602921

FORM 1
REGULATION 9

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-1973

APPLICATION FOR A PATENT

AUSTRALIAN SEC 34(4) PATENT OFFICE

I/We SECTION 34(4)(a) DIRECTION SEE FOLIO 4
NAME DIRECTED Ausimont S.r.l.
of 31 Foro Buonaparte, Milan, Italy

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

CATALYSTS FOR THE PREPARATION OF ELASTOMERIC, SATURATED OR UNSATURATED OLEPHINIC COPOLYMERS, AND COPOLYMERS OBTAINED WITH THEM

which is described in the accompanying complete specification. This Application is a Convention Application and is based on the Application(s) numbered: 21872 A/86 for a Patent or similar protection made in Italy on 2 October 1986.

My/Our address for service is:

GRIFFITH HASSEL & FRAZER
71 YORK STREET
SYDNEY N.S.W. 2000
AUSTRALIA

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 13.8.90

DATED this 30th day of September, 1987.

AUSIMONT S.p.A.

By his/their Patent Attorneys

GRIFFITH HASSEL & FRAZER

TO: THE COMMISSIONER OF PATENTS
COMMONWEALTH OF AUSTRALIA

LODGED AT SUB-OFFICE
30 SEP 1987
Sydney

3126A:rk

ASSIGNEE-APPLICANT

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952 (AS AMENDED)

DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

(Name of applicant) In support of an Application made by: AUSIMONT S.p.A.

(Title) for a patent for an invention entitled: CATALYSTS FOR THE PREPARATION OF ELASTOMERIC, SATURATED OR UNSATURATED OLEPHINIC COPOLYMERS, AND COPOLYMERS OBTAINED WITH THEM

(Full name of signatory) I, Otilio Masseroli

(Address of signatory) of 31 Foro Buonaparte, MILAN, ITALY

do solemnly and sincerely declare as follows:

1. I am authorised by the above mentioned applicant for the patent to make this Declaration on its behalf.

2. The name and address of each actual inventor of the invention is as follows:

(Insert details of inventor/s)

Illaro Cuffiani; Roberto Fabbri; C. Francesco Margelli and Umberto Zucchini

of 33, via Bagaro, 44100 Ferrara, ITALY;
7, via Campanati, 44034 Copparo, Ferrara, ITALY;
1/2, vicolo Degli Estensi, 45030 Occhiobello, Rome, ITALY
and 11, via G. Leopardi, 44100 Ferrara, ITALY, respectively

(Insert details of assignment, etc.) and the fact(s) upon which the applicant is entitled to make this application are as follows:

The applicant is entitled to the invention by virtue of the inventors' contracts of employment with the applicant.

(Delete paragraphs 3 and 4 for Non-Convention application)

3. The basic application(s) as defined by Section 141 of the Act was(were) made as follows:

Country ..... Italy ..... on ... 2 October 1986 .....

in the name(s) ..... Ausimont S.p.A. .....

and in ..... on .....

in the name(s) .....

and in ..... on .....

in the name(s) .....

4. The basic application(s) referred to in the preceding paragraph of this Declaration was(were) the first application(s) made in a Convention country in respect of the invention the subject of this application.

(Place and date of signing) Declared at Milan, Italy this 24th day of September 1987

AUSIMONT S.p.A.

Signed: ing. OTILIO MASSEROLI

Position: Chief Executive Officer

GRIFFITH HASSEL & FRAZER, P.O. BOX 2133, G.P.O., SYDNEY, N.S.W. 2001
AUSTRALIA

(12) PATENT ABRIDGMENT (11) Document No. AU-B-79231/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 602921

(54) Title
CATALYSTS FOR THE PREPARATION OF ELASTOMERIC, SATURATED OR UNSATURATED OLEPHINIC COPOLYMERS, AND COPOLYMERS OBTAINED WITH THEM

(51)[4] International Patent Classification(s)
C08F 004/64 C08F 004/68 C08F 210/12 C08F 210/16
C08F 210/18

(21) Application No. : 79231/87 (22) Application Date : 30.09.87

(30) Priority Data

(31) Number	(32) Date	(33) Country
21872 /86	02.10.86	IT ITALY

(43) Publication Date : 14.04.88

(44) Publication Date of Accepted Application : 01.11.90

(71) Applicant(s)
AUSIMONT S.R.L.

(72) Inventor(s)
ILLARO CUFFIANI; ROBERTO FABBRI; G. FRANCESCO MARGELLI; UMBERTO ZUCCHINI

(74) Attorney or Agent
GRIFFITH HACK & CO., GPO Box 4164, SYDNEY NSW 2001

(57) Claim

1. Solid components of catalysts for the preparation of elastomeric copolymers of ethylene with alpha-olephins, or of ethylene with alpha-olephins and at least a diene, comprising:

A) a magnesium compound containing at least an Mg-halogen bond;

B) a halogenated compound of Ti or V, wherein Ti and V are at least partially trivalent supported onto said magnesium compound, containing metal-oxygen Ti-OR or V-OR bonds, wherein R = alkyl, aryl or cycloalkyl containing from 1 to 20 carbon atoms, in which catalyst components the Mg/Ti(V), halogen/Ti(V), halogen/Mg and OR/Ti(V) atomic ratios are comprised within the following ranges:

- $0.2 \leq Mg/Ti(V) \leq 50$;
- halogen/Ti(V) > 2;
- halogen/Mg > 2;
- OR/Ti(V) ≤ 1.5;

.../2

c) an electron-donor compound, containing one or more oxygen, silicon and/or phosphorus atoms, belonging to the class of ethers or organic and inorganic esters, and in such amount that the electron donor/Mg molar ratio is comprised within the range $0.01 \leqslant \text{donor/Mg} \leqslant 10$.

6. Process for preparing catalytic components according to claim 1, comprising reacting with one another:

(1) an anhydrous magnesium halide, or a compound having formula XMgOR, wherein X = OR, or is a halogen or a radical having the meaning of R, and R is an alkyl, cycloalkyl or aryl radical of from 1 to 20 C atoms;

(2) a compound having the general formula $[MeO_x(OR)_y]_n$, or $Me(\text{acetyl-acetonate})_3^{\beta}$, wherein:

Me = Ti, V:

R = an alkyl, aryl or cycloalkyl radical containing from 1 to 20 C atoms;

x = an integer larger than, or equal to, zero;

y = an integer larger than, or equal to 2;

2x+y = the valence of Me;

n = an integer comprised within the range of from 1 to 6, with the limits being included;

(3) a halogenated compound, capable of substituting in component (2) at least an -OR group with a halogen atom;

(4) an electron-donor compound containing one or more oxygen, silicon and/or phosphorus atoms, constituted by, or comprising an ether or an organic or inorganic ester.

602921

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952 Form 10

COMPLETE SPECIFICATION

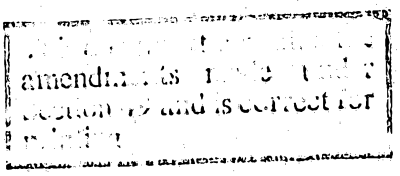
FOR OFFICE USE

Short Title:

Int. Cl:

Application Number:
Lodged:

Complete Specification–Lodged:
Accepted:
Lapsed:
Published:



Priority:

Related Art:

TO BE COMPLETED BY APPLICANT

Name of Applicant: ~~AUSIMONT S.p.A.~~ Ausimont S.r.l.



Address of Applicant: 31, Foro Buonaparte, MILAN, ITALY

Actual Inventor: Illoro Cuffiani ; Roberto Fabbri ; G. Francesco Margelli and Umberto Zucchini

Address for Service: GRIFFITH HASSEL & FRAZER
71 YORK STREET
SYDNEY NSW 2000
AUSTRALIA

Complete Specification for the invention entitled:

CATALYSTS FOR THE PREPARATION OF ELASTOMERIC, SATURATED OR UNSATURATED OLEPHINIC COPOLYMERS, AND COPOLYMERS OBTAINED WITH THEM

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

The copolymerization of ethylene and of alpha-olefins in the presence, or in the absence of diolephins has been carried out heretofore with various types of catalysts: one of the most used of such catalysts is constituted by the product from the reaction of a vanadium compound with an organometallic compound of metals of the I, II, and II Group of the Periodic System (U.K. 1,277,629; IT 890,604; U.K. 1,277,353; IT 879,026; U.K. 1,519,472).

The copolymers obtained with this catalyst are completely amorphous or substantially amorphous; the activity of these catalysts, and consequently, the yield of polymers as referred to the used catalyst is anyway relatively low.

Catalysts for preparing saturated or unsaturated ethylene-propylene elastomers, endowed with a high catalytic activity, have already been disclosed by the present Applicant in some patents, e.g.: FR 2,111,137; U.S. 4,013,823; and Italian Patent Application 20,386 A/85.

The therein disclosed catalysts make it possible, thanks to their high activity, to produce saturated or unsaturated olephinic elastomers, according to simplified, and considerably less expensive processes, which do not comprise any steps of purification of the obtained polymers from the catalytic residues.

Novel catalytic systems have been found now, which, besides being endowed with high catalytic activities, and, consequently, with the above mentioned technical and economical advantages, are capable of producing olefinic elastomers having appreciably improved elastic properties, in particular as relates to the values of tension set of the corresponding cured products.

It was further found that catalysts can be obtained which ~~The catalysts of the present invention~~ comprise the product from the reaction of an Al-alkyl compound (co-catalyst) with a solid catalytic component wherein, as its essential constituents, the following are present:

A) a magnesium compound containing at least an Mg-halogen bond;

B) a halogenated compound of Ti or V, wherein Ti and V are at least partially trivalent, containing metal-oxygen Ti-OR or V-OR bonds, wherein R = alkyl, aryl or cycloalkyl containing from 1 to 20 carbon atoms, in which catalytic component the Mg/Ti(V), halogen/Ti(V), halogen/Mg and OR/Ti(V) atomic ratios are comprised within the following ranges:

- $0.2 \leq Mg/Ti(V) \leq 50$, preferably $0.5 \leq Mg/Ti(V) \leq 5$;
- halogen/Ti(V) >2, preferably 4-10;
- halogen/Mg >2, preferably 4-8;
- $OR/Ti(V) \leq 1.5$, preferably ≤ 1;

C) an electron-donor compound, containing one or more oxygen, silicon and/or phosphorus atoms, belonging to the class of ethers or organic and inorganic esters.

The (C) component is added in such an amount as to supply an electron-donor/Mg molar ratio comprised within the range:

$0.01 \leq Donor/Mg \leq 10$, preferably $0.1 \leq Donor/Mg \leq 1$.

The catalytic components of the present invention can be prepared according to various methods, by preferably operating under such conditions as to have the magnesium compound at least partially dissolved in one of the reactants used.

The preferred preparation methods are:

The First Preparation Method

Reaction between:

(1) an anhydrous magnesium halide, or a compound having formula XMgOR, wherein X = OR, or is a halogen or a radical having the meaning of R, and R is an alkyl, cycloalkyl or aryl radical of from 1 to 20 C atoms.

The magnesium halide is preferably magnesium chloride. Examples of XMgOR compounds are Mg chloro-alkoxides; Mg di-alkoxides; alkyl-alkoxy-magnesium compounds. In case of magnesium compounds not containing an Mg-halogen bond, such a bond is formed by the action of the hereinunder specified compound (3).

(2) a compound having the general formula $[MeO_x(OR)_y]n$, or Me(acetyl-acetonate)$_3$, wherein:

Me = Ti, V:

R = an alkyl. aryl or cycloalkyl radical containing from 1 to 20 C atoms;

x = an integer larger than, or equal to, zero;

y = an integer larger than, or equal to 2;

2x+y = the valence of Me;

n = an integer comprised within the range of from 1 to 6, with the limits being included.

Examples of preferred compounds are:

$Ti(OC^2H^5)^4$,

AUSTRALIAN PATENT OFFICE

$Ti(O\text{-}n\text{-}C_4H_9)_4$,

$Ti(O\text{-}i\text{-}C_3H_7)_4$,

$Ti(OC_6H_5)_4$,

$V(O\text{-}i\text{-}C_3H_7)_4$,

$VO(O\text{-}i\text{-}C_3H_7)_3$,

Ti-triacetylacetonate.

(3) a halogenated, preferably chlorinated, compound, capable of substituting in component (2) at least an -OR group with a halogen atom, such as, e.g., Al-alkyl halides such as $Al\text{-}Et_2Cl$, $Al\text{-}EtCl_2$, Al-alkyl sesquihalide, organic acid halides RCOX (X = halogen, preferably chlorine; R = an aliphatic or aromatic organic radical), hydrogen halides (such as HCl), $SOCl_2$, $COCl_2$, $TiCl_4$, BCl_3, and still others. Particularly interesting results are achieved when Al-alkyl halides, such as $AlEtCl_2$, Al-alkyl sesquihalides, and halogen-containing, or halogen and hydrogen-containing silicon compounds are used; these latter, besides acting as halogenating agents, also perform the function of reducers. As examples of such silicon compounds, there can be mentioned: the silicon halides, having the formula $SiX_{4-n}Y_n$, wherein X, Y represent halogen atoms (e.g., Cl and Br), and n is a number ranging from zero to 3 (with the limits being included), such as $SiCl_4$; the chlorosiloxanes, having the formula $Si_nO_{n-1}Cl_{2n+2}$, wherein n is a number ranging

from 2 to 7 (with the limits being included), such as, e.g., Si_2OCl_6 ; the halogenated polysiloxanes, having the formula Si_nX_{n+2}, wherein X = halogen and n is a number ranging from 2 to 6 (with the limits being included), e.g., Si_4Cl_{10}; the halosilanes, having the formula $SiH_{4-n}X_n$, wherein X = halogen and n is a number ranging from 1 to 3 (with the limits being included), e.g., $SiHCl_3$; the alkyl-halosilanes, having the formula $R_nSiH_xY_y$, wherein R = an aliphatic or aromatic radical, X = halogen, n is a number ranging from 1 to 3 (with the limits being included), x is a number ranging from zero to 2 (with the limits being included), and y is a number ranging from 1 to 3 (with the limits being included), e.g., $C_2H_5SiCl_3$, CH_3SiCl_2H, $(CH_3)_2SiCl_2$; the alkoxy-halosilanes, having the formula $Si(OR)_{4-n}X_n$, wherein X = halogen, R = alkyl or aryl of from 1 to 20 C atoms, and n is a number ranging from 1 to 3 (with the limits being included), e.g., $Si(OC_2H_5)Cl_3$.

(4) an electron-donor compound as defined under above point (C), constituted by, or comprising an ether or an organic or inorganic ester. Examples of such compounds are:

- dialkyl-ethers or aryl-alkyl-ethers, in particular di-n-butyl-ether, diisopropyl-ether, diisoamyl-ether, anisole, dimethylglycol-ether $CH_3-O-CH_2-CH_2-O-CH_3$,

diethyl-polyoxyethylene-glycol-ether

C_2H_5-O-[-CH_2-CH_2-O-]$_n$-C_2H_5;

- organic aliphatic, cycloaliphatic and aromatic esters, in particular ethyl acetate, vinyl acetate, cyclohexyl acetate, methyl p-toluate, ethyl p-anisate, benzyl benzoate;
- inorganic esters, in particular ethyl orthosilicate, diphenyl-dimethoxy-silane, dimethyl-diethoxy-silane, dichloro-dimethoxy-silane, tributyl-phosphate, triphenyl-phosphite.

The reaction conditions, and the ratios between the reactants (1), (2), (3) and (4) are selected in such a way, that in the catalytic component the Mg/Ti(V), halogen/Ti(V), halogen/Mg and OR/Ti(V) ratios are comprised within the above-specified ranges.

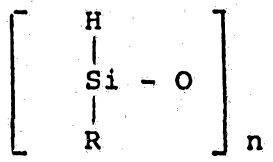
If the components (1) and (2) are reacted with a compound (3) capable of only carrying out a halogenating action, it is necessary that also a reducing compound (3) is used, which is capable of at least partially reducing to the tri-valent state the transition metal persent in component (2).

Silicon compounds which can be used as reducing agents are:

- the silanes Si_nH_{2n+2}, wherein n is a number equal to, or larger than 1, preferably equal to, or larger than 3,

e.g., Si_3H_8;

- the alkyl- or aryl-silanes R_xSiH_{4-x}, wherein R = alkyl or aryl, and x is a number ranging from 1 to 3 (with the limits being included), e.g., $(C_6H_5)_3SiH$;
- the alkoxy- or aryloxy-silanes $(RO)_xSiH_{4-x}$, wherein R = alkyl or aryl, and x is a number ranging from 1 to 3 (with the limits being included), e.g., $(C_2H_5O)_3SiH$;
- the polyalkyl-hydroxy-siloxanes, having the formula:



wherein R is an alkyl radical of from 1 to 10 C atoms, or an aryl, alkoxy or aryloxy, and n is a number lower than 10,000, generally comprised within the range of from 3 to 100.

In order to prepare the catalytic components of the invention, the components (1), (2), (3) and (4) can be reacted either in an aliphatic or aromatic hydrocarbon diluent, when at least one of the reactants is soluble in such a diluent, or in the absence of a diluent, when at least one of the reactants is in the liquid state at reaction pressure and temperature.

Preferably, after reacting the components (1) and (2) until a homogeneous product is obtained, this latter is reacted with the components (3) and (4). According to an

alternative method, which gave very good results, the product from the reaction between (1), (2) and (3) is subsequently treated with (4), optionally in the presence of aromatic, aliphatic and cycloaliphatic hydrocarbon solvents.

The above reactions are carried out at a temperature comprised within the range of from -10°C to +250°C, preferably of from 20°C to 200°C, with the temperature being selected also as a function of the type of components (3) and (4).

The components (1) and (2) are used in such amounts, as to have an Mg/transition metal atomic ratio comprised within the range of from 0.2 to 50, preferably of from 0.5 to 5, whilst the component (3) is used in the amount of at least 2, and preferably 4-10 gram-atoms of halogen per gram-atom of transition metal, and of from 0.1 to 100, preferably 0.5 to 20, gram-equivalents of reducer compound per gram-atom of the transition metal.

The electron-donor compound (4) is used in such a way as to have an electron donor/Mg molar ratio comprised within the range of from 0.01 to 10, and preferably of from 0.1 to 1.

The Second Method

Reaction between:

(I) a Ti compound as defined under (2), concerning the First Method, such as, e.g.

$Ti(O\text{-}n\text{-}C_3H_7)_4$; $Ti(O\text{-}n\text{-}C_4H_9)_4$; $Ti(OC_6H_5)_4$;

polyoxyalkyleneglycol orthotitanates, $V(O\text{-}n\text{-}C_3H_7)_4$;

$VO(O\text{-}n\text{-}C_3H_7)_3$; V(acetylacetonate)$_3$;

(II) a complex having the general formula:

$$MX_2.n(AlRX_2).pAlX_3$$

wherein:

M = Ba, Ca, Mg or Mn;

X = chlorine or bromine;

R = a hydrocarbon radical of from 1 to 20 C atoms, in particular an alkyl of from 1 to 10 C atoms, a cycloalkyl of from 6 to 8 carbon atoms, or an aryl;

n = a number ranging from 1 to 4 (with the limits being included);

p = an integer ranging from zero to 1 (with the limits being included);

n+p = a number comprised within the range of from 1 to 4 (with the limits being included).

Representative examples of component (II) are the following:

$MgCl_2 . 2AlC_2H_5Cl_2$;

$MgCl_2 . 2.5Al\text{-}i\text{-}(C_4H_9)Cl_2$;

$MgCl_2 . 1.5Al\text{-}n\text{-}C_4H_9Cl_2$;

$CaCl_2 . 4AlC_2H_5Cl_2$;

$BaCl_2 . AlCl_3 . AlC_2H_5Cl_2$.

(III) an electron-donor compound, as defined under (4), First Method.

The reaction between components (I), (II) and (III) can be carried out in various ways: the process is anyway performed under such conditions as to secure that the composition of the catalytic component is as above shown as regards the Mg/Ti(V), halogen/Ti(V), halogen/Mg, OR/Ti(V) ratios. The preferred method consists in reacting the mixture of the reactants in an Mg/transition metal atomic ratio generally comprised within the range of from 1 to 10, at a temperature which can be generally comprised within the range of from 0°C to 150°C, or even lower than 0°C, but preferably comprised within the range of from 20°C to 140°C; and in separating the solid reaction product from the liquid phase. The reaction modalities can be different, e.g.:

a) the reaction can be carried out in a hydrocarbon diluent, such as n-hexane, n-heptane, cyclohexane, toluene;

b) the component (II) can be submitted to a [illegible]ation treatment in the presence of components (I) and (III).

In any case, the component (III) is used in such an amount as to have an electron donor/Mg molar ratio comprised within the range of from 0.01 to 10, and preferably of from 0.1 to 1.

A particular advantage of the catalysts of the present invention consists in that the component (II) can be

dissolved in an excess of the Al-alkyl dihalide, and with such solution an inert support can be impregnated, which can already contain the transition metal compound and the electron-donor compound, or these latter can be added to the support at a later time.

Particularly suitable supports are Al_2O_3 and SiO_2 having high values of surface area, and a pore volume larger than 0.3 cc/g, TiO_2, ZrO_2, or polymers.

By operating according to one of the two hereinabove disclosed methods, or still other methods, solid catalytic components are obtained which, in combination with aluminum organometallic compounds, preferably Al-trialkyls, yield catalysts capable of supplying elastomeric copolymers of ethylene and/or alpha-olefins of general formula $R-CH=CH_2$ ($R=C_1-C_6$ alkyl), optionally with conjugated and non-conjugated dienes, endowed with low tension set values.

The preferably used alpha-olephin, in combination with ethylene, is propylene; as the dienes, 1,3-butadiene, 10-methyl-1,9-undecadiene, 1,9-decadiene, 5-ethylidene-2-norbornene, but more preferably 1,3-butadiene or 5-ethylidene-2-norbornene, can be used.

Representative examples of the aluminum organometallic compounds to be used as co-catalysts, together with the solid catalytic components of the present invention, are the following:

$Al(C_2H_5)_3$,

$Al(i\text{-}C_4H_9)_3$,

$Al(n\text{-}C_8H_{17})_3$,

$Al(i\text{-}C_4H_9)_2H$,

$Al(i\text{-}C_4H_9)H_2$.

The molar ratio of such compounds to the transition metal compound exceeds 1, and is generally comprised within the range of from 1 to 100.

The copolymerization of ethylene and/or alpha-olefins, optionally with dienes, is carried out according to known methods, by operating in the presence of an inert hydrocarbon vehicle capable of dissolving the polymer, or in the absence of said solvent. The polymerization is preferably carried out in the presence of liquid propylene as the polymerization vehicle. In this case, the reaction is carried out at a temperature comprised within the range of from 0°C to 60°C. In a continuous process, the excess monomer is flashed off from the obtained polymer, and is then recycled; thanks to the high activity of the catalysts of the present invention, it is not necessary to submit the recovered polymer to purification treatments to remove the catalytic residues.

The following Examples are supplied for illustrative purposes, and are not limitative of the invention.

Preparation of the Catalytic Component "A0"

To a three-necked glass flask, of 100 cm^3 of capacity, and equipped with stirring means, 4.75 g of anhydrous $MgCl_2$ and 38 g of $AlEtCl_2$ are charged under a dry nitrogen atmosphere. With stirring, the mixture is heated to 120°C and is maintained three hours at this temperature, until the complete dissolving of $MgCl_2$ is obtained. In another flask of 250 cm^3 of capacity, a solution of $Ti(O\text{-}n\text{-}Bu)_4$ (25.5 g) in 50 ml of anhydrous n-hexane, is separately prepared.

With this latter solution being kept stirred, and cooled to a temperature of 0°C, to it the previously prepared solution of $MgCl_2$ in $AlEtCl_2$, maintained fluid by being heated at approximately 70°C, is fed. The feeding occurs during a 4-hour time, and the resulting mixture is then heated 1 hour at 60°C.

The top phase is then removed by a siphon, the catalytic solid thus obtained is then repeatedly washed at room temperature with anhydrous n-hexane until all chlorine ions disappear from the washing solvent. The catalytic solid is finally dried 3 hours under vacuum at 40°C. At the analysis, the solid shows the following contents, by weight: Ti = 15.7%; Mg = 4.5%; Al = 2.85%; Cl = 50.5%; OBu = 9.6%.

Preparation of the Catalytic Component "A1"

Inside a glass flask of 100 cm^3 of capacity, equipped with stirring means, 4.75 g of anhydrous $MgCl_2$ and 38 g of

$AlEtCl_2$ are reacted by heating at 120°C for 3 hours, and the complete dissolving of $MgCl_2$ being obtained.

This solution, maintained at 70°C, is then dropwise added, over a 4-hour time, to a stirred flask of 250 cm^3, containing 25.5 g of $Ti(O\text{-}n\text{-}Bu)_4$, 4.05 g of anisole in 50 cm^3 of hexane, maintained cooled at 0°C.

At the end of the addition, the resulting mixture is heated up to 60°C and is maintained 1 hour at this temperature. The formed solid is then filtered off and is repeatedly washed with hexane; finally, it is dried under vacuum at 40°C for 3 hours. At the analysis, the solid shows the following contents, by weight:

Ti = 18.15%; Mg = 6.05%; Al = 0.72%; Cl = 50.3%; OBu = 10.6%; anisole = 3.5%.

Preparation of the Catalytic Component A2"

The process is carried out as disclosed for the preparation of the Catalytic Component "A1", with the only difference that di-isoamyl-ether (5.94 g) is used instead of anisole.

At the analysis, the solid, dried under vacuum at 40°C for 3 hours, shows the following contents, by weight:

Ti = 18.3%; Mg = 6.1%; Al = 0.8%; Cl = 47.7%; OBu = 13.1%;

Preparation of the Catalytic Component "A3"

The Catalytic Component "A3" is prepared according to

the same synthesis modalities as of the Catalytic Component "A1", by using n-butyl ether (4.89 g) instead of anisole.

The catalyst, dried and analysed, shows the following composition, by weight:

Ti = 19.1%; Mg = 5.7%; Al = 0.5%; Cl = 50.2%; OBu = 14.1%; n-butyl ether = 6.0%.

Preparation of the Catalytic Component "A4"

The synthesis is carried according to the same operative modalities as for the Catalytic Component "A1", by using ethyl acetate (4.05 g) instead of anisole.

The dry solid shows the following composition, by weight:

Ti = 17.4%; Mg = 5.5%; Al = 0.6%; Cl = 48.6%; OBu = 11.8%;

Preparation of the Catalytic Component "A5"

The preparation is carried out according to the same synthesis method as of the Catalytic Component "A1", but with anisole being replaced by methyl-p-toluate (MPT) (5.62 g).

The analysis of the dry product shows the following values (by weight):

Ti = 12.7%; Mg = 3.8%; Al = 2.5%; Cl = 38.35%; OBu = 17%; MPT = 19.5%.

Preparation of the Catalytic Component "A6"

By the same operating modalities as used for Component

"A1", the Catalytic Component "A6" is prepared, by using tributyl-phosphate (9.9 g) instead of anisole.

The obtained catalytic, dried and analysed, shows the following composition, by weight:

Ti = 16.8%; Mg = 4.4%; Al = 0.95%; Cl = 41.5%; OBu = 18.3%.

Preparation of the Catalytic Component "A7"

10 g of the Catalytic Component A0 is charged to a glass flask of 250 cm^3 of capacity, and equipped with a mechanical stirrer.

At room temperature, 50 cm^3 of anhydrous toluene and 14.7 g of anisole are added.

The resulting suspension, heated at 80°C, is kept stirred 2 hours.

After decanting the solid, the liquid phase is removed at room temperature. The residue is washed 4 times, each time with 50 cm^3 of anhydrous hexane at room temperature, and is finally dried under vacuum at 40°C for 3 hours.

Its composition by weight results to be the following:

Ti = 17.6%; Mg = 5.7%; Al = 0.56%; Cl = 51.5%; OBu = 9.2%; anisole = 7.6%

Preparation of the Catalytic Component "A8"

13.9 g of the Catalytic Component prepared by the method "A0" is suspended in 50 cm^3 anhydrous toluene, to the suspension 4.52 g of methyl-p [illegible]uate (MPT) is added,

the whole mixture is maintained at 80°C for 2 hours, and is finally washed and dried according to the modalities as already disclosed for the preparation of the Catalytic Component "A7".

The resulting dry solid residue showed the following composition:

Ti = 13.5%; Mg = 4.2%; Al = 2.0%; Cl = 42.9%;

OBu = 4.6%; MPT = 23.8%.

Preparation of the Catalytic Component A9"

To 17.1 g of the Catalytic Component "A0", suspended in 50 cm^3 of anhydrous toluene, 2.15 of dimethoxy-diphenyl-silane (DPMS) was added.

The suspension, slowly heated up to 80°C, was kept stirred at this temperature for 2 hours.

After washing with hexane, and drying according to the same modality as disclosed for the preparation of the Component "A7", the solid showed the following composition, by weight:

Ti = 17.2%; Mg = 5.2%; Al = 1.9%; Cl = 53.3%;

OBu = 6.8%; DPMS = 1.7%.

Preparation of the Catalytic Component "A10"

To a flask of 250 cm^3 of capacity, 3.6 g of $MgCl_2$ and 27 g of $Ti(O\text{-}n\text{-}Bu)_4$ are charged.

The mixture is heated, with stirring, at 140°C for 5 hours, and the resulting solution is diluted, after cooling,

with 53 cm^3 of n-heptane.

At 48°C and with stirring, 15 g of polymethylhydrosiloxane is then added during a 2-hour time, and then 22.5 g of $SiCl_4$ is added during the following two hours.

The temperature is increased to 60°C, and the reaction mixture is stirred for further 2 hours. The whole mixture is transferred on a filtering septum and is repeatedly washed at room temperature with n-hexane, until chlorine ions disappear from the washing solvent.

At the analysis, the solid, dried under vacuum at 40°C for 3 hours, shows the following contents, by weight:

Ti = 14.4%; Cl = 38.3%; Mg = 5.8%; OBu = 28.5%

Preparation of the Catalytic Component All"

13 g of the Catalytic Component "A10" is suspended in 50 cm^3 of anhydrous toluene, to it 8.1 g of anisole is added, the whole mixture is kept stirred at 80°C for 2 hours, and is finally washed and dried according to the same operating modalities as followed for preparing the Catalytic Component "A7".

The resulting product shows the following composition:

Ti = 13.9%; Mg = 5.9%; Cl = 38.7% OBu = 22.0%; anisole = 13.0%.

Preparation of the Catalytic Component "A12"

14 g of Catalyst "A10", suspended in 50 cm^3 of toluene,

is treated at 80°C, for 2 hours, with 3.65 g of methyl-p-toluate (MPT), according the same modalities as already disclosed for the production of the Component "A7".

The composition of the obtained dry product is the following (by weight):

Ti = 9.8%%; Mg = 5.2%; Cl = 31.4% OBu = 14.8%; MPT = 22.6%.

DESCRIPTION OF THE POLYMERIZATION PROCESS

The polymerizations were carried out inside stainless-steel autoclaves, equipped with stirring means, and temperature control system.

The volumes of the autoclaves is specified at Tables I and II, together with the operating conditions, and the amounts of reactants used in the individual polymerization tests.

To the autoclaves, after a suitable purging, the desired amount of propylene, and, optionally, of diene, was charged.

After heating to the desired temperature, ethylene was added, until the desired pressure was reached.

The required amount of the Catalytic Component "A", suspended in 20 cm^3 of anhydrous heptane, also containing aluminum-tributyl (MAB) was charged.

During the polymerization, the pressure was maintained constant by continuously feeding ethylene to the autoclave.

At the end, the catalyst was quenched by injecting 20 cm^3 of acetone containing an amount of Irganox 1010 equivalent to 0.2% by weight, relatively to the produced polymer amount.

After a 5-minute stirring, the monomers are slowly vented, until ambient pressure and temperature are reached.

The recovered polymer is finally dried at 70°C under a nitrogen stream, and is weighed.

The saturated copolymers were cured at 165°C for 40 minutes, on a platen-press, by using the following formulation (previously extruder-homogenised at 80°C for 10 minutes):

COPOLYMER	100	parts by weight
FEF CARBON BLACK	80	parts by weight
CORTIS 100M OIL	30	parts by weight
ZnO	5	parts by weight
SULPHUR	0.4	parts by weight
PEROXIMON F40	5	parts by weight

The unsaturated terpolymers were cured on a platen-press at 160°C for 30 minutes, using the following formulation:

TERPOLYMER	100	parts by weight
ZnO	5	parts by weight
STEARIC ACID	1	part by weight
FEF CARBON BLACK	55	parts by weight

CORTIS 100M OIL	30 parts by weight
TETRAMETHYLTHIURAM DISULPHIDE	1.5 parts by weight
MERCAPTOBENZOTHIAZOLE	0.75 parts by weight
SULPHUR	1.5 parts by weight

EVALUATION OF COPOLYMER PROCESSABILITY

The extrusion performance (extrudability) was evaluated, of two compounds respectively containing the copolymers obtained with the Catalytic Components "A0" and "A1". The compositions of the compounds used, and the results obtained are reported at Table III. To prepare said compounds, a BANBURY mixer was used.

The extrusion was carried out on a TROESTER type extruder, having a screw of 90 mm, with a central body temperature of 40°C, and a head temperature of 80°C; the nozzle had an average diameter of 16 mm. The processability of the compounds was expressed as the revolution speed (revolutions per minute) of the screw, necessary to obtain 14 metres/minute of extruded polymer.

The data obtained (Examples 16 and 17, Table III) shows that the compound containing the copolymer obtained with the Catalytic Component "A1" is endowed with better processability characteristics than the compound containing the copolymer obtained with the Catalyst Component "A0", because it requires a lower extruder revolution speed, i.e.,

shorter extrusion times, with the other operating conditions and the amount of extruded polymer being the same.

TABLE I

Example (No.)	0	1	2	3	4	5
Catalytic Component	A0	A1	A2	A3	A4	A5
Total Reactor Capacity (l)	7.2	7.2	2.5	7.2	7.2	7.2
Propylene Feedstock (g)	2400	2400	720	2400	2400	2400
Charged Catalyst Component (g)	0.011	0.03	0.0042	0.006	0.03	0.017
(1) Charged MAB (g)	0.8	3	1	3	3	3
Polimerization Temperature (°C)	40	40	40	40	40	40
Ethylene Partial Pressure (kg/cm^2)	3.8	3.1	2.5	3.1	3.1	2.5
Total Pressure (kg/cm^2)	19.5	18.8	18.3	18.8	18.8	18.3
Polymerization Time (h)	1	1	1	1	1	1
Produced Polymer (g)	970	710	65	170	630	400
Yield (Polymer g/Catalyst g).10^{-3}	88.2	23.7	15.5	28.3	21	23.5
Bonded Propylene (% by weight)	39	42.8	42.1	41.6	38.2	39.1
$[\eta]^{Tetraline}_{135°C}$ (dl/g)	4.24	3.48	4.05	3.16	2.7	2.65
$ML^{1+4'}_{121°C}$	52	45	69	45	42	32
(2) Tensile Strength (kg/cm^2)	177	161	176	163	161	219
(2) Elongation at break (%)	510	520	505	465	560	315
(2) (3) Tension Set 200% 23°C	14	8	8	10	10	6

(1) 1:1 Molar $Al(iC_4H_9)_3/Al(nC_4H_9)_3$ blend in hexane solution (150 g/l)
(2) Tested on cured polymer
(3) ASTM D. 412/68

TABLE I (cont.d)

Example (No.)	6	7	8	9	10	11	12
Catalytic Component	A6	A7	A8	A9	A10	A11	A12
Total Reactor Capacity (l)	7.2	2.5	1.5	1.5	1.5	1.5	1.5
Propylene Feedstock (g)	2400	720	455	455	455	455	455
Charged Catalyst Component (g)	0.009	0.0045	0.011	0.0037	0.018	0.0215	0.016
(1) Charged MAB (g)	5	1	1	1	1	1	1
Polimerization Temperature (°C)	40	40	40	40	40	40	40
Ethylene Partial Pressure (kg/cm^2)	2.1	2.5	2.8	2.8	2.8	2.8	2.8
Total Pressure (kg/cm^2)	17.8	18.3	18.5	18.5	18.5	18.5	18.5
Polymerization Time (h)	1	1	1	1	1	1	1
Produced Polymer (g)	140	150	110	85	110	120	145
Yield (Polymer g/Catalyst g).10^{-3}	15.6	33.4	10.0	23.0	6.15	5.6	9
Bonded Propylene (% by weight)	48.6	42.7	47.1	42.7	47.4	55	54
$[\eta]^{Tetraline}_{135°C}$ (dl/g)	2.85	3.54	2.98	3.31	3.37	2.43	2.6
$ML^{1+4'}_{121°C}$	36	51	29	37	41	38	22
(2) Tensile Strength (kg/cm^2)	194	167	216	174	203	197	189
(2) Elongation at Break (%)	300	500	340	300	320	330	350
(2) (3) Tension Set 200% 23°C	7	8	6	10	6	8	6

(1) 1:1 Molar $Al(iC_4H_9)_3/Al(nC_4H_9)_3$ blend in hexane solution (150 g/l)
(2) Tested on cured polymer
(3) ASTM D. 412/68

T A B L E I I

Example (No.)	13	14	15
Catalytic Component	AO	A1	A1
Total Reactor Capacity (1)	1.5	1.5	1.5
Propylene Feedstock (g)	455	455	455
Diene Feedstock-Type	1,3-butadiene	1,3-butadiene	ethylidene-norbornene (ENB)
Amount (g)	36	36	19.5
Charged Catalyst Component (g)	0.013	0.026	0.043
(1) Charged MAB (g)	1	1	1
Polymerization Temperature (°C)	40	40	40
Ethylene Partial Pressure (kg/cm^2)	3	2.1	2.5
Total Pressure (kg/cm^2)	17.6	16.7	17.8
Polymerization Time (h)	2	2	2
Produced Polymer (g)	80	70	75
Yield (Polymer g/Catalyst g).10^{-3}	6.2	2.8	1.75
Bonded propylene (% by weight)	35.2	38.8	50.1
Bonded Butadiene (% by weight):			
- in 1,2-position	0.25	0.25	-
- in 1,4-position	1.1	1.8	-
Bonded E.N.B. (%)	-	-	7.1
(2) $[\eta]$ Tetraline 135°C dl/g	3.79	3.85	2.8
(2) Tensile Strength (kg/cm^2)	96	90	93
(2) Elongation at break (%)	815	720	270
(3) Tension Set 200% 23°C	34	20	20

(1) 1:1 Molar $Al(iC_4H_9)_3/Al(nC_4H_9)_3$ blend in hexane solution (150 g/l)
(2) Tested on cured polymer
(3) ASTM D.412/68.PA

T A B L E I I I

COMPOUND FORMULATION (parts by weight)	Example 16	Example 17
Copolymer produced with Component A0 (C_3 = 43%: $[\eta]$ = 2.5 dl/g	85	-
Copolymer produced with Component A1 (C_3 = 46%: $[\eta]$ = 2.6 dl/g	-	85
Irganox 1076	0.2	0.2
ZnO	5	5
Stearic Acid	1	1
Carbowax 4000	2.5	2.5
SRF	58	58
HAF	43	43
Plastikator 32	3	3
Sinfluid AR 25	30	30
Sulphur	0.25	0.25
Caloxol W3	6	6
Peroximon F40	3.6	3.6
Trigonox 29/40	1.8	1.8
Mooney ML (1+4) 100°C	52	51
Screw Revolution Speed to Produce 14 metres of polymer/minute	40	29

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Solid components of catalysts for the preparation of elastomeric copolymers of ethylene with alpha-olephins, or of ethylene with alpha-olephins and at least a diene, comprising:

A) a magnesium compound containing at least an Mg-halogen bond;

B) a halogenated compound of Ti or V, wherein Ti and V are at least partially trivalent supported onto said magnesium compound, containing metal-oxygen Ti-OR or V-OR bonds, wherein R = alkyl, aryl or cycloalkyl containing from 1 to 20 carbon atoms, in which catalyst components the Mg/Ti(V), halogen/Ti(V), halogen/Mg and OR/Ti(V) atomic ratios are comprised within the folLowing ranges:
- $0.2 \leqslant Mg/Ti(V) \leqslant 50$;
- halogen/Ti(V) > 2;
- halogen/Mg > 2;
- $OR/Ti(V) \leqslant 1.5$;

C) an electron-donor compound, containing one or more oxygen, silicon and/or phosphorus atoms, belonging to the class of ethers or organic and inorganic esters, and in such amount that the electron donor/Mg molar ratio is comprised within the range $0.01 \leqslant$ donor/Mg $\leqslant 10$.

2. Solid catalytic components according to claim 1, wherein the Mg/Ti(V) atomic ratio is equal to at least 0.5, the halogen/Ti(V) atomic ratio is comprised within the range of from 4 to 10, the halogen/Mg atomic ratio is comprised

7902S/MS

within the range of from 4 to 8, and the OR/Ti(V) atomic ratio is equal to, or lower than, 1.

3. ~~Catalytic~~ Solid catalytic components according to claim 1 wherein the (C) component/Mg molar ratio is comprised within the range of from 0.01 to 10.

4. ~~Catalytic~~ Solid catalytic components according to claim 1 wherein the magnesium compound is an anhydrous magnesium halide, or a compound having the formula XMgOR, wherein X = OR, or halogen, or R radical, wherein R = an alkyl, cycloalkyl or aryl radical containing from 1 to 20 C atoms.

5. ~~Catalytic~~ Solid Catalytic components according to claim 1 wherein the magnesium compound is magnesium chloride.

6. Process for preparing catalytic components according to claim 1, comprising reacting with one another:

(1) an anhydrous magnesium halide, or a compound having formula XMgOR, wherein X = OR, or is a halogen or a radical having the meaning of R, and R is an alkyl, cycloalkyl or aryl radical of from 1 to 20 C atoms;

(2) a compound having the general formula $[MeO_x(OR)_y]n$, or Me(acetyl-acetonate)$_3$, wherein:

Me = Ti, V:

R = an alkyl, aryl or cycloalkyl radical containing from 1 to 20 C atoms;

x = an integer larger than, or equal to, zero;

y = an integer larger than, or equal to 2;

2x+y = the valence of Me;

n = an integer comprised within the range of from 1 to 6, with the limits being included;

(3) a halogenated compound, capable of substituting in component (2) at least an -OR group with a halogen atom;

(4) an electron-donor compound containing one or more oxygen, silicon and/or phosphorus atoms, constituted by, or comprising an ether or an organic or inorganic ester.

7. Process for preparing catalytic components according to claim 1, comprising reacting with one another:

(I) a Ti or V compound, wherein Ti and V are at least partially trivalent, containing Ti-OR or V-OR bonds, wherein R = an alkyl, aryl or cycloalkyl radical containing from 1 to 20 C atoms;

(II) a complex having the general formula:

$$MX^2.n(AlRX^2).pAlX^3$$

wherein:

M = Ba, Ca, Mg or Mn;

X = chlorine or bromine;

R = a hydrocarbon radical of from 1 to 20 C atoms, in particular an alkyl of from 1 to 10 C atoms, a cycloalkyl of from 6 to 8 carbon atoms, or an aryl;

n = a number ranging from 1 to 4 (with the limits being included);

p = an integer ranging from zero to 1 (with the limits being included);

n+p = a number comprised within the range of from 1 to 4 (with the limits being included);

(III) an electron-donor compound, containing one or more oxygen, silicon and/or phosphorus atoms, constituted by, or comprising an ether or an organic or inorganic ester.

8. Catalysts for preparing elastomeric copolymers of ethylene with alpha-olefins, comprising:

1) an Al-alkyl compound;

2) a catalyst component according to claims from 1 to 5.

9. Elastomeric copolymers of ethylene with alpha-olefins, or of ethylene with alpha-olefins and at least a diene. obtained by using the catalytic compounds according to claim 1.

10. Cured elastomeric copolymers, obtained by curing the copolymers according to claim 9.

Dated this 30th day of September 1987

S.p.A.
AUSIMONT ~~S.p.A.~~
By their Patent Attorney
GRIFFITH HASSEL & FRAZER

AUSTRALIAN PATENT OFFICE
Regd. 34(4)