

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

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

(1) Here insert (in full) Name of Company.

In support of the Convention Application made by(1) UNION CARBIDE CORPORATION

(hereinafter referred to as the applicant) for a Patent for an invention entitled:(2) ETHYLENE POLYMERIZATION CATALYST

(2) Here insert title of Invention.

(3) Here insert full Name and Address, of Company official authorized to make declaration.

I, (3) Timothy N. Bishop of 39 Old Ridgebury Road, Danbury, State of Connecticut, 06817, United States of America

do solemnly and sincerely declare as follows:

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

(4) Here insert basic Country or Countries followed by date or dates and basic Applicant or Applicants.

2. The basic application as defined by Section 141 of the Act was made in(4) the United States of America on the 30th day of September 19 86, by Mary Therese Zoekler; Frederick John Karol on the day of 19, by

(5) Here insert (in full) Name and Address of Actual Inventor or Inventors.

3. (5) Mary Therese Zoekler, Frederick John Karol, residing respectively at: 412 Blue Spring Road, Princeton (08540); 18 Hiland Drive, Belle Mead (08502) State of New Jersey, United States of America

is/are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follow:

The applicant is the assignee of the invention from the said actual inventors.

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at Danbury, Ct., United States of America this 9th day of May 19 88

(6) Signature.

UNION CARBIDE CORPORATION (6) Timothy N. Bishop

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- (57) Claim

1. An ethylene polymerization catalyst comprising:

- (i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is aCl_bR_c wherein
- X = Cl, Br, or I, or mixtures thereof
- ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms
- M = Al or Mg
- R = an alkyl radical having 1 to 14 carbon atoms
- m = an integer from 3 to 6
- ~~a = 1 or 2~~
- b = 2 when M = Al and 3 when M = Mg
- c = 2 when M = Al and 0 when M = Mg,
- said complex impregnated on an

inorganic oxide support;

- (ii) a halocarbon promoter; and
- (iii) a hydrocarbyl aluminum cocatalyst.

4. An ethylene polymerization catalyst comprising:

(i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is

MCl_bR_c wherein

X = Cl, Br, or I, or mixtures thereof

ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

M = Al or Mg

R = an alkyl radical having 1 to 14 carbon atoms

m = an integer from 3 to 6

~~a = 1 or 2~~

b = 2 when M = Al and 3 when M = Mg

c = 2 when M = Al and 0 when M = Mg;

and

(ii) a hydrocarbyl aluminum cocatalyst.

20. An ethylene polymerization catalyst precursor comprising:

a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is

MCl_bR_c wherein

X = Cl, Br, or I, or mixtures thereof

ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

M = Al or Mg

R = an alkyl radical having 1 to 14 carbon atoms

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$m =$ an integer from 3 to 6

~~$a = 1$ or 2~~

$b = 2$ when $M = \text{Al}$ and 3 when $M = \text{Mg}$

$c = 2$ when $M = \text{Al}$ and 0 when $M = \text{Mg}$,

said complex impregnated on an
inorganic oxide support.

PCT

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

<p>(54) Title: ETHYLENE POLYMERIZATION CATALYST</p> <p>(57) Abstract</p> <p>An ethylene polymerization catalyst comprising: (i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is $M_aCl_bR_c$ wherein $X = Cl, Br, \text{ or } I$, or mixtures thereof, $ED =$ an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms, $M = Al \text{ or } Mg$, $R =$ an alkyl radical having 1 to 14 carbon atoms, $m =$ an integer from 3 to 6, $a = 1 \text{ or } 2$, $b = 2$ when $M = Al$ and 3 when $M = Mg$, $c = 2$ when $M = Al$ and 0 when $M = Mg$, said complex impregnated on an inorganic oxide support; (ii) a halocarbon promoter; and (iii) a hydrocarbyl aluminum cocatalyst.</p>

ETHYLENE POLYMERIZATION CATALYSTTechnical Field

This invention relates to a vanadium catalyst useful in ethylene polymerization.

Background Art

While titanium and chromium catalysts are commonly used in ethylene polymerization, vanadium catalysis has received much less attention. In the past, when vanadium catalysts have been used, often it was in a solution process using soluble vanadium catalysts. Under such solution process conditions with soluble vanadium catalysts, the polyethylenes produced had a very narrow molecular weight distribution.

When supported vanadium catalysts have been described in the literature, these catalysts have generally been based on monomeric species such as VCl_4 , VCl_3 , $VOCl_3$, triisobutyl vanadate, and vanadium tris-acetyl acetonate. These vanadium compounds can be reacted with the surface of supports such as silica to form chemically-anchored vanadium species. Ethylene polymerization with these catalysts provides polyethylenes of intermediate or broad molecular weight distribution. Supported vanadium catalysts of the type described above exhibit complex kinetic behavior characterized by erratic reaction rates, lack of reproducibility, attraction to the walls of the reactor causing fouling, and, in general, behavior not regarded as commercially suitable. These features are significant factors responsible

for the lack of commercial use of vanadium catalysts for polyethylene production.

The art is constantly seeking catalysts which combine controllable polymerization kinetics, high hydrogen response for molecular weight control, and high productivities for polyethylene resins having densities ranging from 0.86 to 0.96. Catalysts which display these characteristics as well as providing polyethylene particles of high bulk density and attractive particle size would represent a major advance. Last, but not least, catalysts which contain discrete, isolatable complexes of well-defined compositions are particularly amenable to study, certainly a further advantage from a developmental point of view.

Disclosure of the Invention

An object of this invention, therefore, is to provide an ethylene polymerization catalyst, which meets one, and preferably more, of the aforementioned characteristics. Other objects and advantages will become apparent hereinafter.

According to the present invention, an ethylene polymerization catalyst has been discovered comprising:

- (i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is MCl_bR_c wherein
- X = Cl, Br, or I, or mixtures thereof
- ED = an electron donor selected from the group consisting of ethers, phosphines,



ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

M = Al or Mg

R = an alkyl radical having 1 to 14 carbon atoms

m = an integer from 3 to 6

b = 2 when M = Al and 3 when M = Mg

c = 2 when M = Al and 0 when M = Mg,

said complex impregnated on an inorganic oxide support;

(ii) a halocarbon promoter; and

(iii) a hydrocarbyl aluminum cocatalyst.

According to a second embodiment of this invention there is provided an ethylene polymerization catalyst comprising:

(i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is $MC_{1b}R_c$ wherein

X = Cl, Br, or I, or mixtures thereof

ED = an electron donor selected from the group consisting of ethers, phosphites, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

M = Al or Mg

R = an alkyl radical having 1 to 14 carbon atoms

m = an integer from 3 to 6

b = 2 when M = Al and 3 when M = Mg

c = 2 when M = Al and 0 when M = Mg; and

(ii) a hydrocarbyl aluminum cocatalyst.

According to a third embodiment of this invention there is provided an ethylene polymerization catalyst comprising:



(i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is MCl_bR_c wherein

X = Cl, Br, or I, or mixtures thereof

5 ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

M = Al or Mg

R = an alkyl radical having 1 to 14 carbon atoms

10 m = an integer from 3 to 6

b = 2 when M = Al and 3 when M = Mg

c = 2 when M = Al and 0 when M = Mg,

said complex impregnated on an inorganic oxide support; and

(ii) a hydrocarbyl aluminum cocatalyst.

15 According to a fourth embodiment of this invention there is provided an ethylene polymerization catalyst precursor comprising:

a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is MCl_bR_c wherein

X = Cl, Br, or I, or mixtures thereof

20 ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

M = Al or Mg

R = an alkyl radical having 1 to 14 carbon atoms

25 m = an integer from 3 to 6

b = 2 when M = Al and 3 when M = Mg

c = 2 when M = Al and 0 when M = Mg,



said complex impregnated on an inorganic oxide support.

According to a fifth embodiment of this invention there is provided a process for the polymerization of ethylene or ethylene together with at least one comonomer comprising contacting the monomer(s), in the gas or liquid
5 phase, with a catalyst comprising:

(i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is MCl_bR_c wherein

X = Cl, Br, or I, or mixtures thereof

10 ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

M = Al or Mg

R = an alkyl radical having 1 to 14 carbon atoms

15 m = an integer from 3 to 6

b = 2 when M = Al and 3 when M = Mg

c = 2 when M = Al and 0 when M = Mg,

said complex impregnated on an inorganic oxide support;

(ii) a halocarbon promoter; and

20 (iii) a hydrocarbyl aluminum cocatalyst in such a manner that a polymer or copolymer is produced.

According to a sixth embodiment of this invention there is provided a process for the polymerization of ethylene or ethylene together with at least one comonomer comprising contacting the monomer(s), in the gas or liquid
25 phase, with a catalyst comprising:

(i) a complex having at least one cation and at least one anion

wherein the cation is $V_2X_3(ED)_m$ and the anion is MCl_bR_c wherein



X = Cl, Br, or I, or mixtures thereof

ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

5

M = Al or Mg

R = an alkyl radical having 1 to 14 carbon atoms

m = an integer from 3 to 6

b = 2 when M = Al and 3 when M = Mg

c = 2 when M = Al and 0 when M = Mg; and

10

(ii) a hydrocarbyl aluminum cocatalyst in such a manner that a polymer or copolymer is produced.

According to a seventh embodiment of this invention there is provided a process for the polymerization of ethylene or ethylene together with at least one comonomer comprising contacting the monomer(s), in the gas or liquid phase with a catalyst comprising:

(i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is MCl_bR_c wherein

X = Cl, Br, or I, or mixtures thereof

ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

M = Al or Mg

R = an alkyl radical having 1 to 14 carbon atoms

m = an integer from 3 to 6

b = 2 when M = Al and 3 when M = Mg

c = 2 when M = Al and 0 when M = Mg,

25



said complex impregnated on an inorganic oxide support; and
(ii) a hydrocarbyl aluminum cocatalyst in such a manner that a polymer or copolymer is produced.

5 According to an eighth embodiment of this invention there is provided a process for preparing a catalytic complex comprising refluxing, in solution under an inert atmosphere, a compound having the formula $VX_3(ED)_m$ with a compound having the formula R_2AlOR or R_2AlH wherein

X = Cl, Br, or I, or mixtures thereof

10 ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

R = an alkyl radical having 1 to 14 carbon atoms, each R being alike or different

m = an integer from 3 to 6, until the solution becomes green.

15 According to a ninth embodiment of this invention there is provided a process for preparing a complex comprising reacting, in solution under an inert atmosphere, a compound having the formula $VX_3(ED)_m$ with a compound having the formula R_2AlH wherein

X = Cl, Br, or I, or mixtures thereof

20 ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

R = an alkyl radical having 1 to 14 carbon atoms, each R being alike or different

25 m = an integer from 3 to 6,

until the solution becomes green.



Detailed Description

The vanadium complex can be synthesized as set forth in Cotton et al, Mononuclear and Binuclear Cations Complexes of Vanadium (II), Journal of the American Chemical Society, 1985, Volume 107, pages 3850 to 3855, which is
5 incorporated by reference herein.

Another procedure for the synthesis of the vanadium complex follows:

A 0.05 to 0.10 molar solution of $VCl_3(THF)_3$ in tetrahydrofuran is first prepared. This solution is treated with diethylaluminum ethoxide to provide an aluminum/vanadium atomic ratio between about 0.5 and about 3.0. The
10 aluminum/vanadium atomic ratio is preferably about 0.7 to about 3.0. The solution is then refluxed, under an inert atmosphere such as nitrogen, until it becomes bright green. The reflux time can be in the range of about 15 minutes to about 3 hours depending on the Al/V atomic ratio



selected. Where a hydride is used to provide the anion, the reaction can be carried out at room temperature rather than at reflux temperature. As long as the reactants are in solution, the molarity is not important to the result. Selection of molarity is, then, a matter of practicality. The bright green solution is cooled and hexane or other hydrocarbon solvent is added to precipitate green crystals of the dimeric vanadium salt, i.e., $[V_2Cl_3(THF)_6]^+ [AlCl_2(C_2H_5)_2]^-$ wherein THF = tetrahydrofuran. The crystals are isolated and washed with cold hexane. The components used to provide the complex can be varied as indicated below.

While it is not necessary to support the complex, supported complexes do provide superior performance and are preferred. Silica is the preferred support. Other suitable inorganic oxides are aluminum phosphate, alumina, silica/alumina mixtures, silica modified with an organoaluminum compound such as triethylaluminum (TEAL), silica modified with diethylzinc, and a mixture of silica and calcium carbonate. A typical support is a solid, particulate porous material essentially inert to the polymerization. It is used as a dry powder having an average particle size of about 10 to about 250 microns and preferably about 30 to about 100 microns; a surface area of at least about 3 square meters per gram and preferably at least about 50 square meters per gram; and a pore size of at least about 80 Angstroms and preferably at least about 100 Angstroms.

Generally, the amount of support used is that which will provide about 0.05 to about 0.5 millimole of vanadium per gram of support and preferably about 0.2 to about 0.3 millimole of vanadium per gram of support.

The supported catalyst can be prepared as follows:

(i) A silica gel is first activated at about 600°C under dry, deoxygenated nitrogen for about 20 hours to provide a support free of adsorbed water and containing less than about 0.7 millimole of surface hydroxy groups per gram of silica. The vanadium complex crystals, prepared as above, are redissolved in freshly distilled tetrahydrofuran. This solution of purified dimer is added to the silica in an amount sufficient to provide about 0.3 millimole of vanadium per gram of silica. The resulting slurry is stirred at room temperature (about 20°C) for about 30 minutes under nitrogen. The tetrahydrofuran is then (partially) removed under vacuum to provide a free-flowing, powdered catalyst with a mole ratio of electron donor (in this case, tetrahydrofuran) to vanadium of about 3 to about 15. It is noted that the complex per se contains 3 to 6 moles of the electron donor and the balance is excess.

The preparation of the supported catalyst can be simplified considerably by eliminating the isolation step. In this case, the bright green reaction solution is added to the silica in an amount sufficient to provide about 0.3 millimole of vanadium per gram of silica and the procedure in the

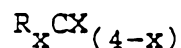
preceding paragraph is then continued. This technique leaves excess diethylaluminum ethoxide in the supported catalyst. The presence of this excess is advantageous because it results in improved hydrogen response. The hydrogen response can also be increased by mix tank treatment with diethylaluminum chloride. In this case, melt flow ratio values are also lowered.

The electron donors incorporated into the vanadium complex are selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms. Among these electron donors, the preferred are alkyl and cycloalkyl ethers having 2 to 20 carbon atoms; alkyl and aryl phosphines having 3 to 20 carbon atoms; dialkyl, diaryl, and alkylaryl ketones having 3 to 20 carbon atoms; alkyl and aryl isocyanides having 2 to 20 carbon atoms; and alkyl, alkoxy, and alkylalkoxy esters of alkyl and aryl carboxylic acids having 2 to 20 carbon atoms. The most preferred electron donors include tetrahydrofuran and triethylphosphine. Other examples of suitable electron donors are methyl formate, ethyl acetate, butyl acetate, ethyl ether, dioxane, di-n-propyl ether, dibutyl ether, ethyl formate, methyl acetate, ethyl anisate, ethylene carbonate, tetrahydropyran, and ethyl propionate. The electron donor will have the proper valence when included in the complex, as will the cation and anion. In its compound form, the electron donor is preferably the solvent for the vanadium compound, which is used to prepare the complex and contains a

like ligand. The vanadium compound is the reaction product of a compound having the formula VX_3 and one of the electron donor compounds mentioned above. Where $VCl_3(THF)_3$ is the initial vanadium compound, tetrahydrofuran is used as the solvent. Alternately, the electron donor can be introduced in a ligand exchange reaction with a preformed complex, e.g., treating the $[V_2Cl_3(THF)_6]^+$ ion with triethylphosphine to yield the $[V_2Cl_3(\text{triethylphosphine})_6]^+$ ion.

Compounds which can be used to provide the anion portion of the complex have the formula R_2AlOR or R_2AlH wherein R is an alkyl radical having 1 to 14 carbon atoms, and preferably 1 to 4 carbon atoms, and each R is alike or different. Preferred alkyl radicals are ethyl and isobutyl. Examples of suitable anion providing compounds are diethyl aluminum ethoxide, diisobutyl aluminum ethoxide, dimethyl aluminum ethoxide, diethyl aluminum methoxide, diethyl aluminum propoxide, diethyl aluminum butoxide, diethyl aluminum hydride, and diisobutyl aluminum hydride.

The halocarbon promoter can have the following formula:



wherein R = hydrogen or an unsubstituted or halogen substituted alkyl radical having 1 to 6 carbon atoms;

X = a halogen; and

x = 0, 1, or 2.

Preferred promoters include fluoro-, chloro-, and bromo-substituted methane or ethane having at least 2 halogen atoms attached to a carbon atom, e.g., methylene dichloride, 1,1,1-trichloroethane, chloroform, CBr_4 , CFCl_3 , CH_3CCl_3 , and $\text{CF}_2\text{ClCCl}_3$. The first three mentioned promoters are especially preferred. About 0.1 to about 10 moles, and preferably about 0.2 to about 2 moles, of promoter can be used per mole of cocatalyst.

The hydrocarbyl aluminum cocatalyst can be represented by the formula R_3Al wherein each R is an alkyl, cycloalkyl, aryl, or hydride radical; at least one R is a hydrocarbyl radical; two or three R radicals can be joined in a cyclic radical forming a heterocyclic structure; each R can be alike or different; and each R, which is a hydrocarbyl radical, has 1 to 20 carbon atoms, and preferably 1 to 10 carbon atoms. Further, each alkyl radical can be straight or branched chain and such hydrocarbyl radical can be a mixed radical, i.e., the radical can contain alkyl, aryl, and/or cycloalkyl groups. Examples of suitable radicals are: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, 2-methylpentyl, heptyl, octyl, isooctyl, 2-ethylhexyl, 5,5-dimethylhexyl, nonyl, decyl, isodecyl, undecyl, dodecyl, phenyl, phenethyl, methoxyphenyl, benzyl, tolyl, xylyl, naphthyl, naphthal, methylnaphthyl, cyclohexyl, cycloheptyl, and cyclooctyl.

Examples of suitable hydrocarbyl aluminum compounds are as follows: triisobutylaluminum

(TIBA), trihexylaluminum, di-isobutylaluminum hydride, dihexylaluminum hydride, isobutylaluminum dihydride, hexylaluminum dihydride, di-isobutylhexylaluminum, isobutyl dihexylaluminum, trimethylaluminum, triethylaluminum, tripropylaluminum, triisopropylaluminum, tri-n-butylaluminum, trioctylaluminum, tridecylaluminum, tridodecylaluminum, tribenzylaluminum, triphenylaluminum, trinaphthylaluminum, and tritolylaluminum. The preferred hydrocarbyl aluminums are triethylaluminum, triisobutylaluminum, trihexylaluminum, di-isobutylaluminum hydride, and dihexylaluminum hydride.

The cocatalyst and promoter can be added to the supported vanadium complex either before or during the polymerization reaction. They can be added together or separately, simultaneously or sequentially. The cocatalyst and promoter are preferably added separately as solutions in an inert solvent, such as isopentane, to the polymerization reaction at the same time as the flow of the ethylene is initiated. The cocatalyst is necessary to obtain any significant polymerization. The promoter, on the other hand, can be considered a preferred option. About 5 to about 500 moles, and preferably about 10 to about 40 moles, of cocatalyst can be used per mole of vanadium complex.

The ethylene polymerization can be conducted in the gas phase or liquid phase using conventional techniques such as fluidized bed, slurry, or solution processes. A continuous,

fluidized bed process is preferred. Using this fluidized bed process, the vanadium complex, the cocatalyst, the promoter, the ethylene monomer, and any comonomers are continuously fed into the reactor and polyethylene product is continuously removed. The density of the ethylene copolymer produced may be varied over a wide range depending upon the amount of alpha-olefin comonomer added and upon the particular comonomer employed. The greater the mole percent of alpha-olefin, the lower the density.

The fluidized bed polymerization is conducted at a temperature below the sintering temperature of the product. The operating temperature is generally in the range of about 10°C to about 115°C. Preferred operating temperatures will vary depending upon the density desired. High density polyethylenes of greater than about 0.94 grams per cubic centimeter (g/cc) are produced at operating temperatures of about 85°C to about 115°C, and preferably about 90°C to about 100°C. Low density polyethylenes ranging in density from about 0.91 to about 0.94 g/cc are preferably produced at an operating temperature of about 75°C to about 90°C. Very low density polyethylenes of less than about 0.91 g/cc are preferably produced at an operating temperature of about 10°C to about 80°C. In the case of very low density polyethylenes, it is necessary to dilute the reaction mixture with a large quantity of a diluent gas in order to prevent the formation of polymer agglomerates and sustain polymerization on a continuous basis.

The fluidized bed reactor is typically operated at pressures of up to about 1,000, and preferably about 50 to about 350, psig.

A chain transfer agent, such as hydrogen, can be used to terminate the polymer chain. Usually the ratio of hydrogen to ethylene will vary between about 0.001 to about 2.0 moles of hydrogen per mole of ethylene.

The invention is illustrated by the following examples.

EXAMPLE 1

Preparation of catalyst precursors (THF = tetrahydrofuran):

(i) In a dry, nitrogen-purged flask fitted with a reflux condenser and nitrogen inlet are placed 20 milliliters of $VCl_3(THF)_3$ (0.06 molar solution in THF, 1.2 millimoles V) and 2.65 milliliters of $(C_2H_5)_2AlOC_2H_5$ (1.36 molar solution in hexane, 3.6 millimoles Al). The reaction solution is refluxed under nitrogen for 35 minutes during which time the color changes to a bright green. The solution is cooled to room temperature and an equal volume of hexane is added. Bright green crystals of the vanadium (II) dimeric complex are isolated, washed with cold hexane, and redissolved in freshly distilled THF.

Silica, predried and activated at 600°C, is slurried in THF under nitrogen. The silica used is a dry powder having an

average particle size of about 30 to about 100 microns. It has a surface area greater than or equal to about $50 \text{ m}^2/\text{g}$ and pore sizes of greater than or equal to about 100 Angstroms. A portion of the solution of purified dimer is added to give a vanadium loading of 0.30 millimole of vanadium per gram of silica. The slurry is stirred at room temperature for 30 minutes, and dried to a free-flowing, pale green powder under vacuum.

(ii) The same procedure as described in paragraph (i) above is followed except that 50 milliliters of $\text{VCl}_3(\text{THF})_3$ (0.07 molar solution, 3.5 millimoles V) and 1.80 milliliters of $(\text{C}_2\text{H}_5)_2\text{AlOC}_2\text{H}_5$ (1.36 molar solution, 2.4 millimoles Al) are used. At the lower Al/V ratio, four hours at reflux are required for a complete reaction to form the dimer. Rather than isolating the crystalline dimer, the reaction solution is cooled to room temperature and added directly to a slurry of silica in THF. After stirring for 30 minutes at room temperature, the catalyst precursor is dried under vacuum to a free-flowing pale green powder.

(iii) The procedure described in paragraph (ii) is followed except that 15 milliliters of $\text{VCl}_3(\text{THF})_3$ (0.06 molar solution, 0.9 millimoles V) and 1.6 milliliters of $(\text{C}_2\text{H}_5)_2\text{AlH}$ (1.0 molar

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solution, 1.6 millimoles Al) are used. The reaction is complete after 20 minutes at reflux.

(iv) The procedure described in paragraph (ii) is followed except that 20 milliliters of $VCl_3(THF)_3$ (0.06 molar solution, 1.2 millimoles V) and 1.6 milliliters of $(isobutyl)_2AlH$ (1.0 molar solution, 1.6 millimoles Al) are combined and stirred at room temperature under nitrogen for one hour. A dark green solution is formed. This solution is added to a slurry of silica (3.80 grams) in THF. The slurry is stirred for 10 minutes at room temperature, then dried under vacuum to a free-flowing pale green powder.

EXAMPLE 2

Preparation of catalyst precursor:

A 0.06 molar solution of $VCl_3(THF)_3$ is prepared by dissolving 23.60 grams VCl_3 (0.15 mole) in 2,500 milliliters THF at 70°C under nitrogen over several hours. The solution is cooled to 60°C, and $(C_2H_5)_2AlOC_2H_5$ (25 weight percent in hexane) is added to give an atomic ratio of Al/V = 0.7. The mixture is stirred at 70°C under 1 psig nitrogen for 24 hours resulting in a clear green solution. 500 grams of silica, activated at 600°C, are added. After stirring for 30 minutes, the catalyst precursor is dried at 70°C under a slow nitrogen purge to give a THF level of 12 weight percent. The dried catalyst is a pale beige, free-flowing powder.

EXAMPLES 3 TO 17

To a slurry reactor are added sufficient catalyst precursor to give 0.03 millimole of vanadium, prepared by one of the procedures in Example 1 or 2; 480 milliliters of hexane; 20 milliliters of 1-hexene as comonomer; 40 equivalents of triethylaluminum; 40 equivalents of CFCl_3 ; ethylene at a partial pressure of 143 psig; and hydrogen at a partial pressure of 1 psig.

The following variables are set forth in Table I below:

1. In example 3, the cocatalyst is triisobutylaluminum instead of triethylaluminum.
2. In example 12, triethylphosphine is used instead of THF.
3. The reducing agent and support are those used in the preparation of the catalyst precursor.
4. The activation temperature is given for the support.
5. The activity of the catalyst is measured in grams of polyethylene per millimole of vanadium per hour per 100 psig of ethylene.
6. Melt index: ASTM D-1238, Condition E. Measured at 190°C and reported as grams per 10 minutes.
7. Melt flow ratio: Ratio of Flow Index to Melt Index. Flow index: ASTM D-1238, Condition F. Measured at 10 times the weight used in the melt index test above.
8. Polymer density: ASTM D-1505 procedure is followed for polymers having a density of less

than 0.940 gram per cubic centimeter and a modified procedure is used for polymers having a density equal to or greater than 0.940 gram per cubic centimeter. For the low density polymers, a plaque is made and conditioned for one hour at 100°C to approach equilibrium crystallinity. For the high density polymers, the plaque is conditioned for one hour at 120°C to approach equilibrium crystallinity, and is then quickly cooled to room temperature. Measurement for density is then made in a density gradient column and density values are reported as grams per cubic centimeter.

9. Catalyst preparation refers to the procedures in Examples 1 and 2.

10. The aluminum to vanadium ratio is an atomic ratio.

11. i-Bu = isobutyl.

12. The silica is as described in example 1(i).

TABLE I

Example	Reducing Agent	Support	Activation Temperature (°C)	Catalyst Activity	Melt Index	Melt Flow Ratio	Polymer Density	Catalyst Preparation	Al/V
3	$(C_2H_5)_2AlOC_2H_5$	Silica	600	3200	0.35	112	0.9657	Example 1(i)	0.5
4	$(C_2H_5)_2AlOC_2H_5$	Silica	600	2300	5.50	64	0.9547	Example 1(i)	0.5
5	$(C_2H_5)_2AlOC_2H_5$	Silica modified with TEAL	600	1700	11.2	90	0.9546	Example 1(i)	0.5
6	$(C_2H_5)_2AlOC_2H_5$	Aluminum Phosphate	600	1900	12.3	44	0.9560	Example 1(i)	0.5
7	$(C_2H_5)_2AlOC_2H_5$	Silica	600	2900	0.35	100	0.9462	Example 1(ii)	0.7
8	$(C_2H_5)_2AlOC_2H_5$	Silica	800	3600	0.89	72	0.9462	Example 1(ii)	0.7
9	$(C_2H_5)_2AlOC_2H_5$	Silica	600	3500	0.21	90	--	Example 2	0.7
10	$(C_2H_5)_2AlOC_2H_5$	Silica	800	2600	27.3	37	--	Example 1(ii)	3.0
11	$(C_2H_5)_2AlOC_2H_5$	Silica modified with TEAL	600	2800	20.9	54	0.9562	Example 1(ii)	2.4
12	$(C_2H_5)_2AlOC_2H_5$	Silica	600	1100	3.07	76	0.9596	Example 1(i)	0.5
13	$(C_2H_5)_2AlH$	Silica	800	3100	0.34	97	--	Example 1(iii)	0.5
14	$(C_2H_5)_2AlH$	Silica	800	2700	0.40	78	--	Example 1(iii)	1.0
15	$(i-Bu)_2AlH$	Silica	600	3500	2.09	62	0.9509	Example 1(iv)	1.3
16	$(i-Bu)_2AlOC_2H_5$	Silica	600	2800	4.54	62	--	Example 1(iv)	2.7
17	Mg	Silica	800	2100	43.3	20	--		

EXAMPLES 18 TO 21

Ethylene polymerization is carried out in a fluidized bed as described above using the catalyst prepared by the procedure of Example 2, the comonomer is 1-hexene; the cocatalyst is triethylaluminum; and the promoter is CFCl_3 .

The variables are set forth in Table II.

Notes concerning Table II;

1. Vanadium loading is given in millimole of vanadium per gram of catalyst.

2. The diethylaluminum chloride is added to the catalyst precursor in a mix tank treatment prior to its use in the polymerization process.

3. Fluidized bed pressure is 315 psia.

4. Melt index, flow index, melt flow ratio, and polymer density are described above.

5. Bulk density: ASTM D-1895, Method B. The resin is poured via a 3/8-inch diameter funnel into a 400 milliliter graduated cylinder to the 400 milliliter line without shaking the cylinder, and weighed by difference. Density values are reported as pounds per cubic foot.

6. Tetrahydrofuran is given in weight percent based on catalyst.

TABLE II

<u>Example</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Vanadium loading (millimole/gram)	0.27	0.27	0.35	0.27
Tetrahydrofuran (weight percent)	12	12	30	10
Diethylaluminum chloride to vanadium (molar ratio)	0	0	0	1.5
Fluidized bed temperature (°C)	90	100	90	90
H ₂ /C ₂ ratio	0.030	0.036	0.032	0.021
C ₆ /C ₂ ratio	0.007	0.005	0.006	0.006
C ₂ H ₄ partial pressure (%)	73.6	72.6	74.0	72.5
Resin production rate (pounds/hour)	24.9	20.8	17.4	23.4
Cocatalyst feed rate (cc/hour)	160	130	150	140
Melt index (grams/10 minutes)	0.291	0.346	0.290	0.409
Flow index	27.1	27.5	24.9	25.5
Melt flow ratio	93	79	86	62
Polymer density (grams/cc)	0.954	0.953	0.953	0.953
Vanadium in resin (ppm)	3.8	3.8	4.5	4.1
Ash in resin (weight percent)	0.045	0.044	0.045	0.049
Bulk density (pounds/cubic foot)	17.5	17.6	18.5	21.5
Average particle size of resin (inch)	0.039	0.036	0.052	0.043

CLAIMS

1. An ethylene polymerization catalyst comprising:

(i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is aCl_bR_c wherein

X = Cl, Br, or I, or mixtures thereof

ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

M = Al or Mg

R = an alkyl radical having 1 to 14 carbon atoms

m = an integer from 3 to 6

~~a = 1 or 2~~

b = 2 when M = Al and 3 when M = Mg

c = 2 when M = Al and 0 when M = Mg,

said complex impregnated on an inorganic oxide support;

(ii) a halocarbon promoter; and

(iii) a hydrocarbyl aluminum cocatalyst.

2. The catalyst defined in claim 1 wherein ED is selected from the group consisting of alkyl and cycloalkyl ethers having 2 to 20 carbon atoms; alkyl and aryl phosphines having 3 to 20 carbon atoms; dialkyl, diaryl, and alkylaryl ketones having 3 to 20 carbon atoms; alkyl and aryl isocyanides having 2 to 20 carbon atoms; and alkyl, alkoxy, and alkylalkoxy esters of alkyl and aryl carboxylic acids having 2 to 20 carbon atoms.



3. The catalyst defined in claim 1 wherein ED is selected from the group consisting of tetrahydrofuran and triethylphosphine.

4. An ethylene polymerization catalyst comprising:

(i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is MCl_bR_c wherein
 $X = Cl, Br, \text{ or } I, \text{ or mixtures thereof}$
 $ED = \text{an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms}$

$M = Al \text{ or } Mg$

$R = \text{an alkyl radical having 1 to 14 carbon atoms}$

$m = \text{an integer from 3 to 6}$

~~$a = 1 \text{ or } 2$~~

$b = 2 \text{ when } M = Al \text{ and } 3 \text{ when } M = Mg$

$c = 2 \text{ when } M = Al \text{ and } 0 \text{ when } M = Mg;$

and

(ii) a hydrocarbyl aluminum cocatalyst.

5. The catalyst defined in claim 4 wherein ED is selected from the group consisting of alkyl and cycloalkyl ethers having 2 to 20 carbon atoms; alkyl and aryl phosphines having 3 to 20 carbon atoms; dialkyl, diaryl, and alkylaryl ketones having 3 to 20 carbon atoms; alkyl and aryl isocyanides having 2 to 20 carbon atoms; and alkyl, alkoxy, and alkylalkoxy esters of alkyl and aryl carboxylic acids having 2 to 20 carbon atoms.



6. The catalyst defined in claim 4 wherein ED is selected from the group consisting of tetrahydrofuran and triethylphosphine.

7. An ethylene polymerization catalyst comprising:

(i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is MCl_bR_c wherein
 $X = Cl, Br, \text{ or } I, \text{ or mixtures thereof}$
 $ED = \text{an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms}$

$M = Al \text{ or } Mg$

$R = \text{an alkyl radical having 1 to 14 carbon atoms}$

$m = \text{an integer from 3 to 6}$

~~$a = 1 \text{ or } 2$~~

$b = 2 \text{ when } M = Al \text{ and } 3 \text{ when } M = Mg$

$c = 2 \text{ when } M = Al \text{ and } 0 \text{ when } M = Mg,$

said complex impregnated on an inorganic oxide support; and

(ii) a hydrocarbyl aluminum cocatalyst.

8. The catalyst defined in claim 7 wherein ED is selected from the group consisting of alkyl and cycloalkyl ethers having 2 to 20 carbon atoms; alkyl and aryl phosphines having 3 to 20 carbon atoms; dialkyl, diaryl, and alkylaryl ketones having 3 to 20 carbon atoms; alkyl and aryl isocyanides having 2 to 20 carbon atoms; and alkyl,



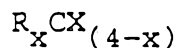
alkoxy, and alkylalkoxy esters of alkyl and aryl carboxylic acids having 2 to 20 carbon atoms.

9. The catalyst defined in claim 7 wherein ED is selected from the group consisting of tetrahydrofuran and triethylphosphine.

10. The catalyst defined in claim 1 wherein the support is silica.

11. The catalyst defined in claim 7 wherein the support is silica.

12. The catalyst defined in claim 1 wherein the promoter is represented by the formula:



wherein R = hydrogen or an unsubstituted or halogen substituted alkyl radical having 1 to 6 carbon atoms;

X = a halogen; and

x = 0, 1, or 2.

13. The catalyst defined in claim 12 wherein the promoter is a fluoro-, chloro-, or bromo-substituted methane or ethane having at least 2 halogen atoms attached to a carbon atom.

14. The catalyst defined in claim 1 wherein the cocatalyst is represented by the formula R_3Al wherein each R is an alkyl, cycloalkyl, aryl, or hydride radical; at least one R is a hydrocarbyl radical; two or three R radicals can be joined in a

cyclic radical forming a heterocyclic structure; each R can be alike or different; and each R, which is a hydrocarbyl radical, has 1 to 20 carbon atoms.

15. The catalyst defined in claim 14 wherein the cocatalyst is selected from the group consisting of triethylaluminum and triisobutylaluminum.

16. The catalyst defined in claim 4 wherein the cocatalyst is represented by the formula R_3Al wherein each R is an alkyl, cycloalkyl, aryl, or hydride radical; at least one R is a hydrocarbyl radical; two or three R radicals can be joined in a cyclic radical forming a heterocyclic structure; each R can be alike or different; and each R, which is a hydrocarbyl radical, has 1 to 20 carbon atoms.

17. The catalyst defined in claim 16 wherein the cocatalyst is selected from the group consisting of triethylaluminum and triisobutylaluminum.

18. The catalyst defined in claim 7 wherein the cocatalyst is represented by the formula R_3Al wherein each R is an alkyl, cycloalkyl, aryl, or hydride radical; at least one R is a hydrocarbyl radical; two or three R radicals can be joined in a cyclic radical forming a heterocyclic structure; each R can be alike or different; and each R, which is a hydrocarbyl radical, has 1 to 20 carbon atoms.

19. The catalyst defined in claim 18 wherein the cocatalyst is selected from the group

consisting of triethylaluminum and triisobutylaluminum.

20. An ethylene polymerization catalyst precursor comprising:

a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is

MCl_bR_c wherein

X = Cl, Br, or I, or mixtures thereof

ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

M = Al or Mg

R = an alkyl radical having 1 to 14 carbon atoms

m = an integer from 3 to 6

~~a = 1 or 2~~

b = 2 when M = Al and 3 when M = Mg

c = 2 when M = Al and 0 when M = Mg,

said complex impregnated on an inorganic oxide support.

21. The catalyst precursor defined in claim 20 wherein ED is selected from the group consisting of alkyl and cycloalkyl ethers having 2 to 20 carbon atoms; alkyl and aryl phosphines having 3 to 20 carbon atoms; dialkyl, diaryl, and alkylaryl ketones having 3 to 20 carbon atoms; alkyl and aryl isocyanides having 2 to 20 carbon atoms; and alkyl, alkoxy, and alkylalkoxy esters of alkyl and aryl carboxylic acids having 2 to 20 carbon atoms.



22. The catalyst precursor defined in claim 20 wherein ED is selected from the group consisting of tetrahydrofuran and triethylphosphine.

23. A process for the polymerization of ethylene or ethylene together with at least one comonomer comprising contacting the monomer(s), in the gas or liquid phase, with a catalyst comprising:

(i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is MCl_bR_c wherein

X = Cl, Br, or I, or mixtures thereof

ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

M = Al or Mg

R = an alkyl radical having 1 to 14 carbon atoms

m = an integer from 3 to 6

~~a = 1 or 2~~

b = 2 when M = Al and 3 when M = Mg

c = 2 when M = Al and 0 when M = Mg,

said complex impregnated on an

inorganic oxide support;

(ii) a halocarbon promoter; and

(iii) a hydrocarbyl aluminum cocatalyst

in such a manner that a polymer or copolymer is produced.

24. A process for the polymerization of ethylene or ethylene together with at least one



comonomer comprising contacting the monomer(s), in the gas or liquid phase, with a catalyst comprising:

- (i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is MCl_bR_c wherein
- X = Cl, Br, or I, or mixtures thereof
- ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms
- M = Al or Mg
- R = an alkyl radical having 1 to 14 carbon atoms
- m = an integer from 3 to 6
- ~~a = 1 or 2~~
- b = 2 when M = Al and 3 when M = Mg
- c = 2 when M = Al and 0 when M = Mg;

and

(ii) a hydrocarbyl aluminum cocatalyst in such a manner that a polymer or copolymer is produced.

25. A process for the polymerization of ethylene or ethylene together with at least one comonomer comprising contacting the monomer(s), in the gas or liquid phase with a catalyst comprising:

- (i) a complex having at least one cation and at least one anion wherein the cation is $V_2X_3(ED)_m$ and the anion is MCl_bR_c wherein
- X = Cl, Br, or I, or mixtures thereof



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ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

M = Al or Mg

R = an alkyl radical having 1 to 14 carbon atoms

m = an integer from 3 to 6

~~a = 1 or 2~~

b = 2 when M = Al and 3 when M = Mg

c = 2 when M = Al and 0 when M = Mg,

said complex impregnated on an inorganic oxide support; and

(ii) a hydrocarbyl aluminum cocatalyst in such a manner that a polymer or copolymer is produced.

26. A process for preparing a catalytic complex comprising refluxing, in solution under an inert atmosphere, a compound having the formula $VX_3(ED)_m$ with a compound having the formula R_2AlOR or R_2AlH wherein

X = Cl, Br, or I, or mixtures thereof

ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

R = an alkyl radical having 1 to 14 carbon atoms, each R being alike or different

m = an integer from 3 to 6,

until the solution becomes green.



27. The process defined in claim 26 wherein the aluminum/vanadium atomic ratio is in the range of about 0.5:1 to about 3:1.

28. A process for preparing a complex comprising reacting, in solution under an inert atmosphere, a compound having the formula $VX_3(ED)_m$ with a compound having the formula R_2AlH wherein

X = Cl, Br, or I, or mixtures thereof

ED = an electron donor selected from the group consisting of ethers, phosphines, ketones, isocyanides, and esters, each electron donor having 2 to 20 carbon atoms

R = an alkyl radical having 1 to 14 carbon atoms, each R being alike or different

m = an integer from 3 to 6,
until the solution becomes green.

29. The process defined in claim 26 wherein (i) the solvent is the electron donor; (ii) the green solution is impregnated on an inorganic oxide support; and (iii) the impregnated support is dried to remove excess electron donor.

30. The process defined in claim 28 wherein (i) the solvent is the electron donor; (ii) the green solution is impregnated on an inorganic oxide support; and (iii) the impregnated support is dried to remove excess electron donor.

31. An ethylene polymerization catalyst, substantially as hereindescribed with reference to any one of the Examples.

32. A process for the polymerization of ethylene or ethylene together with at least one comonomer which process is substantially as hereindescribed with reference to any one of the Examples.

33. A process for preparing a catalytic complex which process is substantially as hereindescribed with reference to Example 1 or Example 2.

DATED this 7th day of December 1989.

UNION CARBIDE CORPORATION

By Their Patent Attorneys:

CALLINAN LAWRIE

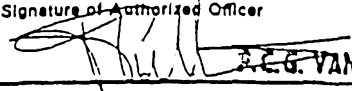
Michael J. Houlihan.



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 87/02462

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 08 F 4/68; C 08 F 10/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 08 F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	Journal of the American Chemical Society, vol. 107, 1985, American Chemical Society (US) F.A. Cotton et al.: "Mononuclear and binuclear cationic complexes of vanadium (II)", pages 3850-3855, see the whole article	1
Y	EP, A, 0123317 (PHILLIPS PETROLEUM) 31 October 1984 see the claims	1

<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
12th January 1988	9 FEB 1988	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 A.E.G. VAN DER PUTTEN	

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 8702462
SA 19085

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 01/02/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0123317	31-10-84	JP-A- 59206412	22-11-84
		US-A- 4559318	17-12-85
		CA-A- 1225983	25-08-87
