of transition metal used
15 usually exceeds 50,000 and in many cases 100,000. In the most favourable cases it is greater than 1,000,000.

20 For this reason, the content of catalytic residues in polymers produced by a process according to the invention can be extremely low. More particularly, the residual content of transition metal can be extremely low. Now it is the derivatives of transition metals which
25 are particularly troublesome in catalytic residues, because of certain coloured complexes which they form with the phenolic antioxidants which are commonly included in polyolefin compositions. It is for this reason that
30 in the well-known processes for the polymerisation of olefins by means of catalysts containing a transition metal compound, the polymers have to be purified from the catalytic residues which they contain, for example by a treatment with alcohol. In the process of the invention, the content of troublesome residues
35 is so low that it is possible to omit the purification treatment, which is a costly operation in view of the raw materials and energy which it consumes and the considerable capital investment which it entails.

40 The polyolefins produced according to the invention are characterised by a remarkably high impact resistance. Thus homopolymers of ethylene produced by a process according
45 to the invention, having a melt index of about 5, possess an impact resistance measured by the Izod test of approximately 10 kg cm/cm notch. The polyethylenes of the same melt index produced by the use of known high-activity catalytic systems do not have an impact resistance (measured by the same test)
50 greater than approximately 6 kg cm/cm notch.

55 The polyolefins obtained by the process of the invention may generally be used in any moulding technique; thus they may be used in extrusion, injection, extrusion blow-moulding, or calendering processes for example. They
60 may be used advantageously in applications in which a good impact resistance is required, and in particular for manufacturing crates, tubs, pallets and bottles.

The Examples which follow are intended to illustrate the invention.

Examples 1 to 5.

The following reactants were used:

- 1) magnesium ethylate, $Mg(OC_2H_5)_2$ (sold by Dynamit Nobel);
- 2) titanium tetrabutylate, $Ti(On-C_4H_9)_4$ (sold by Titangesellschaft);
- 3) ethyl aluminium dichloride, $Al(C_2H_5)_2Cl_2$ (sold by Schering).

114 g of magnesium ethylate was added to 170 g of titanium tetrabutylate. The mixture was heated to 170° C with agitation for 2½ hours. It was observed that there was almost complete dissolution of the magnesium ethylate. In the mixture the atomic ratio
75 Ti/Mg was 0.5 gram atom/gram atom $\pm 10\%$ error due to impurities in the reactants.

To the mixture thus made, and previously cooled to ambient temperature, 400 mls. of hexane at 20° C was added, and then, gradually, varying quantities of ethyl aluminium dichloride in the form of a solution in hexane containing 400 g/litre.

An exothermic reaction took place, leading to the formation of the catalytic complex in the form of a precipitate.

The catalytic complex thus formed was separated by filtration and washed with hexane. It was then dried *in vacuo* at 70° C until its weight was constant.

Varying quantities of catalytic complex and 200 mg. of triisobutyl aluminium were introduced into a 1.5-litre autoclave containing 0.5 litres of hexane. The temperature of the autoclave was then brought to about 85° C. Ethylene was introduced under a partial pressure of 10 kg/cm² and hydrogen under a partial pressure of 4 kg/cm².

The polymerisation was continued for one hour with agitation, the total pressure being kept constant by the continuous addition of ethylene. After 1 hour the autoclave was degassed and the polyethylene produced was collected.

Table 1 shows the particular conditions for each experiment and also the results obtained. The ratio $Al/Mg + Ti$ represents the number of moles of ethyl aluminium dichloride used per gram equivalent of magnesium and titanium present in the mixture. This ratio is also accurate to within $\pm 10\%$.

The results given in Table 1 show that the productivity of the catalytic complexes (weight of polymer obtained per gram of complex used) and their specific activity (weight of polymer obtained per hour, per gram of transition metal used, per kg/cm² of ethylene) vary according to the ratio $Al/Mg + Ti$ defined above. They are at a maximum for values of this ratio of between 0.75 and 2 moles/gram equivalent.

TABLE 1

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Quantity of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ used, g		159	318	635	879	1270
Al/Mg + Ti ratio mole/g.-eq		0.31	0.62	1.25	1.75	2.50
Elementary analysis of the catalytic complex						
magnesium	mg/g	90	96	105	88	29
titanium	mg/g	76	92	113	114	202
aluminium	mg/g	48	41	36	40	49
chlorine	mg/g	263	384	573	603	563
Specific surface area of the catalytic complex m^2/g		19	22	273	339	221
Quantity of catalytic complex used mg		27	11	5	5	12
Quantity of polyethylene obtained g		32	65	138	127	121
Productivity gPE/g complex		1200	5900	27 600	25 400	10 100
Specific activity gPE/hr $\times$ g Ti $\times$ kg/cm ² C_2H_4		1600	6400	24 400	22 300	5 000
Fluidity index of the PE g/10 mins (ASTM Standard D 1238-57 T)		0.20	0.77	1.06	0.56	0.27

Examples 6 to 8.

A catalytic complex was prepared as in Examples 1 to 5, except that the quantities of titanium tetrabutylate and ethyl aluminium dichloride were varied.

The polymerisation was carried out under the same conditions as in Examples 1 to 5.

Table 2 shows the particular conditions for

each experiment as well as the results obtained.

The results shown in Table 2, as well as those of Examples 4, 9 and 10, show that the productivity of the catalytic complexes according to the invention is at a maximum for values of the atomic ratio Ti/Mg between 0.10 and 2.

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TABLE 2

		Ex. 6	Ex. 7	Ex. 8
Quantity of Ti (On-C ₄ H ₉) ₄ used	g	85	340	680
Atomic ratio Ti/Mg	g-at/g-at	0.25	1	2
Quantity of Al(C ₂ H ₅)Cl ₂ used	g	635	1270	2540
Ratio Al/Mg + Ti	mole/g-eq	1.66	1.66	2
Elementary analysis of the catalytic complex				
magnesium	mg/g	104	50	23
titanium	mg/g	76	165	216
aluminium	mg/g	43	36	23
chlorine	mg/g	616	593	495
Specific surface area of the catalytic complex	m ² /g	340	320	249
Quantity of catalytic complex used	mg	4	5	6
Quantity of polyethylene obtained	g	131	130	66
Productivity	gPe/g complex	32 800	26 000	11 000
Specific activity gPE/hr × g Ti × kg/cm ² C ₂ H ₄		43 000	15 750	5 100
Fluidity index of the PE	g/10 mins.	0.37	0.34	0.09

Example 9.

The same reagents as in Examples 1 to 5 were used.

5 A mixture containing 100 mls. of hexane, 15 g of magnesium ethylate and 4.5 g of titanium tetrabutylate was kept under agitation and at the boiling point (approximately 69° C) for 0.75 hours. In this mixture the atomic ratio Ti/Mg was 0.10 gram atom/gram atom.

10 To the mixture thus obtained 75 g of ethyl aluminium dichloride were added in the form of a 400 g/litre solution in hexane. This mixture was heated with agitation and under reflux (approximately 73° C) for one hour. The Al/(Mg + Ti) ratio of the mixture was 2.10 moles/gram equivalent. The catalytic complex appeared in the form of a precipitate, which was separated by filtration. It was then dried *in vacuo* at 70° C until its weight was constant.

The elementary analysis of the catalytic complex showed that it contained:

25	magnesium	219 mg/g
	titanium	14 mg/g
	aluminium	23 mg/g
	chlorine	703 mg/g

30 A polymerisation experiment was carried out under conditions identical to those of Ex-

amples 1 to 5. 21 mg of catalytic complex was used.

169 g of polyethylene was obtained, whose melt index was 0.15 g/10 mins. The productivity was therefore 8000 gPE/g catalytic complex, and the specific activity was 57,500 gPE/hr. × g Ti × kg/cm² C₂H₄.

Example 10.

The same reactants were used as in Examples 1 to 5, except that the titanium tetrabutylate was replaced by titanium tetranonylate of the formula Ti(OC₉H₁₉)₄.

114 g of magnesium ethylate were added to 87 g of titanium tetranonylate. The mixture was heated to 195° C with agitation for 2½ hours. It was found that there was almost complete dissolution of the magnesium ethylate. In the mixture the Ti/Mg atomic ratio was 0.14 gram atoms/gram atom to within an error of ± 10% due to impurities in the reactants.

To this mixture, which had previously been cooled to ambient temperature, 1600 mls. of hexane at 20° C were added, and then, gradually, 635 g of ethyl aluminium dichloride in the form of a 400 g/litre solution in hexane.

This mixture was heated with agitation and under reflux (approximately 69° C) for 0.75 hours. The Al(Mg+Ti) ratio of the mixture was 2 moles/gram equivalent. The catalytic

complex appeared in the form of a precipitate. It was separated by filtration and washed with hexane. It was then dried *in vacuo* at 70° C until its weight was constant.

- 5 The elementary analysis of the catalytic complex thus formed showed that it contained:

10	magnesium	165 mg/g
	titanium	41 mg/g
	aluminium	45 mg/g
	chlorine	641 mg/g

A polymerisation test was carried out under identical conditions to those of Examples 1 to 5. 4 mg of catalytic complex was used.

- 15 144 g of polyethylene was obtained whose melt index was 1.09 g/10 mins. The productivity was therefore 36,000 gPE/g catalytic complex and the specific activity was 88,000 gPE/hr. x gTi x kg/cm² C₂H₄.

20 Examples 11 to 14.

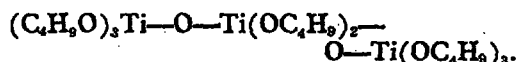
As in Examples 1 to 5, magnesium ethylate and ethyl aluminium dichloride were used. However, the transition-metal compound used was varied, as follows:

- 25 *Example 11:* titanium tetraethylate, (Ti(OC₂H₅)₄) (sold by Titangesellschaft).

Example 12: vanadium oxyoctylate, VO(OC₈H₁₇)₃.

- 30 *Example 13:* zirconium tetrabutylate, Zr(OC₄H₉)₄.

Example 14: a condensed titanium butylate of the average formula:



(Sold by Titangesellschaft); this butylate 35 was heated to 90° C before being used.

114 g of magnesium ethylate was added to various quantities of the above mentioned transition-metal compounds. The mixture was heated to 170° C with agitation for 2½ hours. 40 The almost complete dissolution of the magnesium ethylate was observed.

After the mixture had been cooled, 400 mls. of hexane at 60° C were added to it, and, gradually, various quantities of ethyl aluminium dichloride in the form of a 400 g/litre solution in hexane. 45

An exothermic reaction took place, and gave a catalytic complex in the form of a precipitate. 50

The catalytic complex thus formed was separated by filtration and washed with hexane. It was then dried *in vacuo* at 70° C until its weight was constant.

Polymerisation tests were carried out under conditions identical to those of Examples 1 to 5. 55

Table 3 shows the particular conditions for each test as well as the results obtained.

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TABLE 3

		Ex. 11	Ex. 12	Ex. 13	Ex. 14
Nature of the derivative of transition metal		Ti(OEt) ₄	VO(OOct) ₄	Zr(Obu) ₄	condensed Ti butylate
Quantity of this derivative used g		114	573	383	253
Atomic ratio Tr/Mg	g-at/g-at	0.5	1	1	1
Quantity of Al(C ₂ H ₅) ₂ Cl ₂ used	g	635	635	635	635
Ratio Al/Mg + Tr mole/g-eq		1.25	0.71	0.83	0.83
Elementary analysis of the catalytic complex	magnesium	mg/g	90	44	88
	transition metal				60
	Tr	mg/g	106	89	181
	aluminium	mg/g	34	73	29
	chlorine	mg/g	539	317	480
Specific surface area of the complex	m ² /g	343		140	
Quantity of catalytic complex used g		5	28	20	4
Quantity of polyethylene obtained g		197	84	62	104
Productivity gPE/g complex		39 400	3 000	3 100	26 000
Specific activity gPE/hr × g Tr × kg/cm ² C ₂ H ₄		37 200	3 370	1 700	20 300
Fluidity index of the PE		0.50	0.05	0.51*	0.70

* Fluidity index measured under heavy load (21.6 kg).

Example 15.

The same reactants were used as in Examples 1 to 5, with the addition of zirconium tetrabutylate of formula Zr(OC₄H₉)₄.

114 g of magnesium ethylate were mixed with 100 g of titanium tetrabutylate and 153 g of zirconium tetrabutylate. The mixture was heated to 170° C with agitation for 2½ hours. It was found that there was almost complete dissolution of the magnesium ethylate. In the mixture the (Ti+Zr)/Mg atomic ratio was approximately 0.7 to within an error of ± 10% due to impurities in the reactants. The Ti/Zr atomic ratio was approximately 0.75.

To the mixture thus prepared and previously cooled to ambient temperature, 400 mls. of hexane at 20° C were added, and then, gradually, 635 g of ethyl aluminium dichloride in the form of a 400 g/litre solution in hexane.

An exothermic reaction took place and gave a catalytic complex in the form of a precipitate. The precipitate was separated by filtration and washed with hexane. It was then

dried *in vacuo* at 70° C until its weight was constant.

A polymerisation test was then carried out under conditions identical to those of Examples 1 to 5 except that the partial pressure of ethylene was 5 kg/cm² and that of hydrogen was 2 kg/cm². 6 mg of catalytic complex was used.

61 g of polyethylene was obtained with a melt index of 0.44 g/10 mins. The productivity was therefore 10,000 gPE/g catalytic complex.

Example 16.

The catalytic complex was prepared as in Example 3 except that the ethyl aluminium dichloride was replaced by diethyl aluminium chloride, Al(C₂H₅)₂Cl.

The catalytic complex thus formed had the following elementary composition:

magnesium	67 mg/g
titanium	92 mg/g
aluminium	92 mg/g
chlorine	385 mg/g

A polymerisation experiment was carried out as in Example 3. 147 g of polyethylene were collected, with a melt index of 1.34 g/10 mins. The productivity was therefore 29,400 gPE/g complex, and the specific activity was 32,000 gPE/hr x g Ti x kg/cm² C₂H₄.

Example 17.

The catalytic complex was prepared as in Example 3, except that the ethyl aluminium dichloride was replaced by aluminium trichloride. The latter was used in the solid state in an amount of 665 g.

The catalytic complex thus formed had the following elementary composition:

15	magnesium	66 mg/g
	titanium	1.6 mg/g
	aluminium	96 mg/g
	chlorine	713 mg/g

A polymerisation experiment was carried out as in Example 3. 11 mg of catalytic complex was used.

17 g of polyethylene was produced, having a melt index of 0.08 g/10 mins. The productivity was therefore 1500 gPE/g catalytic complex, and the specific activity was 96,500 gPE/hr x g Ti x kg/cm² C₂H₄.

Examples 18 to 24.

As in Examples 1 to 5, titanium tetra-

butylate and ethyl aluminium dichloride were used. However, the following oxygen-containing organic compounds (M) were used:

<i>Example 18:</i>	potassium ethylate	KOC ₂ H ₅	
<i>Example 19:</i>	calcium ethylate	Ca(OC ₂ H ₅) ₂	35
<i>Example 20:</i>	aluminium propylate	Al(OC ₃ H ₇) ₃	
<i>Example 21:</i>	silicon butylate	Si(OC ₄ H ₉) ₄	
<i>Example 22:</i>	manganese ethylate	Mn(OC ₂ H ₅) ₂	40
<i>Example 23:</i>	iron ethylate	Fe(OC ₂ H ₅) ₃	

Various quantities of these oxygen-containing organic compounds (M) were added to 340 g of titanium tetrabutylate. The preparation of the catalytic complexes was otherwise carried out as in Examples 1 to 5. The polymerisation tests were also as in Examples 1 to 5.

In Example 21, a partially condensed silicon butylate/titanium butylate complex (of a commercial type sold by Dynamit Nobel) was used. This complex contained 84 g of titanium and 28 g of silicon per kg.

Table 4 shows the special conditions in each experiment as well as the results obtained.

TABLE 4

	Ex. 18	Ex. 19	Ex. 20	Ex. 21	Ex. 22	Ex. 23
Nature of compound (M)	KOC ₂ H ₅	Ca(OC ₂ H ₅) ₂	Al(OC ₂ H ₅) ₃	Si(OC ₂ H ₅) ₄	Mn(OC ₂ H ₅) ₂	Fe(OC ₂ H ₅) ₃
Quantity of this compound used g	168	130	408	185	145	190
Atomic ratio Ti/Me g-at/g-at	0.5	1	0.5	1.75	1	1
Quantity of Al(C ₂ H ₅)Cl ₃ used g	635	320	1270	635	635	635
Ratio Al/Me + Ti mole/g-eq	0.85	0.40	1	0.45	0.85	0.70
Elementary analysis of the catalytic complex						
Metal Me mg/g	139	101	—	12	127	182
Titanium mg/g	83	129	209	239	104	92
Aluminum mg/g	93	17	74	44	19	71
Chlorine mg/g	623	378	517	410	457	377
Specific surface area of the catalytic complex m ² /g	74	10	192	50	147	56
Quantity of catalytic complex used mg	30	22	20	25	11	51
Quantity of polyethylene obtained g	18	77	69	70	55	93
Productivity gPE/g complex	600	3500	3500	2800	5000	1800
Specific activity gPE/hr × g Ti × kg/cm ² C ₂ H ₄	700	2700	1650	1170	4760	2020
Fluidity index of the PE g/10mins	0.08	1.4	0.11	1.99*	0.63	1.08*

* Fluidity index measured under heavy load (21.6 kg).

Example 24.

The same reactants were used as in Examples 1 to 5, with the addition of aluminium ethylate, $\text{Al}(\text{OC}_2\text{H}_5)_3$.

- 5 114 g of magnesium ethylate were added to 144 g of titanium tetrabutylate mixed with 284 g of aluminium ethylate. The mixture was heated to 170° C with agitation for 2½ hours. It was observed that there was almost complete dissolution of the magnesium ethylate. In the mixture the $\text{Ti}/(\text{Mg}+\text{Al})$ atomic ratio was 0.15 gram atom/gram atom to within an error of $\pm 10\%$ due to impurities in the reactants.

- 15 To the mixture thus made and previously cooled to ambient temperature, 400 mls. of hexane at 20° C were added, and then gradually 635 g of ethyl aluminium dichloride in the form of a 400 g per litre solution in hexane.

- 20 This mixture was heated with agitation and under reflux (approx. 69° C) for 0.75 hours. The $\text{Al}/(\text{Mg}+\text{Al}+\text{Ti})$ ratio of the mixture was approximately 0.60 moles/gram equivalent. The catalytic complex appeared in the form of a precipitate. It was separated by filtration and washed with hexane. It was then dried *in vacuo* at 70° C until its weight was constant.

- 30 The elementary analysis of the complex thus formed showed that it contained:

35	magnesium	47 mg/g
	titanium	54 mg/g
	aluminium	92 mg/g
	chlorine	502 mg/g

A polymerisation test was carried out under conditions identical with those of Examples 1 to 5. 7 mg of catalytic complex was used.

155 g of polyethylene was produced, having a melt index of 3.04 g/10 mins. The productivity was therefore 22,200 gPE/g catalytic complex and the specific activity was 41,000 gPE/hr. x Ti x kg/cm² C₂H₄.

Examples 25 and 26.

The following reactants were used:

- | | | |
|--------------------------------|--|----|
| (1) magnesium ethylate | $\text{Mg}(\text{OC}_2\text{H}_5)_2$ | |
| (2) aluminium butylate | $\text{Al}(\text{OC}_4\text{H}_9)_3$ | |
| (3) titanium tetranonylate | $\text{Ti}(\text{OC}_9\text{H}_{19})_4$ | |
| (4) ethyl aluminium dichloride | $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ | 50 |

114 g of magnesium ethylate was added to 234 g of aluminium butylate mixed with various quantities of titanium tetranonylate. The mixture was heated to 190° C with agitation for 1½ hours. It was observed that there was almost complete dissolution of the magnesium ethylate.

To the mixture thus formed and previously cooled to ambient temperature, 6 litres of hexane at 20° C was added, and then, gradually, 635 g of ethyl aluminium dichloride in the form of a 400 g per litre solution in hexane.

This mixture was heated to 65° C with agitation for one hour. The catalytic complex appeared in the form of a precipitate. It was separated by filtration and washed with hexane. It was then dried *in vacuo* at 70° C until its weight was constant.

A polymerisation test was carried out under conditions identical to those of Examples 1 to 5 except that only 100 mg of triisobutyl aluminium was used.

Table 5 shows the special conditions for each experiment and also the results obtained.

TABLE 5

		Ex. 25	Ex. 26
Quantity of $\text{Ti}(\text{OC}_2\text{H}_5)_4$ used	g	31	62
Atomic ratio Ti/Mg + Al	g-at/g-at	0.025	0.05
Elementary analysis of the catalytic complex			
magnesium	mg/g	67	93
titanium	mg/g	15	24
aluminium	mg/g	119	130
chlorine	mg/g	479	438
Specific surface area of the catalytic complex			
	m^2/g	—	—
Quantity of catalytic complex used	mg	7.2	3.3
Quantity of polyethylene obtained	g	132	83
Productivity	gPE/g complex	18 400	25 200
Specific activity	$\text{gPE/hr} \times \text{g Ti} \times \text{kg/cm}^2 \text{ C}_2\text{H}_4$	122 000	105 000
Fluidity index of the PE	g/10 mins	1.02	0.52

Examples 25 and 26 show that the specific activity is extremely high when the Ti/(Mg+Al) ratio is between 0.025 and 0.10 gram atom/gram atom.

Examples 27 to 31.

The same reactants were used as in Examples 1 to 5, except that the magnesium ethylate was replaced by:

- 10 *Example 27:* magnesium phenate: $\text{Mg}(\text{OC}_6\text{H}_5)_2$
Example 28: magnesium formate: $\text{Mg}(\text{OOCH})_2$
15 *Example 29:* magnesium benzoate: $\text{Mg}(\text{OOCOC}_6\text{H}_5)_2$
Example 30: magnesium hydroxymethylate: $\text{Mg}(\text{OH})(\text{OCH}_3)$

Example 31: magnesium acetylacetonate $\text{Mg}(\text{C}_5\text{H}_7\text{O}_2)_2$ 20

The catalytic complexes were prepared as in Examples 1 to 5 under the conditions given in Table 6, except that one litre of hexane was used. It was not possible to observe the complete dissolution of the $\text{Ti}(\text{OC}_2\text{H}_5)_4$ even after the addition of the hexane. On the contrary, a suspension of very fine particles was formed, to which the solution of ethyl aluminium dichloride was added. The catalytic complexes obtained were similar to those of the preceding Examples. With each of these complexes, a polymerisation test was carried out under the conditions of Examples 1 to 5. 25 30

Table 6 shows the special conditions for each experiment and the results obtained. 35

TABLE 6

	Ex. 27	Ex. 28	Ex. 29	Ex. 30	Ex. 31
Nature of compound (M)	Mg(OC ₂ H ₅) ₂	Mg(OOCH) ₂	Mg(OOCC ₆ H ₅) ₂	Mg(OH)OCH ₃	Mg(C ₆ H ₅ O ₂) ₂
Quantity of this compound used g	210	57	133	36	111
Atomic ratio Ti/Me g-at/g-at	0.5	1	1	1	1
Quantity of Al(C ₂ H ₅)Cl ₂ used g	635	318	318	318	318
Ratio Al/Me + Ti mole/g-eq	1.25	0.85	0.85	0.85	0.85
Elementary analysis of the catalytic complex					
Magnesium mg/g	99	93	66	45	48
Titanium mg/g	92	152	126	167	97
Aluminum mg/g	39	10	11	27	150
Chlorine mg/g	530	395	402	454	168
Specific surface area of the catalytic complex m ² /g					
	—	111	24	149	—
Quantity of the catalytic complex used mg	5	7	7	12	32
Quantity of polyethylene obtained g	126	60	157	60	113
Productivity gPE/g complex	25 200	8 600	22 400	5 000	3 500
Specific activity gPE/hr × g Ti × kg/cm ² C ₂ H ₄	27 400	5 530	17 500	3 050	3 600
Fluidity index of the PE g/10 mins.	0.83	0.20	2.08	0.20	0.59

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Example 32.

The procedure of Example 1 was again followed, except that 10 mg of the catalytic complex was used, and the 200 mg of triisobutyl aluminium was replaced by 72 mg of trimethyl aluminium.

76 g of polyethylene was obtained, having a melt index of 0.59 g/10 mins. The productivity was therefore 7600 gPE/g complex, and the specific activity was 10,000 gPE/hr. x g Ti x kg/cm² C₂H₄.

Example 33.

The procedure of Example 16 was again followed, except that 8 mg of the catalyst was used, and the 200 mg of triisobutyl aluminium was replaced by 120 mg of diethyl aluminium chloride.

61 g of polyethylene was obtained, having a melt index of 0.08 g/10 mins. The productivity was therefore 7600 gPE/g complex.

Example 34.

The same reactants were used as in Examples 1 to 5.

To 500 mls. of a 400 g/litre solution of ethyl aluminium dichloride in hexane, there were successively added 1 litre of hexane and 75 g of titanium tetrabutylate diluted in 100 mls. of hexane. The latter addition was carried out gradually. The temperature of the mixture at the end was about 35° C. The formation of a precipitate was observed. 36 g of magnesium ethylate was then added, in the solid state. The mixture was then heated to 60° C with agitation for one hour.

The catalytic complex was filtered and washed with hexane. It was then dried *in vacuo* at 70° C until its weight was constant.

The elementary analysis of the catalytic complex showed that it contained:

40	magnesium	111 mg/g
	titanium	109 mg/g
	chlorine	393 mg/g

Its specific surface area was 137 m²/g.

A polymerisation experiment was carried out under the same conditions as in Examples 1 to 5, except that 100 mg of triisobutyl aluminium was used, and the partial pressures of ethylene and hydrogen were 5 and 2 kg/cm² respectively. 7 mg of catalytic complex was used.

64 g of polyethylene was produced, having a melt index of 0.82 g/10 mins. The productivity was 9100 gPE/g catalytic complex, and the specific activity was 16,800 gPE/hr x g Ti x kg/cm² C₂H₄.

Example 35.

A catalytic complex prepared as in Example 12 was used.

A co-polymerisation experiment with

ethylene and propylene was carried out.

Into a 5-litre autoclave, 1.2 g of trihexyl aluminium and 2175 mls. of propylene were successively introduced. The temperature was raised to 40° C with the concurrent introduction of ethylene until the total pressure was 18.1 kg/cm². 254 mg of catalytic complex was then added.

The polymerisation was carried on for 6 hours, with agitation, at 40° C.

At the end of the polymerisation the autoclave was de-gassed, and 384 g of an ethylene/propylene co-polymer containing 41 moles per cent of propylene was obtained.

Example 36.

A catalytic complex was prepared as in Examples 1 to 5, except that, for 114 g of magnesium ethylate, 680 g of titanium tetrabutylate and 635 g of ethyl aluminium dichloride were used. The Ti/Mg atomic ratio was therefore 2 gram atoms/gram atom to within an error of ± 10%. The Al/(Mg+Ti) ratio was 0.5 moles/gram equivalent to within ± 10% error.

The catalytic complex was used for a polymerisation experiment carried out continuously in a 300-litre reactor of the "liquid-full" type provided with very effective agitation and cooling devices. The cooling device was regulated so as to maintain the temperature in the reactor at 90° C. The polymerisation was carried out in suspension in hexane, which was introduced continuously into the reactor at the rate of 52 kg/hr.

There were also introduced:

ethylene, sufficient to maintain the concentration in the reactor at 41 g ethylene per kg. of diluent, hydrogen, sufficient to maintain the concentration in the reactor at 0.21 g of hydrogen per kg. of diluent, and trimethyl aluminium, sufficient to maintain the concentration in the reactor at 26 mg of Al(CH₃)₃ per kg. of diluent.

The resulting suspension of the polymer in the diluent was discharged as necessary to maintain the pressure in the reactor at 30 kg/cm².

6.8 kg of polyethylene were obtained per hour. This polyethylene had a density of 0.965 and a melt index of 5.1 g/10 mins. It contained only 2 ppm of titanium originating from catalytic residues, even without purification.

Its Izod impact strength measured according to ASTM Standard D 256 was 10.5 kgcm/cm notch.

By way of comparison a similar polymerisation test was carried out using a catalytic complex prepared in accordance with Example 3 of Belgian Patent Specification No. 767586.

The special conditions of this comparative experiment were as follows:

	rate of feed of hexane:	54.8 kg/hr
	concentration of ethylene:	34 g/kg. of diluent
5	concentration of hydrogen:	0.26 g/kg of diluent
	concentration of $\text{Al}(\text{CH}_3)_3$:	17 mg/kg of diluent

6.7 kg of polyethylene were obtained per hour. This polyethylene had a density of 0.965 and a melt index of 5.8 g/10 mins. It contained 3 ppm of titanium. Its Izod impact strength was only 6.4 kg cm/cm notch.

It will be seen that the catalytic complexes according to the invention make it possible to obtain, with still further improved catalytic activities, polymers which for more or less equivalent melt indices have an Izod impact strength which is distinctly greater than that of the best polymers of the prior art.

WHAT WE CLAIM IS:—

1. Process for the polymerisation of alpha-olefins whose molecule contains from 2 to 20 carbon atoms, wherein the polymerisation is carried out in the presence of a catalytic system comprising: an organometallic compound of a metal (as herein defined) of group Ia, IIa, IIb, IIIb or IVb of the Periodic Table and a solid catalytic complex being a complex insoluble in alkanes and cycloalkanes) prepared by reacting:

(1) an oxygen-containing organic compound (M) of a metal (as herein defined) (Me) of group Ia, IIa, IIIb, IVb, VIIa or VIII of the Periodic Table comprising only sequences of metal-oxygen-organic radical bonds with:

(2) a non-halogenated oxygen-containing organic compound (T) of a metal (Tr) of group IVa, Va or VIa of the Periodic Table in which an organic radical is attached to the metal (Tr) via oxygen, and with:

(3) a halide of aluminium (A) as herein defined).

2. Process in accordance with Claim 1, wherein the metal (Me) is magnesium, calcium, manganese, iron, nickel, cobalt or tin.

3. Process in accordance with Claim 1, wherein the metal (Me) is aluminium or silicon.

4. Process in accordance with Claim 2, wherein the metal (Me) is magnesium.

5. Process in accordance with Claim 1, wherein, in order to prepare the catalytic complex, two oxygen-containing organic compounds (M) are used, of which one is an oxygen-containing organic compound of metal (Me) of group IIa of the Periodic Table and the other is an oxygen-containing organic compound of a metal (Me) of group IIIb or IVb of the Periodic Table.

6. Process in accordance with Claim 5,

wherein the metal (Me) of Group IIa is magnesium and the metal (Me) of group 65 IIIb or IVb is aluminium or silicon.

7. Process in accordance with any of Claims 1 to 6, wherein the oxygen-containing organic compound (M) is an alkoxide.

8. Process in accordance with any of Claims 1 to 6, wherein the oxygen-containing organic compound (M) is a phenate.

9. Process in accordance with any of Claims 1 to 6, wherein the oxygen-containing organic compound (M) is a salt of a carboxylic acid.

10. Process in accordance with any of Claims 1 to 9, wherein the metal (Tr) is titanium, zirconium or vanadium.

11. Process in accordance with Claim 10, wherein the metal (Tr) is titanium.

12. Process in accordance with any preceding Claim, wherein the oxygen-containing organic compound (T) is an alkoxide, oxy-alkoxide or condensed alkoxide.

13. Process in accordance with any preceding Claim, wherein the aluminium halide (A) corresponds to the general formula $\text{AlR}'_n\text{X}_{3-n}$ in which R' is a hydrocarbon radical containing 1 to 6 carbon atoms, X is a halogen and n is a number such that $0 \leq n < 3$.

14. Process in accordance with Claim 13, wherein X is chlorine.

15. Process in accordance with any preceding Claim, wherein the quantities of the oxygen-containing organic compounds (M) and (T) used for preparing the solid catalytic complex are such that the atomic ratio Tr/Me between the quantities of metal (Tr) and metal (Me) present is between 0.01 and 100.

16. Process in accordance with Claim 15, wherein the atomic ratio Tr/Me is between 0.10 and 2.

17. Process in accordance with Claim 15, wherein the atomic ratio Tr/Me is between 0.025 and 0.10.

18. Process in accordance with any preceding Claim, wherein the quantities of the oxygen-containing organic compounds (M) and (T) and of the aluminium halide (A) used for preparing the solid catalytic complex are such that the ratio $\text{Al}/(\text{Me} + \text{Tr})$ between the quantity of the aluminium compound and the quantity of the metals (Me) and (Tr) is between 0.10 and 10 moles/gram equivalent.

19. Process in accordance with Claim 18, wherein the ratio $\text{Al}/(\text{Me} + \text{Tr})$ is between 0.75 and 2 moles/gram equivalent.

20. Process in accordance with any preceding Claim, wherein the organometallic compound of a metal of group Ia, IIa, IIb, IIIb or IVb of the Periodic Table is an organo-aluminium.

21. Process for the preparation of solid catalytic complexes (being complexes insoluble



* C L M S *

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rate of feed
of hexane: 54.8 kg/hr
concentration of
ethylene: 34 g/kg. of diluent
5 concentration of
hydrogen: 0.26 g/kg of diluent
concentration of
Al(CH₃)₃: 17 mg/kg of diluent

6.7 kg of polyethylene were obtained per
10 hour. This polyethylene had a density of
0.965 and a melt index of 5.8 g/10 mins. It
contained 3 ppm of titanium. Its Izod im-
pact strength was only 6.4 kg cm/cm notch.

It will be seen that the catalytic complexes
15 according to the invention make it possible to
obtain, with still further improved catalytic
activities, polymers which for more or less
equivalent melt indices have an Izod impact
strength which is distinctly greater than that
20 of the best polymers of the prior art.

WHAT WE CLAIM IS:—

1. Process for the polymerisation of alpha-
olefins whose molecule contains from 2 to 20
25 carbon atoms, wherein the polymerisation is
carried out in the presence of a catalytic sys-
tem comprising: an organometallic compound
of a metal (as herein defined) of group Ia,
IIa, IIb, IIIb or IVb of the Periodic Table
and a solid catalytic complex being a complex
30 insoluble in alkanes and cycloalkanes) pre-
pared by reacting:

(1) an oxygen-containing organic compound
(M) of a metal (as herein defined) (Me)
35 of group Ia, IIa, IIb, IVb, VIIa or
VIII of the Periodic Table compris-
ing only sequences of metal-oxygen-or-
ganic radical bonds with:

(2) a non-halogenated oxygen-containing or-
ganic compound (T) of a metal (Tr) of
40 group IVa, Va or VIa of the Periodic
Table in which an organic radical is at-
tached to the metal (Tr) via oxygen, and
with:

(3) a halide of aluminium (A) as herein
45 defined).

2. Process in accordance with Claim 1,
wherein the metal (Me) is magnesium, cal-
cium, manganese, iron, nickel, cobalt or tin.

3. Process in accordance with Claim 1,
50 wherein the metal (Me) is aluminium or
silicon.

4. Process in accordance with Claim 2,
wherein the metal (Me) is magnesium.

5. Process in accordance with Claim 1,
55 wherein, in order to prepare the catalytic
complex, two oxygen-containing organic com-
pounds (M) are used, of which one is an
oxygen-containing organic compound of metal
(Me) of group IIa of the Periodic Table
60 and the other is an oxygen-containing organic
compound of a metal (Me) of group IIIb
or IVb of the Periodic Table.

6. Process in accordance with Claim 5,

wherein the metal (Me) of Group IIa is
magnesium and the metal (Me) of group
IIIb or IVb is aluminium or silicon. 65

7. Process in accordance with any of Claims
1 to 6, wherein the oxygen-containing organic
compound (M) is an alkoxide.

8. Process in accordance with any of Claims
1 to 6, wherein the oxygen-containing organic
compound (M) is a phenate. 70

9. Process in accordance with any of Claims
1 to 6, wherein the oxygen-containing organic
compound (M) is a salt of a carboxylic acid. 75

10. Process in accordance with any of
Claims 1 to 9, wherein the metal (Tr) is
titanium, zirconium or vanadium.

11. Process in accordance with Claim 10,
wherein the metal (Tr) is titanium. 80

12. Process in accordance with any preced-
ing Claim, wherein the oxygen-containing or-
ganic compound (T) is an alkoxide, oxy-
alkoxide or condensed alkoxide.

13. Process in accordance with any pre-
ceding Claim, wherein the aluminium halide
(A) corresponds to the general formula
AlR'_nX_{3-n} in which R' is a hydrocarbon
radical containing 1 to 6 carbon atoms, X is
a halogen and n is a number such that
0 ≤ n < 3. 85

14. Process in accordance with Claim 13,
wherein X is chlorine. 90

15. Process in accordance with any preced-
ing Claim, wherein the quantities of the
oxygen-containing organic compounds (M)
and (T) used for preparing the solid cat-
alytic complex are such that the atomic ratio
Tr/Me between the quantities of metal (Tr)
and metal (Me) present is between 0.01 and
10. 95

16. Process in accordance with Claim 15,
wherein the atomic ratio Tr/Me is between
0.10 and 2.

17. Process in accordance with Claim 15,
105 wherein the atomic ratio Tr/Me is between
0.025 and 0.10.

18. Process in accordance with any preced-
ing Claim, wherein the quantities of the
oxygen-containing organic compounds (M)
and (T) and of the aluminium halide (A)
used for preparing the solid catalytic com-
plex are such that the ratio Al/(Me + Tr)
between the quantity of the aluminium com-
pound and the quantity of the metals (Me)
and (Tr) is between 0.10 and 10 moles/gram
equivalent. 110

19. Process in accordance with Claim 18,
wherein the ratio Al/(Me + Tr) is between
0.75 and 2 moles/gram equivalent. 115

20. Process in accordance with any preced-
ing Claim, wherein the organometallic com-
pound of a metal of group Ia, IIa, IIb, IIIb
or IVb of the Periodic Table is an organo-
aluminium. 120

21. Process for the preparation of solid
catalytic complexes (being complexes insolu- 125

ble in alkanes and cycloalkanes), comprising reacting:

- 5 (1) an oxygen-containing organic compound (M) of a metal (as herein defined) (Me) of group Ia, IIa, IIb, IVb, VIIa or VIII of the Periodic Table comprising only sequences of metal-oxygen-organic radical bonds, with:
- 10 (2) a non-halogenated oxygen-containing organic compound (T) of a metal (Tr) of group IVa, Va or VIa of the Periodic Table in which an organic radical is attached to the metal (Tr) *via* oxygen; and with
- 15 (3) a halide of aluminium (A) (as herein defined).

22. Solid catalytic complexes (being complexes insoluble in alkanes and cycloalkanes) for the polymerisation of alpha-olefins whose molecule contains from 2 to 20 carbon atoms prepared by reacting:

- 20 (1) an oxygen-containing organic compound (M) of a metal (as herein defined) (Me) of group Ia, IIa, IIb, IVb, VIIa or VIII of the Periodic Table comprising only sequences of metal-oxygen-organic radical bonds, with:
- 25 (2) a non-halogenated oxygen-containing organic compound (T) of a metal (Tr) of

group IVa, Va or VIa of the Periodic Table in which an organic radical is attached to the metal (Tr) *via* oxygen, and with:

- 30 (3) a halide of aluminium (A) (as herein defined).

23. A process according to any of Claims 1 to 20, wherein the polymerisation is that of ethylene.

24. Polymers of alpha-olefins prepared by a process according to any of Claims 1 to 20.

25. Process for the polymerisation of alpha-olefins as in claim 1, substantially as described in any of Examples 1 to 17, 19, 22, 27 and 32—36.

26. Process for the polymerisation of alpha-olefins as in Claim 1, substantially as described in any of Examples 18, 20, 23, 24—26 and 28—31.

27. Polymers of alpha-olefins prepared by a process according to Claim 25.

28. Polymers of alpha-olefins prepared by a process according to Claim 26.

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