

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
11 March 2004 (11.03.2004)

PCT

(10) International Publication Number
WO 2004/020486 A1

(51) International Patent Classification⁷: **C08F 10/00**, 2/34

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(21) International Application Number:
PCT/CA2003/001227

(22) International Filing Date: 19 August 2003 (19.08.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2,399,753 27 August 2002 (27.08.2002) CA

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ANTISTATIC FOR GAS PHASE SINGLE SITE CATALYST POLYMERIZATION

(57) Abstract: An antistatic suitable for use in gas phase polymerization in the presence of a single site catalyst comprises a mixture of a polysulphone, a polyamide and a sulphonic acid. The antistatic may be added to the reactor as a part of the gases being polymerized and reduced the reactor fouling attributable to the build up of static in the reactor.

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**ANTISTATIC FOR GAS PHASE SINGLE SITE CATALYST
POLYMERIZATION**

TECHNICAL FIELD

The present invention relates the gas phase polymerization of olefins, and particularly alpha olefins in the presence of a single site catalyst. Processes for the gas phase polymerization of olefins are well known and described in a number of patents including for example U.S. Patents 4,543,399 and 4,588,790 issued to Jenkins, III et al., September 24, 1985 and May 13, 1986, respectively, assigned to Union Carbide.

BACKGROUND ART

United States Patent 4,182,810 issued January 8, 1980, assigned to Phillips Petroleum Company teaches the use of antifouling agents comprising a mixture of a polysulphone copolymer, a polyamide and a sulphonic acid in a slurry phase polymerization. The Patent does not teach or suggest the use of similar systems in a gas phase polymerization.

United States Patent 5,026,795 issued June 25, 1991 assigned to Phillips Petroleum Company teaches the use of an antistatic agent comprising of a polysulphone copolymer, a polyamide and a sulphonic acid in a gas phase polymerization. The only teaching of a catalyst in the disclosure is a silica/titanium/chromium oxide catalyst. This is not the single site catalyst of the present invention.

United States Patent 5,030,700 issued July 9, 1991 assigned to Exxon and immediately withdrawn apparently related to a process to control static in a gas phase process in which the catalyst was a metallocene catalyst. Applicant references the case but has been unable to obtain a copy of the Patent or even an abstract of the Patent.

WO 01/18067 published March 15, 2001 in the name of BP Chemicals Limited discloses similar compositions may be used to control static in gas phase reactors using Ziegler Natta type catalysts. The reference does not teach or suggest the antistatic agent would be useful in conjunction with single site catalysts.

DISCLOSURE OF INVENTION

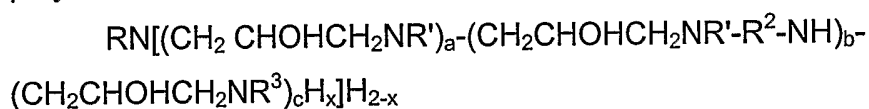
The present invention provides In a process for the fluidized bed gas phase polymerization of one or more C₂₋₈ alpha in the presence of a single site catalyst and an activator the improvement comprising including in the gas phase from 0.5 to 20,000 ppm based on the weight of the olefin in the reactor of an anti static agent comprising:

(i) from 3 to 48 parts by weight of one or more polysulfones comprising:

- (a) 50 mole % of sulphur dioxide;
- (b) 40 to 50 mole % of a C₆₋₂₀ an alpha olefin; and
- (c) from 0 to 10 mole % of a compound of the formula

ACH=CHB where A is selected from the group consisting of a carboxyl radical and a C₁₋₁₅ carboxy alkyl radical; and B is a hydrogen atom or a carboxyl radical provided if and B are carboxyl radicals A and B may form an anhydried;

(ii) from 3 to 48 parts by weight of one or more polymeric polyamides of the formula:



wherein R¹ is an aliphatic hydrocarbonyl group of 8 to 24 carbon atoms, R² is an alkylene group of 2 to 6 carbon atoms, R³ is the group-R²-HNR¹, R is R¹ or an N-aliphatic hydrocarbonyl alkylene group having the formula R¹NHR²; a, b and c are integers from 0 to 20 and x is 1 or 2 ; with the proviso that when R is R¹ then a is greater than 2 and b = c = 0, and when R is R¹NHR²-then a is 0 and the sum of b + c is an integer from 2 to 20;

(iii) from 3 to 48 parts by weight of C₁₀₋₂₀ alkyl or arylalkyl sulphonic acid,
and optionally from 0 to 150 parts by weight of a solvent or diluent.

BEST MODE FOR CARRYING OUT THE INVENTION

As used in this specification the term single site catalyst includes homogeneous catalysts producing under typical conditions a polymer having a polydispersity (Mw/Mn) of less than 7, preferably less than 4.

Such catalysts tend to be complexes of transition metals, preferably an early transition metal (e.g. Ti, V, Zr and Hf) and generally having two bulky ligands. In many of the well known single site catalysts typically one of the bulky ligands is a cyclopentadienyl-type ligand. These cyclopentadienyl-type ligands comprise a C₅₋₁₃ ligand containing a 5-membered carbon ring having delocalized bonding within the ring and bound to the metal atom through covalent η^5 bonds which are unsubstituted or may be further substituted (sometimes referred to in a short form as Cp ligands). Cyclopentadienyl-type ligands include unsubstituted cyclopentadienyl, substituted cyclopentadienyl, unsubstituted indenyl, substituted indenyl, unsubstituted fluorenyl and substituted fluorenyl. An exemplary list of substituents for a cyclopentadienyl-type ligand includes the group consisting of C₁₋₁₀ hydrocarbyl radicals (including phenyl and benzyl radicals), which hydrocarbyl substituents are unsubstituted or further substituted by one or more substituents selected from the group consisting of a halogen atom, preferably a chlorine or fluorine atom and a C₁₋₄ alkyl radical; a C₁₋₈ alkoxy radical; a C₆₋₁₀ aryl or aryloxy radical; an amido radical which is unsubstituted or substituted by up to two C₁₋₈ alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C₁₋₈ alkyl radicals; silyl radicals of the formula $-\text{Si}-(\text{R})_3$ wherein each R is independently selected from the group consisting of hydrogen, a C₁₋₈ alkyl or alkoxy radical, and C₆₋₁₀ aryl or aryloxy radicals; and germanyl radicals of the formula $\text{Ge}-(\text{R})_3$ wherein R is as defined directly above.

If there are two such bulky ligands (i.e. bis Cp) the catalysts are metallocene-type catalysts. The Cp ligand may be bridged to another Cp ligand by a silyl bridge or a short chain (C₁₋₄) alkyl radical. The Cp-type ligand may be bridged to an amido radical which may be further substituted by up to two additional substituents. Such bridged complexes are sometimes referred to as constrained geometry catalysts. The catalyst may contain a CP type ligand together with other bulky ligands such as a

phosphinimine ligand or a ketimide ligand. All of the foregoing types of catalyst are intended to come within the phrase single site catalyst.

Gas phase polymerization of olefins is well known. Typically, in gas phase polymerization of polyolefins (such as polyethylene) a gaseous feed stream comprising ethylene and one or more C₃₋₆ copolymerizable monomers typically butene or hexene or both, together with a ballast gas such as nitrogen, optionally a small amount of C₁₋₂ alkanes (i.e. methane and ethane) and further optionally a molecular weight control agent (typically hydrogen) is fed to a reactor. Typically the feed stream passed through a distributor plate at the bottom of the reactor and traverses a catalyst bed, typically a fluidized catalyst bed. A small proportion of the olefin monomers in the feed stream react with the catalyst. The unreacted monomer and the other non-polymerizable components in the feed stream exit the bed and typically enter a disengagement zone where the velocity of the feed stream is reduced so that entrained polymer falls back into the fluidized bed. Typically the gaseous stream leaving the top of the reactor is then passed through a compressor. The compressed gas is then cooled by passage through a heat exchanger to remove the heat of reaction. The heat exchanger may be operated at temperatures below about 65°C, preferably at temperatures from 20°C to 50°C.

Polymer is removed from the reactor through a series of vessels in which monomer is separated from the off gases. The polymer is recovered and further processed. The off gases are fed to a monomer recovery unit. The monomer recovery unit may be selected from those known in the art including a distillation tower (i.e. a C₂ splitter), a pressure swing adsorption unit and a membrane separation device. Ethylene and hydrogen gas recovered from the monomer recovery unit are fed back to the reactor. Finally, make up feed stream is added to the reactor below the distributor plate.

The polymerization is a particulate polymerization and there is a static electricity build up on the polymer particles in the reactor bed. The

particles may tend to be attracted to the walls of the reactor and this over the long run may result in sheeting and formation of agglomerates.

It has now been found that an antistatic aid comprising:

- (1) a polysulphone copolymer;
- (2) a polymeric polyamine; and
- (3) an oil-soluble sulphonic acid,

may be used to reduce static (or static electricity) in the gas phase polymerization of olefins in the presence of a single site catalyst.

The antistatic can be added at any location of the fluidized bed polymerization process, including but not limited to the reactor itself, below the distributor plate or above the distributor plate in the fluidized bed, above the fluidized bed, in the velocity reduction zone, anywhere in the reaction loop or recycle line, etc. According to a preferred embodiment of the present invention, the process aid additive is directly added into the polymerization zone, more preferably directly into the fluidized bed. The antistatic may be added near the distributor plate typically the bottom third of the bed. The antistatic may be added at several different locations of the process.

Care should be taken if the antistatic is to be added in admixture with the catalyst component or the cocatalyst.

The polysulphone component of the antistatic in accordance with the present invention is typically a linear polymer believed to be alternating copolymers of the olefins and sulphur dioxide, having a 1:1 molar ratio of the comonomers with the olefins in head to tail arrangement. The polysulphone should consist of about 50 mole percent of units derived from sulphur dioxide; about 40 to 50 mole percent of units derived from one or more C₆₋₂₀ alpha olefins, and optionally from about 0 up to about 10 mole percent of units derived from an olefinic compound having the formula ACH=CHB where A is a group having the formula (C_xH_{2x})-COOH wherein x is from 0 to about 17, and B is hydrogen or carboxyl, with the proviso that when B is carboxyl, x is 0, and wherein A and B together can be a dicarboxylic anhydride group.

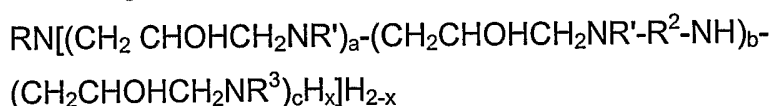
The polysulphone used in the present invention generally has a weight average molecular weight in the range 30,000 to 1,000,000, preferably from 50,000 to 500,000. Preferably, the alpha olefins in the sulphone are straight chain olefins having up to 18 carbon atoms, including 1-hexene, 1-heptene, 1-octene, 1-decene, 1-dodecene, 1-hexadecene and 1-octadecene.

If present the ACH=CHB components of the sulphone polymer may be derived from maleic acid, acrylic acid, and 5-hexenoic acid.

The manufacture of polysulphones is more fully described in U.S. Patent specifications 3,811,848 and 3,917,466. The text of which is herein incorporated by reference.

A particularly useful polysulphone is a copolymer of 1-decene and sulphur dioxide having an inherent viscosity (measured as a 0.5 weight percent solution in toluene at 30°C) ranging from about 0.04 dl/g to 1.6 dl/g.

The polyamine component in accordance with the present invention has the general formula:



wherein R¹ is an aliphatic hydrocarbyl group of 8 to 24 carbon atoms, R² is an alkylene group of 2 to 6 carbon atoms, R³ is the group R²-HNR¹, R is R¹ or an N-aliphatic hydrocarbyl alkylene group having the formula R¹NHR²; a, b and c are integers from 0 to 20 and x is 1 or 2; with the proviso that when R is R¹ then a is greater than 2 and b=c=0, and when R is R¹NHR² then a is 0 and the sum of b+c is an integer from 2 to 20.

U.S. Patent 3,917,466 discloses the polyamines which can be used in the present invention.

One method of preparing the polyamine comprises heating an aliphatic primary monoamine or N-aliphatic hydrocarbyl alkylene diamine with epichlorohydrin in 1:1 to 1:1.5 molar ratio at a temperature of 50°C to 100°C in a solvent, such as xylene and isopropanol, and adding a strong base, such as sodium hydroxide and continuing the heating for about 2

hours. The product containing the polymeric polyamine is then separated by decanting and flashing off the solvent.

The amine used to make the polyamine is preferably an N-aliphatic alkaline diamine or a primary aliphatic amine containing at least 8 carbon atoms and preferably 12 or more carbon atoms with epichlorohydrin. The primary aliphatic amines include those derived from fatty acids such as tall oil, tallow, soy bean oil, coconut oil and cotton seed oil. Preferably the polyamine is the reaction of N-tallowamine (N-tallow-1, 3-diaminopropane) with epichlorohydrin in a molar ratio of from 1:1 to 1:2 preferably 1:1.5 mole. One method of preparing such a polyamine is disclosed in U.S. Patent 3,917,466. One such reaction product is "Polyflo 130" sold by Universal Oil Company.

The oil-soluble sulphonic acid in the antistatic may be any oil-soluble sulphonic acid such as a C₁₀₋₂₀ alkyl or arylalkyl sulphonic acid. A useful sulphonic acid is petroleum sulphonic acid resulting from treating oils with sulphuric acid. Preferred oil-soluble sulphonic acids are dodecylbenzene sulphonic acid and dinonylnaphthyl sulphonic acid.

The antistatic of the present invention comprises from 3 to 48, preferably from 5 to 40, most preferably from 10 to 40 parts by weight of polysulphone; from 3 to 48, preferably from 5 to 40, most preferably from 10 to 40 parts by weight of polymeric polyamine and from 3 to 48, preferably from 5 to 40, most preferably from 10 to 40 parts by weight of sulphonic acid. The antistatic may be dissolved or dispersed in from 0 to 150, preferably 100 to 150 parts by weight of a solvent or diluent.

Suitable solvents include aromatic, paraffin and cycloparaffin compounds.

The solvents are preferably selected from the group consisting of benzene, toluene, xylene, cyclohexane, fuel oil, isobutane, kerosene and mixtures thereof. According to one embodiment of the present invention, the anti static is diluted in a conventional hydrocarbon diluent, which can be the same or different from the solvents listed above, preferably butane, pentane or hexane. When a diluent is used, the antistatic (including the

solvent therefor) is preferably present in an amount comprised between 0.1 and 500 g per litre of diluent, preferably between 1 and 50 g per litre of diluent.

The catalyst may be a single site type catalyst typically comprising a transition metal, preferably an early transition metal (e.g. Ti, V, Zr and Hf) and generally having two bulky ligands. In many of the well known single site catalysts typically one of the bulky ligands is a cyclopentadienyl-type ligand. These cyclopentadienyl-type ligands comprise a C₅₋₁₃ ligand containing a 5-membered carbon ring having delocalized bonding within the ring and bound to the metal atom through covalent η^5 bonds which are unsubstituted or may be further substituted (sometimes referred to in a short form as Cp ligands). Cyclopentadienyl-type ligands include unsubstituted cyclopentadienyl, substituted cyclopentadienyl, unsubstituted indenyl, substituted indenyl, unsubstituted fluorenyl and substituted fluorenyl. An exemplary list of substituents for a cyclopentadienyl-type ligand includes the group consisting of C₁₋₁₀ hydrocarbyl radicals (including phenyl and benzyl radicals), which hydrocarbyl substituents are unsubstituted or further substituted by one or more substituents selected from the group consisting of a halogen atom, preferably a chlorine or fluorine atom and a C₁₋₄ alkyl radical; a C₁₋₈ alkoxy radical; a C₆₋₁₀ aryl or aryloxy radical; an amido radical which is unsubstituted or substituted by up to two C₁₋₈ alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C₁₋₈ alkyl radicals; silyl radicals of the formula -Si-(R)₃ wherein each R is independently selected from the group consisting of hydrogen, a C₁₋₈ alkyl or alkoxy radical, and C₆₋₁₀ aryl or aryloxy radicals; and germanyl radicals of the formula Ge-(R)₃ wherein R is as defined directly above.

If there are two such bulky ligands (i.e. bis Cp) the catalysts are metallocene-type catalysts. The Cp ligand may be bridged to another Cp ligand by a silyl bridge or a short chain (C₁₋₄) alkyl radical. The Cp-type ligand may be bridged to an amido radical which may be further

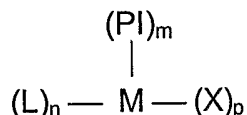
substituted by up to two additional substituents. Such bridged complexes are sometimes referred to as constrained geometry catalysts.

Broadly, the transition metal complex (or catalyst) suitable for use in the present invention has the formula:



wherein M is a transition metal preferably selected from Ti, Hf and Zr (as described below); L is a monanionic ligand selected from the group consisting of a cyclopentadienyl-type ligand, a bulky heteroatom ligand (as described below) and a phosphinimine ligand (as described below); X is an activatable ligand which is most preferably a simple monanionic ligand such as alkyl or a halide (as described below); n may be from 1 to 3, preferably 2 or 3; and p may be from 1 to 3, preferably 1 or 2, provided that the sum of n+p equals the valence state of M, and further provided that two L ligands may be bridged by a silyl radical or a C₁₋₄ alkyl radical.

If one or more of the L ligands is a phosphinimine ligand the transition metal complex may be of the formula:



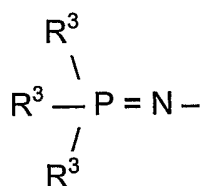
wherein M is a transition metal preferably selected from Ti, Hf and Zr (as described below); PI is a phosphinimine ligand (as described below); L is a monanionic ligand selected from the group consisting of a cyclopentadienyl-type ligand or a bulky heteroatom ligand (as described below); X is an activatable ligand which is most preferably a simple monanionic ligand such as an alkyl or a halide (as described below); m is 1 or 2; n is 0 or 1; and p is an integer fixed by the valence of the metal M (i.e. the sum of m+n+p equals the valence state of M).

In one embodiment the catalysts are group 4 metal complexes in the highest oxidation state. For example, the catalyst may be a bis (phosphinimine) dichloride complex of titanium, zirconium or hafnium. Alternately, the catalyst contains one phosphinimine ligand, one "L" ligand

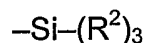
(which is most preferably a cyclopentadienyl-type ligand) and two "X" ligands (which are preferably both chloride).

The preferred metals (M) are from Group 4, (especially titanium, hafnium or zirconium) with titanium being most preferred.

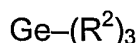
The catalyst may contain one or two phosphinimine ligands, which are covalently bonded to the metal. The phosphinimine ligand is defined by the formula:



wherein each R^3 is independently selected from the group consisting of a hydrogen atom; a halogen atom; C_{1-20} , preferably C_{1-10} hydrocarbyl radicals which are unsubstituted by or further substituted by a halogen atom; a C_{1-8} alkoxy radical; a C_{6-10} aryl or aryloxy radical; an amido radical; a silyl radical of the formula:



wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, and C_{6-10} aryl or aryloxy radicals; and a germanyl radical of the formula:



wherein R^2 is as defined above.

The preferred phosphinimines are those in which each R^3 is a hydrocarbyl radical, preferably a C_{1-6} hydrocarbyl radical. A particularly preferred phosphinimine is tri-(tertiary butyl) phosphinimine (i.e. wherein each R^3 is a tertiary butyl group).

Preferred phosphinimine catalysts are Group 4 organometallic complexes which contain one phosphinimine ligand (as described above) and one ligand L which is either a cyclopentadienyl-type ligand or a heteroligand.

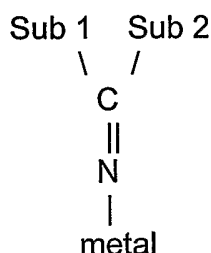
As used herein, the term "heteroligand" refers to a ligand which contains at least one heteroatom selected from the group consisting of

boron, nitrogen, oxygen, phosphorus or sulfur. The heteroligand may be sigma or pi-bonded to the metal. Exemplary heteroligands include ketimide ligands, silicone-containing heteroligands, amido ligands, alkoxy ligands, boron heterocyclic ligands and phosphole ligands, all as described below.

As used herein, the term "ketimide ligand" refers to a ligand which:

- (a) is bonded to the transition metal via a metal-nitrogen atom bond;
- (b) has a single substituent on the nitrogen atom, (where this single substituent is a carbon atom which is doubly bonded to the N atom); and
- (c) has two substituents Sub 1 and Sub 2 (described below) which are bonded to the carbon atom.

Conditions a, b and c are illustrated below:



The substituents "Sub 1" and "Sub 2" may be the same or different. Exemplary substituents include hydrocarbyls having from 1 to 20 carbon atoms, silyl groups, amido groups and phosphido groups. For reasons of cost and convenience it is preferred that these substituents both be hydrocarbyls, especially simple alkyls and most preferably tertiary butyl.

Silicon containing hetroligands are defined by the formula:



wherein the – denotes a bond to the transition metal and μ is sulfur or oxygen.

The substituents on the Si atom, namely R_x , R_y and R_z are required in order to satisfy the bonding orbital of the Si atom. The use of any particular substituent R_x , R_y or R_z is not especially important to the success of this invention. It is preferred that each of R_x , R_y and R_z is a C_{1-2}

hydrocarbyl group (i.e. methyl or ethyl) simply because such materials are readily synthesized from commercially available materials.

The term "amido" is meant to convey its broad, conventional meaning. Thus, these ligands are characterized by (a) a metal-nitrogen bond; and (b) the presence of two substituents (which are typically simple alkyl or silyl groups) on the nitrogen atom.

The terms "alkoxy" and "aryloxy" is also intended to convey its conventional meaning. Thus, these ligands are characterized by (a) a metal oxygen bond; and (b) the presence of a hydrocarbyl group bonded to the oxygen atom. The hydrocarbyl group may be a C₁₋₁₀ straight chained, branched or cyclic alkyl radical or a C₆₋₁₃ aromatic radical which radicals are unsubstituted or further substituted by one or more C₁₋₄ alkyl radicals (e.g. 2, 6 di-tertiary butyl phenoxy).

Boron heterocyclic ligands are characterized by the presence of a boron atom in a closed ring ligand. This definition includes heterocyclic ligands, which also contain a nitrogen atom in the ring. These ligands are well known to those skilled in the art of olefin polymerization and are fully described in the literature (see, for example, U.S. Patents 5,637,659, 5,554,775 and the references cited therein).

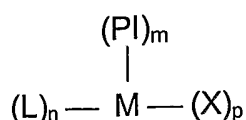
The term "phosphole" is also meant to convey its conventional meaning. "Phospholes" are cyclic dienyli structures having four carbon atoms and one phosphorus atom in the closed ring. The simplest phosphole is C₄PH₄ (which is analogous to cyclopentadiene with one carbon in the ring being replaced by phosphorus). The phosphole ligands may be substituted with, for example, C₁₋₂₀ hydrocarbyl radicals (which may, optionally, contain halogen substituents); phosphido radicals; amido radicals; or silyl or alkoxy radicals. Phosphole ligands are also well known to those skilled in the art of olefin polymerization and are described as such in U.S. Patent 5,434,116 (Sone, to Tosoh).

The term "activatable ligand" or "leaving ligand" refers to a ligand which may be activated by the alumoxane, (also referred to as an "activator"), to facilitate olefin polymerization. Exemplary activatable

ligands are independently selected from the group consisting of a hydrogen atom; a halogen atom, preferably a chlorine or fluorine atom; a C₁₋₁₀ hydrocarbyl radical, preferably a C₁₋₄ alkyl radical; a C₁₋₁₀ alkoxy radical, preferably a C₁₋₄ alkoxy radical; and a C₅₋₁₀ aryl oxide radical; each of which said hydrocarbyl, alkoxy, and aryl oxide radicals may be unsubstituted by or further substituted by one or more substituents selected from the group consisting of a halogen atom, preferably a chlorine or fluorine atom; a C₁₋₈ alkyl radical, preferably a C₁₋₄ alkyl radical; a C₁₋₈ alkoxy radical, preferably a C₁₋₄ alkoxy radical; a C₆₋₁₀ aryl or aryloxy radical; an amido radical which is unsubstituted or substituted by up to two C₁₋₈, preferably C₁₋₄ alkyl radicals; and a phosphido radical which is unsubstituted or substituted by up to two C₁₋₈, preferably C₁₋₄ alkyl radicals.

The number of activatable ligands depends upon the valence of the metal and the valence of the activatable ligand. The preferred catalyst metals are Group 4 metals in their highest oxidation state (i.e. 4⁺) and the preferred activatable ligands are monoanionic (such as a halide – especially chloride, or C₁₋₄ alkyl – especially methyl). One useful group of catalysts contain a phosphinimine ligand, a cyclopentadienyl ligand and two chloride (or methyl) ligands bonded to the Group 4 metal. In some instances, the metal of the catalyst component may not be in the highest oxidation state. For example, a titanium (III) component would contain only one activatable ligand.

As noted above, one group of catalysts is a Group 4 organometallic complex in its highest oxidation state having a phosphinimine ligand, a cyclopentadienyl-type ligand and two activatable ligands. These requirements may be concisely described using the following formula for the preferred catalyst:



wherein M is a metal selected from Ti, Hf and Zr; PI is as defined above, but preferably a phosphinimine wherein R³ is a C₁₋₆ alkyl radical, most

preferably a t-butyl radical; L is a ligand selected from the group consisting of cyclopentadienyl, indenyl and fluorenyl ligands which are unsubstituted or substituted by one or more substituents selected from the group consisting of a halogen atom, preferably chlorine or fluorine; C₁₋₄ alkyl radicals; and benzyl and phenyl radicals which are unsubstituted or substituted by one or more halogen atoms, preferably fluorine; X is selected from the group consisting of a chlorine atom and C₁₋₄ alkyl radicals; m is 1; n is 1; and p is 2.

In one embodiment of the present invention the transition metal complex may have the formula $[(Cp)_qM[N=P(R^3)]_fX_g]$ wherein M is the transition metal; Cp is a C₅₋₁₃ ligand containing a 5-membered carbon ring having delocalized bonding within the ring and bound to the metal atom through covalent η^5 bonds and said ligand being unsubstituted or up to fully substituted with one or more substituents selected from the group consisting of a halogen atom, preferably chlorine or fluorine; C₁₋₄ alkyl radicals; and benzyl and phenyl radicals which are unsubstituted or substituted by one or more halogen atoms, preferably fluorine; R³ is a substituent selected from the group consisting of C₁₋₁₀ straight chained or branched alkyl radicals, C₆₋₁₀ aryl and aryloxy radicals which are unsubstituted or may be substituted by up to three C₁₋₄ alkyl radicals, and silyl radicals of the formula $-Si-(R)_3$ wherein R is C₁₋₄ alkyl radical or a phenyl radical; L is selected from the group consisting of a leaving ligand; q is 1 or 2; f is 1 or 2; and the valence of the transition metal $-(q+f) = g$.

Typically the single site catalysts are activated using alumoxanes. Alumoxanes have the formula $(R^4)_2AlO(R^4AlO)_mAl(R^4)_2$ wherein each R⁴ is independently selected from the group consisting of C₁₋₂₀ hydrocarbyl radicals, m is from 3 to 50. Preferably m is from 5 to 30. Most preferably R⁴ is selected from the group consisting of C₁₋₆, most preferably C₁₋₄ straight chained or branched alkyl radicals. Suitable alkyl radicals include a methyl radical, an ethyl radical, an isopropyl radical and an isobutyl radical. In some commercially available alumoxanes R⁴ is a methyl radical.

The catalyst useful in accordance with the present invention may have a molar ratio of aluminum from the alumoxane to transition metal from 5 to 300: 1, preferably from 25 to 200:1, most preferably from 50 to 120:1. Typically the alumoxane loading on the support will be from 1 to 40 weight % based on the (weight of the) support, preferably from 2 to 30 weight % based on the (weight of the) support, most preferably from 5 to 20 weight % based on the (weight of the) support. The corresponding loading of transition metal from the single site catalyst will be within the above specified ratio of Al:transition metal. Generally the loading of transition metal on the support will be from 0.01 to 5 weight % based on the (weight of the) support, preferably from 0.05 to 2 weight % of transition metal based on the (weight of the) support, most preferably from 0.1 to 1 weight % of transition metal based on the (weight of the) support.

The catalysts are supported. The supports useful in accordance with the present invention typically comprise a substrate of aluminum or silica having a pendant reactive moiety. The reactive moiety may be a siloxy radical or more typically is a hydroxyl radical. The preferred support is silica or alumina. The support should have a particle size from about 10 to 250 microns, preferably from about 30 to 150 microns. The support should have a large surface area typically greater than about 3 m²/g, preferably greater than about 50 m²/g, most preferably from 100 m²/g to 1,000 m²/g. The support will be porous and will have a pore volume from about 0.3 to 5.0 ml/g, typically from 0.5 to 3.0 ml/g. Supports, which are specifically designed to be an agglomeration of subparticles are also useful.

It is important that the support be dried prior to the initial reaction with the catalyst or a catalyst component such as an aluminum compound. Generally the support may be heated at a temperature of at least 200°C for up to 24 hours, typically at a temperature from 500°C to 800°C for times from about 2 to 20 hours. The resulting support will be free of adsorbed water and should have a surface hydroxyl content from about 0.1 to 5 mmol/g of support, preferably from 0.5 to 3 mmol/g.

The present invention will be illustrated by the following non-limiting examples in which unless otherwise indicated parts is parts by weight (e.g. g) and % is weight %.

EXAMPLES

Example 1

A technical scale reactor similar to that disclosed in EP 0 659,773, was used to polymerize polyethylene (hexene:ethylene molar ratio of about 0.0109) using a supported catalyst which was a dichloro CpC₆F₅ tri-*t*-butyl phosphinimido titanium complex supported on silica activated with MAO at a 1:120 molar ratio of Ti:Al. The reactor was operated in a conventional mode.

During the polymerization an anti static of the present invention commercially available under the Trademark STADIS 425 was feed to the reactor in an amount varying from 0 to 100 parts per million (ppm) based on the bed weight.

The anti static agent of the present invention exhibited minimum effects on the polymerization. After the experiment the reactor was clear of polymer residue normally attributed to static.

Example 2

To more clearly demonstrate the antistatic properties of the compositions of the present invention a further experiment was conducted. Several grams of polymer prepared with the same catalyst as used in experiment 1 were placed in two plastic test tubes. A wooden applicator was dipped into Stadis 425 and briefly stirred in one of the samples. The test tubes were then sealed and shaken for about 5 minutes after which they were examined for static. The polymer in the test tube treated with the STADIS 425 had lower levels of static demonstrated by significantly low levels of attraction of polymer to the hand of the experimenter when the test tube was touched.

INDUSTRIAL APPLICABILITY

The present invention enhances productivity in gas phase polymerizations.

CLAIMS

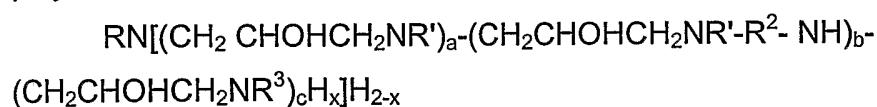
1. In a process for the fluidized bed gas phase polymerization of one or more C₂₋₈ alpha in the presence of a single site catalyst and an activator the improvement comprising including in the gas phase from 0.5 to 20,000 ppm based on the weight of the olefin in the reactor of an anti static agent comprising:

(i) from 3 to 48 parts by weight of one or more polysulfones comprising:

- (a) 50 mole % of sulphur dioxide;
- (b) 40 to 50 mole % of a C₆₋₂₀ an alpha olefin; and
- (c) from 0 to 10 mole % of a compound of the formula

ACH=CHB where A is selected from the group consisting of a carboxyl radical and a C₁₋₁₅ carboxy alkyl radical; and B is a hydrogen atom or a carboxyl radical provided if A and B are carboxyl radicals A and B may form an anhydried;

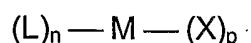
(ii) from 3 to 48 parts by weight of one or more polymeric polyamides of the formula:



wherein R¹ is an aliphatic hydrocarbyl group of 8 to 24 carbon atoms, R² is an alkylene group of 2 to 6 carbon atoms, R³ is the group-R²-HNR¹, R is R¹ or an N-aliphatic hydrocarbyl alkylene group having the formula R¹NHR²; a, b and c are integers from 0 to 20 and x is 1 or 2; with the proviso that when R is R¹ then a is greater than 2 and b = c = 0, and when R is R¹NHR²-then a is 0 and the sum of b+c is an integer from 2 to 20;

(iii) from 3 to 48 parts by weight of C₁₀₋₂₀ alkyl or arylalkyl sulphonic acid and optionally from 0 to 150 parts by weight of a solvent or diluent.

2. The process according to claim 2, wherein the single site catalyst has the formula:



wherein M is a transition metal L is a monanionic ligand selected from the group consisting of a cyclopentadienyl-type ligand, a bulky heteroatom ligand and a phosphinimine ligand; X is an activatable ligand; n may be from 1 to 3, and p may be from 1 to 3, provided that the sum of n+p equals the valence state of M, and further provided that two L ligands may be bridged by a silyl radical or a C₁₋₄ alkyl radical.

3. The process according to claim 2, wherein said one or more alpha olefins are selected from the group consisting of ethylene, butene and hexene.
4. The process according to claim 3, wherein in the polysulphone compounds having the formula ACH=CHB are units derived from maleic acid, acrylic acid, 5-hexenoic acid.
5. The process according to claim 3, wherein the sulphonic acid is selected from the group consisting of dodecylbenzene sulphonic acid and dinonylnaphthyl sulphonic acid.
6. The process according to claim 5, wherein the polysulphon is a copolymer of 1-decene and sulphur dioxide having an inherent viscosity (measured as a 0.5 weight percent solution in toluene at 30°C) ranging from about 0.04 dl/g to 1.6 dl/g.
7. The process according to claim 5, wherein the polyamide is the reaction product of N-tallow-1, 3-diaminopropane with epichlorohydrin. polymeric in a 1:1.5 mole ratio.
8. The process according to claim 7, wherein the catalyst is a transition metal complex containing at least one C₅₋₁₃ ligand selected from the group consisting of a cyclopentadienyl radical, an indenyl radical and a fluorenyl radical which are unsubstituted or further substituted by up to the number of available carbon atoms with substituents selected from the group consisting of a halogen atom, and C₁₋₄ alkyl radicals, and mixtures thereof.
9. The process according to claim 8, wherein the catalyst has phosphinimine ligand.

10. The process according to claim 8, wherein the catalyst has a ketimide ligand.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 03/01227

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F10/00 C08F2/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

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Y	WO 02 46250 A (UNIVATION TECH LLC) 13 June 2002 (2002-06-13) page 32, line 27 -page 33, line 5 page 33, line 23 - line 26; claims 1,11,12	1-9
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

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

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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.

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Date of the actual completion of the international search

12 November 2003

Date of mailing of the international search report

26/11/2003

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INTERNATIONAL SEARCH REPORT

Internatic lication No
PCT/CA 03/01227

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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