

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
10 June 2010 (10.06.2010)

PCT

(10) International Publication Number
WO 2010/063090 A1

(51) International Patent Classification:

C08F 2/01 (2006.01) *C08F 4/6592* (2006.01)
C08F 10/00 (2006.01) *C08F 4/69* (2006.01)
C08F 2/34 (2006.01) *C09K 3/16* (2006.01)
C08F 4/24 (2006.01)

(21) International Application Number:

PCT/CA2009/001584

(22) International Filing Date:

3 November 2009 (03.11.2009)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2,645,516 1 December 2008 (01.12.2008) CA

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: CLAY AS AN ANTI-STATIC AGENT IN A GAS PHASE POLYMERIZATION REACTOR

(57) Abstract: The addition of small amounts of surface charged clay to a gas phase polyolefin polymerization reactor in the presence of a chromium based catalyst or a single site catalyst including metallocene and constrained geometry catalysts can be used to control static electricity in the polymer bed.



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CLAY AS AN ANTI-STATIC AGENT IN A GAS PHASE POLYMERIZATION REACTOR**TECHNICAL FIELD**

5 The present invention relates to a process to control static electricity in the gas phase polymerization of alpha olefins such as co (including terpolymers) and homopolymers of ethylene and co (including terpolymers) and homopolymers of propylene.

BACKGROUND ART

10 The build up of static electricity (static) in a gas phase fluidized or stirred bed reactor during the polymerization of alpha olefins leads to a number of different problems such as formation of sheets (sheeting), polymer build up in parts of the reactor and product quality issues. These problems tend to require that the reactor be shut down and cleaned on a periodic basis.

15 United States patent 4,792,592 issued Dec. 20, 1988 to Fulks, et al. assigned to Union Carbide Corporation teaches applying and maintaining a static electric charge to a fluid bed gas phase polymerization reactor at locations where sheet build up is expected to occur at a level below that at which sheeting will occur.

20 United States patent 4,855,370 issued Aug. 8, 1989 to Chirillo, et al. assigned to Union Carbide teaches reducing sheeting during a fluid bed gas phase polymerization using a titanium or vanadium catalyst by adding small amounts of water to the reactor (sometimes called water add back) to maintain the static levels sufficiently low to prevent or reduce sheeting.

25 United States patent 4,532,311 issued July 30, 1985 to Fulks, et al. teaches treating the internal surface of a reactor with a solution of a chromocene compound prior to fluid bed polymerization of alpha olefins in the presence of a titanium containing catalyst. The patent teaches the treatment to reduce static and consequently sheeting.

30 U.S. patent 5,034,481 issued July 23, 1991 to Funk et al. assigned to BASF teaches adding chromium salts of salicylic acid to a fluid bed gas phase reactor as an antistat agent in the presence of a titanium containing catalyst.

 United States Patent 5,731,392 issued March 24, 1998 to Ali, et al. assigned to Mobil Oil Company teaches adding TEOS (tetraethylorthosilicate) as an antistatic agent (or antistat) to a fluid bed gas phase reactor in an amount from 16 to 40 ppm based on the ethylene feed stream. The tetraethylorthosilicate may be used in conjunction with

water add back to control negative and positive static respectively. The patent does not teach adding clay as an antistatic agent.

U.S. patent 6,201,076 issued March 13, 2001 to Etherton, et al. assigned to Equistar teaches adding from about 10 to 75 weight % based on the weight of the support of a fatty amine to reduce fouling and sheeting in the polymerization of olefins in the presence of a single site catalyst.

There are a number of patents, which teach the use of a combination of polysulfones, polyamides and sulphonic acid as antistat in gas phase and slurry polymerization of alpha olefins. These include United States Patents 4,182,810 and 5,026,795 issued Jan. 8, 1980 to Wilcox and June 25, 1991 to Hogan both assigned to Phillips Petroleum Company.

U.S. patent 6,689,846 issued Feb. 10, 2004, to Leskinen et al. assigned to Borealis teaches adding an antistat and catalyst deactivator to the second reactor of a tandem reactor polymerization process. The antistat agent is a STADIS[®] type antistat (a mixture of lower alkanol (C₁₋₆); aromatic (C₆₋₁₂) sulphonic acid(s); polymeric polyamines; and polysulfone copolymers).

WO 0142320 published June 14, 2001 in the name of The Dow Chemical Company teaches the use of clay supports for single site catalysts. However, the patent does not teach or suggest that the use of one or more clays as a support or being added to the reactor reduces static in the reactor.

United States Patent 5,225,458 issued July 6, 1993 in the names of Bailly et al. assigned to BP Chemicals Limited teaches the addition of 0.005 to 0.2 weight % of a pulverulent inorganic material to a gas phase polymerization. The pulverulent material may be mineral oxides such as silica, alumina or magnesium oxide. However, the patent does not expressly teach that clays can be use as antistatic agents. The polymerization catalyst seems to be limited to Ziegler Natta catalyst and specifically prepolymerized catalyst.

None of the above art suggests clays per se could be useful as an antistatic agent in gas phase, typically fluidized bed but also stirred bed polymerization typically of alpha olefin homo or copolymers.

The present invention seeks to provide a simple, inexpensive method to help control static in a gas phase polymerization process for alpha olefins.

DISCLOSURE INVENTION

The present invention seeks to provide a process to control static in a gas phase olefin polymerization reactor comprising feeding to the reactor clay or modified clay or mixtures of the two where the rate of addition of the clay component, to the reactor is in an amount from 0.001 to 1.0 weight % of the polymer production rate. (e.g. typically pounds or tonnes per hour). Modified clays are clays in which the clay has undergone some type of chemical or physical transformation. This can include but is not limited to mixing with additives, adjuvants, inorganic compounds and the like or partaken in some form of a chemical reaction such as being modified with an exchangeable cation, reacted with a surface modifying reagent and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a plot of the electrostatic charge in a technical scale stirred tank reactor of granular resin produced with a chromium catalyst before and after the addition of clay.

Figure 2 is a plot of the electrostatic charge in a technical scale stirred tank reactor of granular resin produced with single site catalyst before and after the addition of clay.

BEST MODE FOR CARRYING OUT THE INVENTION

There are a number of types of catalyst which may be used in gas phase polymerization, either in stirred or fluidized reactor, of alpha olefins such as ethylene or propylene or copolymerization of ethylene or propylene with one or more monomers selected from the group consisting of C₃₋₈ alpha olefins such as 1-butene, 1-pentene, isopentene, 4-methyl-1-pentene, 1-hexene and 1-octene, preferably 1-butene and 1-hexene. Typically, polyethylene has a density from 0.910 to 0.960 g/cc. Typically the polyolefin may comprise from 100 to 80, preferably from 100 to 85 most preferably from 100 to 90 weight % of ethylene and from 0 to 20, preferably less than 15, most preferably less than 10 weight % of one or more comonomers selected from the group consisting of C₃₋₈ alpha olefins. Generally, the polymers having a higher amount of comonomer, typically from about 85 to 95 weight % of ethylene and from about 15 to 5 weight % of one or more C₃₋₈ alpha olefins will have a density of less than 0.930 g/cc and polymers comprising from 100 to 95 weight % of ethylene and from 0 to 5 weight % of one or more C₃₋₈, preferably C₄₋₆, alpha olefins prepared with a chrome catalyst (which is not a single site type catalyst) will have a density of greater than 0.930 g/cc typically greater than 0.940, preferably greater than 0.945 g/cc. Similar compositions

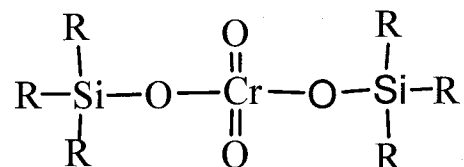
prepared in the presence of a single site catalyst will have a lower density (e.g. for 6 weight % of hexene in the copolymer may have a density in the range of about 0.920 g/cc).

The gas phase polymerization process may be a stirred bed or fluidized bed process. Such processes are well known in the art. Fluidized bed polymerization processes are discussed in a number of patents including the above noted U.S. patents to Union Carbide. Generally, in the gas phase polymerization process the temperature of the reactor for single site and/or chromium catalyst will be from 75 to 120°C, typically from 80 to 115°C, preferably from 85 to 110°C. The reactor pressure (e.g. total pressure in the reactor) will be from 100 to 500 psi (689 to 3,445 kPa), typically from 150 to 300 psi (1,033 to 2,067 kPa), preferably from 200 to 300 psi (1,378 to 2,067 kPa). The reaction may be in dry mode, condensed mode (e.g. U.S. patents to Jenkins III et al., such as U.S. patent 4,543,399) or super condensed mode (U.S. patent to Griffin or DeChellis such as U.S. patent 5,352,749). The reaction may take place in the presence of hydrogen and a non-polymerizable gas, which may be inert or may be an alkane, or a mixture thereof.

The catalyst for the polymerization may comprise a Phillips type chromium oxide catalyst, a hydrocarbylsilyl chromium catalyst (e.g. silyl chromate type catalysts), a Ziegler Natta supported catalyst such as disclosed in United States Patent 7,211,535 issued May 1, 2007 to Kelly et al., assigned to NOVA Chemicals Corporation and Ineos Europe Limited, or a single site, a metallocene, a constrained geometry, or a bulky ligand single site catalyst and conventional activators/co-catalysts and mixtures thereof. Reviews by Mülhaupt, R. *Macromol. Chem. Phys.* 2004, 289 – 327, **2003** and Boussie, T.R. et al. in *J. Am Chem. Soc.*, 125, 4306 - 4317, **2003** and references within give a good understanding by what is meant by single site catalysts.

The chromium-based catalysts may comprise chromium oxide on a support as described below. The oxide catalysts are typically prepared by contacting the support as described below with a solution comprising an inorganic (e.g. $\text{Cr}(\text{NO}_3)_3$ or an organometallic (e.g. chromium acetate, silyl chromate – e.g. a bis hydrocarbyl silyl chromate) chromium compound.

The bis hydrocarbyl silyl chromate compound may be of the formula



wherein each R is selected from the group consisting of C₁₋₁₄ alkyl or aromatic radicals preferably C₁₋₆ alkyl or aromatic compounds. Some suitable silyl chromates include

bis(trimethylsilyl)chromate; bis(triethylsilyl)chromate; bis(tributylsilyl)chromate; bis(tripentylsilyl)chromate, bis(triphenylsilyl)chromate, bis(tritolylsilyl)chromate, bis(triethylhexylsilyl)chromate, and bis(tridecylsilyl)chromate, bis(tritetradecylsilyl)chromate, bis(tribenzylsilyl)chromate, preferably bis(triphenylsilyl)chromate

The inorganic chromium catalysts and chromium acetate type catalysts are activated by being oxidized in air at elevated temperatures (e.g. 400 to 800°C). The silyl chromate compounds may also be activated through a reduction with an aluminum compound preferably to provide a molar ratio of Al:Cr from 0.5:1 to 30:1, preferably from 1:1 to 10:1, most preferably from 1:1 to 6:1. The aluminum compound may be of the formula R¹_bAl(OR¹)_a wherein a is from 0 to 2, typically 0 or 1, b is an integer from 1 to 3, a+b is equal to 3, R¹ is independently selected from a C₁₋₁₀ alkyl radical. Some activators include tri alkyl aluminums such as triethylaluminum or triisobutylaluminum and dialkyl aluminum alkoxides such as diethyl aluminum ethoxide. The aluminum activator may be added to the support prior to the chromium compound.

Single site, metallocene, constrained geometry and bulky ligand single site catalyst may have the formula :



wherein M is selected from the group consisting of Ti, Zr, and Hf; L is a monoanionic ligand independently selected from the group consisting of cyclopentadienyl-type

ligands and bulky heteroatom ligands containing not less than five atoms in total (typically of which at least 20%, preferably at least 25% numerically are carbon atoms)

and further containing at least one heteroatom selected from the group consisting of boron, nitrogen, oxygen, phosphorus, sulfur and silicon, said bulky heteroatom ligand being sigma or pi-bonded to M, Y is independently selected for the group consisting of

activatable ligands; 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.

Non-limiting examples of bridging groups include bridging groups containing at least one Group 13 to 16 atom, often referred to as a divalent moiety such as but not limited to at least one of a carbon, oxygen, nitrogen, silicon, boron, germanium and tin atom or a combination thereof. Preferably the bridging group contains a carbon, silicon or germanium atom, most preferably at least one silicon atom or at least one carbon atom. The bridging group may also contain substituent radicals as defined above including halogens.

Some bridging groups include but are not limited to a di C_{1-6} alkyl radical (e.g. an alkylene radical such as an ethylene bridge), a di C_{6-10} aryl radical (e.g. a benzyl radical having two bonding positions available), silicon or germanium radicals substituted by one or more radicals selected from the group consisting of C_{1-6} alkyl, C_{6-10} aryl, phosphine or amine radical which are unsubstituted or up to fully substituted by one or more C_{1-6} alkyl or C_{6-10} aryl radicals, or a hydrocarbyl radical such as a C_{1-6} alkyl radical or a C_{6-10} arylene (e.g. divalent aryl radicals); divalent C_{1-6} alkoxide radicals and the like.

Exemplary of the silyl species of bridging groups are dimethylsilyl, methylphenylsilyl, diethylsilyl, ethylphenylsilyl or diphenylsilyl radicals. Most preferred of the bridged species are dimethylsilyl, diethylsilyl and methylphenylsilyl bridging radicals.

Exemplary hydrocarbyl radicals for bridging groups include methylene, ethylene, propylene, butylene, phenylene and the like, with methylene being preferred.

Exemplary bridging amides include dimethylamide, diethylamide, methylethylamide, di-*t*-butylamide, diisopropylamide and the like.

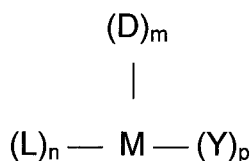
The term "cyclopentadienyl" refers to a 5-member carbon ring having delocalized bonding within the ring and typically being bound to the active catalyst site, generally a group 4 metal (M) through η^5 - bonds. The cyclopentadienyl ligand may be unsubstituted or up to fully substituted with one or more substituents selected from the group consisting of C_{1-10} hydrocarbyl radicals in which hydrocarbyl substituents are unsubstituted or further substituted by one or more substituents selected from the group consisting of a halogen atom; a C_{1-4} alkyl radical; a C_{1-8} alkoxy radical; a C_{6-10} aryl or aryloxy radical; an amido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C_1 .

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 C_{1-8} alkyl or alkoxy radical, and C_{6-10} aryl or aryloxy radicals; and germanyl radicals of the formula $\text{Ge}-(\text{R})_3$ wherein R is as defined above.

5 Typically the cyclopentadienyl-type ligand is selected from the group consisting of a cyclopentadienyl radical, an indenyl radical and a fluorenyl radical where the radicals are unsubstituted or up to fully substituted by one or more substituents selected from the group consisting of a fluorine atom, a chlorine atom; C_{1-4} alkyl radicals; and a phenyl or benzyl radical which is unsubstituted or substituted by one or
10 more fluorine atoms.

In the above formula for the single site catalysts if none of the L ligands is a bulky heteroatom ligand then the catalyst could be a bis Cp catalyst (a traditional metallocene) or a bridged constrained geometry type catalyst or tris Cp catalyst.

15 If the catalyst contains one or more bulky heteroatom ligands the catalyst would have the formula:

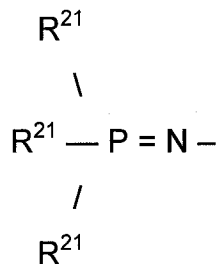


20 wherein M is a transition metal selected from the group consisting of Ti, Hf and Zr; D is independently a bulky heteroatom ligand (as described below); L is a monoanionic ligand selected from the group consisting of cyclopentadienyl-type ligands (as described above); D and L may optionally be joined by a bridging group as described above; Y is independently selected from the group consisting of activatable ligands; m is 1 or 2; n is 0, 1 or 2 and p is an integer and the sum of $m+n+p$ equals the valence
25 state of M, provided that when m is 2, D may be the same or different bulky heteroatom ligands and may optionally be bridged.

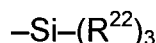
For example, the catalyst may be a bis (phosphinimine), or a mixed phosphinimine ketimide dichloride complex of titanium, zirconium or hafnium. Alternately, the catalyst could contain one phosphinimine ligand or one ketimide ligand,
30 one "L" ligand (which is most preferably a cyclopentadienyl-type ligand) and two "Y" ligands (which are preferably both chloride).

The preferred metals (M) are from Group 4 (especially titanium, hafnium or zirconium) with titanium being most preferred. In one embodiment the catalysts are group 4 metal complexes in the highest oxidation state.

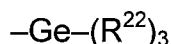
The bulky heteroatom ligands (D) include but are not limited to phosphinimine ligands (PI) and ketimide (ketimine) ligands. The phosphinimine ligand (PI) is defined by the formula:



wherein each R^{21} is independently selected from the group consisting of a hydrogen atom; a halogen atom; C_{1-20} , preferably C_{1-10} straight chain or branched 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^{22} 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^{22} is as defined above.

The preferred phosphinimines are those in which each R^{21} is a hydrocarbyl radical, preferably a C_{1-6} straight chained or branched (e.g. secondary or tertiary) hydrocarbyl radical.

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

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:

Sub 1 Sub 2

\ /

C

||

N

|

metal

The substituents "Sub 1" and "Sub 2" may be the same or different and may be further bonded together through a bridging group to form a ring. Exemplary substituents include hydrocarbyls having from 1 to 20, preferably from 3 to 6, carbon atoms, silyl groups (as described below), amido groups (as described below) and phosphido groups (as described below). For reasons of cost and convenience it is preferred that these substituents both be hydrocarbyls, especially simple alkyls and most preferably tertiary butyl.

Suitable ketimide catalysts of the present invention are Group 4 organometallic complexes that contain one ketimide ligand (as described above) and one ligand L that is either a cyclopentadienyl-type ligand or a heteroatom ligand.

The term bulky heteroatom ligand (D) is not limited to phosphinimine or ketimide ligands and includes ligands that contains at least one heteroatom selected from the group consisting of boron, nitrogen, oxygen, phosphorus, sulfur and silicon. The heteroatom ligand may be sigma or pi-bonded to the metal. Exemplary heteroatom ligands include silicon-containing heteroatom ligands, amido ligands, alkoxy ligands, boron heterocyclic ligands and phosphole ligands, as all described below.

Silicon containing heteroatom ligands are defined by the formula:



wherein the – denotes a bond to the transition metal and Y 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 that 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. Patent's 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 dienyl structures having four carbon atoms and one phosphorus atom in the closed ring. The simplest phosphole is C₄H₄P (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 single site type catalysts may be activated with an activator selected from the group consisting of:

(i) a complex aluminum compound of the formula $R^{12}_2AlO(R^{12}AlO)_mAlR^{12}_2$ wherein each R¹² is independently selected from the group consisting of C₁₋₂₀ hydrocarbyl radicals and m is from 3 to 50, and optionally a hindered phenol to provide a molar ratio of Al:hindered phenol from 2:1 to 5:1 if the hindered phenol is present;

(ii) ionic activators selected from the group consisting of:

(A) compounds of the formula $[R^{13}]^+ [B(R^{14})_4]^-$ wherein B is a boron atom, R¹³ is a cyclic C₅₋₇ aromatic cation or a triphenyl methyl cation and each R¹⁴ is independently selected from the group consisting of phenyl radicals which are unsubstituted or substituted with 3 to 5 substituents selected from the group consisting of a fluorine atom, a C₁₋₄ alkyl or alkoxy radical which is unsubstituted or substituted by a fluorine atom; and a silyl radical of the formula $-Si-(R^{15})_3$;

wherein each R^{15} is independently selected from the group consisting of a hydrogen atom and a C_{1-4} alkyl radical; and

(B) compounds of the formula $[(R^{18})_t ZH]^+[B(R^{14})_4]^-$ wherein B is a boron atom, H is a hydrogen atom, Z is a nitrogen atom or phosphorus atom, t is 2 or 3 and R^{18} is independently selected from the group consisting of C_{1-18} alkyl radicals, a phenyl radical which is unsubstituted or substituted by up to three C_{1-4} alkyl radicals, or one R^{18} taken together with the nitrogen atom may form an anilinium radical and R^{14} is as defined above; and

(C) compounds of the formula $B(R^{14})_3$ wherein R^{14} is as defined above;

and

(iii) mixtures of (i) and (ii).

Preferably the activator is a complex aluminum compound of the formula $R^{12}_2AlO(R^{12}AlO)_mAlR^{12}_2$ wherein each R^{12} is independently selected from the group consisting of C_{1-4} hydrocarbonyl radicals and m is from 3 to 50, and optionally a hindered phenol to provide a molar ratio of Al:hindered phenol from 2:1 to 5:1 if the hindered phenol is present. In the aluminum compound, preferably R^{12} is methyl radical and m is from 10 to 40. The preferred molar ratio of Al:hindered phenol, if it is present, is from 3.25:1 to 4.50:1. Preferably the phenol is substituted in the 2, 4 and 6 position by a C_{2-6} alkyl radical. Desirably the hindered phenol is 2,6-di-tert-butyl-4-ethyl-phenol.

The aluminum compounds (alumoxanes and optionally hindered phenol) are typically used as activators in substantial molar excess compared to the amount of the transition metal in the catalyst. Aluminum:transition metal molar ratios of from 10:1 to 10,000:1 are preferred, most preferably 10:1 to 500:1 especially from 10:1 to 120:1.

Ionic activators are well known to those skilled in the art. The "ionic activator" may abstract one activatable ligand so as to ionize the catalyst center into a cation, but not to covalently bond with the catalyst and to provide sufficient distance between the catalyst and the ionizing activator to permit a polymerizable olefin to enter the resulting active site.

Examples of ionic activators include:

triethylammonium tetra(phenyl)boron,
tripropylammonium tetra(phenyl)boron,
tri(n-butyl)ammonium tetra(phenyl)boron,
trimethylammonium tetra(p-tolyl)boron,
trimethylammonium tetra(o-tolyl)boron,

- tributylammonium tetra(pentafluorophenyl)boron,
 tripropylammonium tetra(o,p-dimethylphenyl)boron,
 tributylammonium tetra(m,m-dimethylphenyl)boron,
 tributylammonium tetra(p-trifluoromethylphenyl)boron,
 5 tributylammonium tetra(pentafluorophenyl)boron,
 tri(n-butyl)ammonium tetra(o-tolyl)boron,
 N,N-dimethylanilinium tetra(phenyl)boron,
 N,N-diethylanilinium tetra(phenyl)boron,
 N,N-diethylanilinium tetra(phenyl)n-butylboron,
 10 di-(isopropyl)ammonium tetra(pentafluorophenyl)boron,
 dicyclohexylammonium tetra(phenyl)boron,
 triphenylphosphonium tetra(phenyl)boron,
 tri(methylphenyl)phosphonium tetra(phenyl)boron,
 tri(dimethylphenyl)phosphonium tetra(phenyl)boron,
 15 tropillium tetrakis(pentafluorophenyl) borate,
 triphenylmethylium tetrakis(pentafluorophenyl) borate,
 tropillium phenyltris(pentafluorophenyl) borate,
 triphenylmethylium phenyltris(pentafluorophenyl) borate,
 benzene (diazonium) phenyltris(pentafluorophenyl) borate,
 20 tropillium tetrakis (2,3,5,6-tetrafluorophenyl) borate,
 triphenylmethylium tetrakis (2,3,5,6-tetrafluorophenyl) borate,
 tropillium tetrakis (3,4,5-trifluorophenyl) borate,
 benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) borate,
 tropillium tetrakis (1,2,2-trifluoroethenyl) borate,
 25 triphenylmethylium tetrakis (1,2,2-trifluoroethenyl) borate,
 tropillium tetrakis (2,3,4,5-tetrafluorophenyl) borate, and
 triphenylmethylium tetrakis (2,3,4,5-tetrafluorophenyl) borate.

Readily commercially available ionic activators include:

- N,N-dimethylaniliniumtetrakis(pentafluorophenyl) borate;
 30 triphenylmethylium tetrakis(pentafluorophenyl) borate (tritylborate); and
 tris(pentafluorophenyl) borane.

Ionic activators may also have an anion containing at least one group comprising an active hydrogen or at least one of any substituent able to react with the support. As a result of these reactive substituents, the ionic portion of these ionic activators may

become bonded to the support under suitable conditions. One non-limiting example includes ionic activators with tris (pentafluorophenyl) (4-hydroxyphenyl) borate as the anion. These tethered ionic activators are more fully described in U.S. Patents 5,834,393; 5,783,512; and 6,087,293.

5 The ionic activators may be used in amounts to provide a molar ratio of transition metal to boron from 1:1 to 1:6, preferably from 1:1 to 1:2.

 The catalysts of the present invention are typically used on an inorganic oxide support. Typically the support comprises an inorganic substrate usually of alumina or silica having a pendant reactive moiety. The reactive moiety may be a siloxyl radical or
10 more typically is a hydroxyl radical. The preferred support is silica. The support should have an average particle size from about 10 to 150 microns, preferably from about 20 to 100 microns. The support should have a large surface area typically greater than about 100 m²/g, preferably greater than about 200 m²/g, most preferably from 250 m²/g to 1,000 m²/g. The support will be porous and will have a pore volume from about 0.3
15 to 5.0 ml/g, typically from 0.5 to 3.0 ml/g.

 It is also believed titanium silicates such as those disclosed in U.S. Patent 4,853,202 issued Aug. 1, 1989 to Kuznicki assigned to Engelhard Corporation would be useful as supports in accordance with the present invention.

 It is important that the support be dried prior to contact with the catalyst or
20 catalyst components. 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 about 2 to 20, preferably 4 to 10 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.

25 Silicas suitable for use in the present invention have high surface area and are amorphous. For example, commercially available silicas are marketed under the trademark of Sylopol[®] 958 and 955 by the Davison Catalysts a Division of W. R. Grace and Company and ES-70W by Ineos Silica.

 The amount of the hydroxyl groups in silica may be determined according to the
30 method disclosed by J. B. Peri and A. L. Hensley, Jr., in *J. Phys. Chem.*, 72 (8), 2926, 1968, the entire contents of which are incorporated herein by reference.

 While heating is the most preferred means of removing OH groups inherently present in many carriers, such as silica, the OH groups may also be removed by other removal means, such as chemical means. For example, a desired proportion of OH

groups may be reacted with a suitable chemical agent, such as a hydroxyl reactive aluminum compound (e.g. triethylaluminum) or a silane compound. This method of treatment has been disclosed in the literature and two relevant examples are: U.S. Patent 4,719,193 to Levine in 1988 and by Noshay A. and Karol F.J. in *Transition Metal*
 5 *Catalyzed Polymerizations*, Ed. R. Quirk, 396, **1989**. For example the support may be treated with an aluminum compound of the formula $R^1_bAl(OR^1)_aX_{3-(a+b)}$ wherein a is 0 to 2, preferably 0 or 1, b is an integer from 1 to 3, a+b is from 1 to 3, R^1 is a independently selected from C_{1-10} alkyl radicals and X is a chlorine atom.

Clay has an amorphous or crystalline layered mineral structure, having the
 10 strongest chemical bonds in two dimensions (e.g. forming planes or sheets of material which are stacked on top of each other to form a three dimensional structure). Sheets or layers may typically be of two types of structure. The plane or sheet may have a tetrahedral structure in which a central silicon atom coordinates oxygen atoms or an octahedral structure in which a central aluminum, magnesium or iron atom coordinates
 15 oxygen or hydroxide. Adjacent planes are held together by weaker chemical bonds such as Van der Waals forces, electrostatic interactions, and hydrogen bonding. There may also be inter-lamina bridging molecules between layers. Ions are generally located between the layers or planes. In this respect, the clay mineral is substantially different from metal oxides having a three-dimensional structure such as silica, alumina, and
 20 zeolite.

Clay is typically composed of crystalline hydrated silicates of aluminum, magnesium and iron. Most clays have a surface electrical charge typically, negative. In the present invention the clay should have a negative surface charge. Negatively surfaced charged clays typically have cations (+) between the planes. Such cations
 25 can be ion-exchanged by other organic or inorganic cations. Typically the clays useful in the present invention have the ability to exchange cations typically. H^+ , Na^+ , K^+ , Ca^{2+} , Al^{3+} , $Fe^{2+, \text{ or } 3+}$, $Ti^{3+ \text{ or } 4}$ or NR_4^+ and phosphonium (R_4P^+) compounds wherein R is selected from the group consisting of hydrogen, C_{1-12} alkyl and C_{6-12} aryl. The ability to exchange cations between the layers is the cation exchange capacity (CEC) in
 30 milliequivalents per 100 g of clay. Different clays have different CEC's. Some representative CEC's are kaolinite: 3 to 15 meq/100 g, halloysite: 5 to 40 meq/100 g, montmorillonite: 80 to 150 meq/100 g, illite: 10 to 40 meq/100 g, vermiculite: 100 to 150 meq/100 g, chlorite: 10 to 40 meq/100 g, zeolite, attapulgite: 20 to 30 meq/100 g.

Clay useful in accordance with the present invention may be classified by the amount of negative surface charge: (1) biophilite, kaolinite, dickalite, and talc have no negative surface charge (e.g. charge of 0 (zero)), (2) smectite clays have a negative surface charge of from -0.25 to -0.6, (3) vermiculite clays have a negative surface charge of from -0.6 to -0.9, (4) mica clays have a negative surface charge of from about -1, and (5) brittle mica clays have a negative surface charge of about -2. Each of the above groups includes various sub groups of clays. For example, the smectite group includes montmorillonite, bentonite, beidellite, saponite, nontronite, hectorite, teniolite, suconite and related analogues; the mica group includes white mica, palagonite and illite. While these clays are naturally occurring they may also be artificially synthesized with a high purity.

Any of the natural or synthetic clays having a negative surface charge may be used in accordance with the present invention. Preferred clays are of the smectite family, including the most preferred montmorillonite (e.g., sodium montmorillonite). The clays may be used as they are without subjecting them to any further treatment. Alternatively, they may be ball milled, screened, acid treated or the like prior to use. They may have water added and adsorbed or may be dehydrated typically by heating to a moisture content of less than 1 weight %, preferably less than 0.05 weight %. The clays may be used alone or in combination.

Typically the clays have pores having a diameter from about 4×10^{-3} microns to 1×10^{-1} microns. (e.g., 40-1000 angstroms) as measured using a mercury porosimeter and a pore volume of at least 0.1 cc/g, more preferably from 0.1 to 1 cc/g. The clay may have an average particle size from about 0.01 to about 50, preferably from about 0.1 to about 25, and most preferably from about 0.5 to about 15 microns, desirably from 0.5 to 10 microns (micrometers).

The clays should be dried prior to use under conditions that may be comparable to or different from drying the support.

The clay may be used alone or in combination with other conventional additives or adjuvants such as heat and light stabilizers, UV stabilizers, other anti static agents, inorganic agents including catalysts and activators as described above, typically oxides such as alumina, silica (as described above) and magnesium oxide, and organic materials such as polymeric supports including polyethylene, polystyrene, acrylamides and functionalized (e.g. typically acid or ester copolymers) derivatives thereof. The clay is fed to the reactor as a component (stream) separate from the catalyst and support.

The clay may be used in the polymerization reaction in an amount from 0.001 to 1 weight %, preferably from 0.002 to 0.5 weight % most preferably from 0.005 to 0.3 weight % of the polymer production rate.

The clay is independently fed to the reactor using a feeder such as a catalyst feeder, for example the solid catalyst feeder disclosed in U.S. patent 3,779,712 issued Dec. 18, 1973 to Calvert et al. assigned to Union Carbide Corporation. This approach requires two catalyst feeders per reactor; however, it gives the flexibility of being able to change the ratio of clay to catalyst in the reactor giving one more control parameter than the situation when the clay is premixed with the catalyst.

The clay and supported catalyst could be dry blended (homogeneously mixed) and fed using one catalyst feeder. In this approach care needs to be taken that the clay and catalyst support do not segregate. While the particles should be attracted to each other by electrostatic charges, the particle size and flow properties of the different particles may lead to separation or segregation during the storage and feeding process.

The resulting granular polymer (powder) is recovered in the normal manner and is useful for conventional applications for polyolefins of comparable density and molecular weight. Properties such as tear properties, dart impact, Environmental Stress Crack Resistance (ESCR), tensile strength, elongation, gloss, clarity etc. are not compromised.

The present invention will now be illustrated by the following non-limiting examples.

EXAMPLES

Example 1

Two kg of polyethylene resin in granular form (i.e. not pelletized), having an Melt Flow Rate (ASTM D1238 I₂₁ 190° C /21.6 kg) of 5, and a density of 0.955 g/cc, prepared with a chrome-based catalyst were dried in a vacuum oven at 60°C for at least 3 hours to remove any residual moisture. It was then loaded to a gas phase technical scale reactor (TSR) as described in European Patent 0 659 773 equipped with an electrostatic monitoring probe (Correstat 3410, Progression, Inc., Haverhill, MA). The reactor was pressurized with dry nitrogen (to 2000 kPa) and the temperature was raised to 80°C. The granular material was stirred for 60 minutes prior to the injection of 1g of montmorillonite clay (sold under the trademark CLOISITE® Na⁺ from Southern Clay Products Inc.). Both clay and resin had been dried and kept in an oven

for several days. Ninety per cent by volume of the particles of the clay have particle size less than 13 micrometers.

The electrostatic response was monitored throughout the experiment as shown in Figure 1. Figure 1 shows that upon injection of the clay at point A, the polarity of the signal reversed and did not change back to its initial condition. Subsequent addition of more clay (1g) at point B after 45 minutes had little effect on the electrostatic signal.

The experiment shows the addition of a very small amount of clay having a negative surface charge into a stirred bed gas phase reactor can alter electrification patterns in the reactor to control static charge in the polymer bed.

Example 2

Two kg of PE resin (MI=1, density = 0.918 g/cc), prepared with a single-site phosphinimide catalyst (as described in NOVA Chemicals United States Patent 5,965,677) in granular form was dried in a vacuum oven for at least 3 hours. It was then loaded to the TSR equipped with an electrostatic monitoring probe as described above. The reactor was pressurized with dry nitrogen (to 2000 kPa) and the temperature was raised to 80°C. The granular material was stirred for 60 minutes prior to the injection of 0.62g of montmorillonite clay at point A in Figure 2. The clay and resin were predried as in Example 1.

The electrostatic response was monitored throughout the experiment. Figure 2 shows that upon injection of the clay, the polarity of the signal reversed. Furthermore, the electrostatic signal became less agitated as time progressed. Even though addition of more clay (0.98g) after 45 minutes at point B resulted in a more agitated electrostatic response, the signal started to pacify as time progressed.

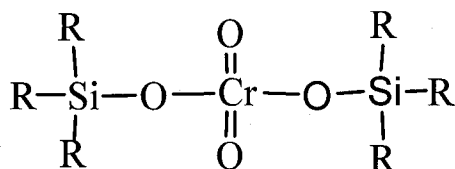
Again the results show that the addition of very small amounts of clay having a negative surface charge into a stirred bed reactor can reduce static significantly.

INDUSTRIAL APPLICABILITY

The present invention is useful in the commercial gas phase polymerization of olefins to reduce static in the reactor and product discharge systems, which reduces fouling in these locations.

CLAIMS

1. A process to control static electricity in a gas phase olefin polymerization reactor comprising feeding to the reactor clay or modified clay or mixtures of the two where the rate of addition of clay to the reactor is in an amount from 0.001 to 1.0 weight % of the polymer production rate.
2. The process according to claim 1 wherein the clay is selected from the group consisting of smectite clays, vermiculite clays and mica which are untreated or treated.
3. The process according to claim 2, wherein the clay is treated with a cation selected from the group consisting of H^+ , Na^+ , K^+ , Ca^{2+} , Al^{3+} , Fe^{2+} , Fe^{3+} , Ti^{3+} or 4^+ , NR_4^+ and phosphonium (R_4P^+) compounds wherein R is selected from the group consisting of hydrogen, C_{1-12} alky, and C_{6-12} aryl.
4. The process according to claim 2, wherein the rate of addition of clay to the reactor is in an amount from 0.002 to 0.5 weight % of the polymer production rate.
5. The process according to claim 4, wherein the reactor contains a polymerization catalyst comprising a chromium compound.
6. The process according to claim 5, wherein the catalyst is chrome oxide.
7. The process according to claim 6, wherein clay is fed to the reactor.
8. The process according to claim 6, wherein modified clay is fed to the reactor.
9. The process according to claim 5, wherein the catalyst comprises a silyl chromate of the formula



wherein each R is selected from the group consisting of C_{1-14} alkyl or aromatic radicals.

10. The process according to claim 9, wherein the silyl chromate is used in conjunction with an aluminum compound of the formula



wherein a is from 0 to 2, b is an integer from 1 to 3, a+b is equal to 3, R^1 is a independently selected from C_{1-10} alkyl radical to provide a molar ratio of Al:Cr from 0.5:1 to 30:1

11. The process according to claim 10, wherein the silyl chromate is selected from the group consisting of bis(trimethylsilyl)chromate; bis(triethylsilyl)chromate;

bis(tributylsilyl)chromate; bis(tripentylsilyl)chromate, bis(triphenylsilyl)chromate, bis(tritolylsilyl)chromate, bis(triethylhexylsilyl)chromate, bis(tridecylsilyl)chromate, bis(tritetradecylsilyl)chromate, and bis(tribenzylsilyl)chromate.

12. The process according to claim 11, wherein clay is fed to the reactor.

5 13. The process according to claim 11, wherein modified clay is fed to the reactor.

14. The process according to claim 12 or 13, wherein the clay is from the smectite group.

15. The process according to claim 12 or 13, wherein the clay is montmorillonite or bentonite.

10 16. The process according to claim 7 or 8, wherein the clay is from the smectite group.

17. The process according to claim 7 or 8, wherein the clay is montmorillonite or bentonite.

18. The process according to claim 4, wherein the reactor contains a catalyst is selected from the group consisting of single site, metallocene, constrained geometry and bulky ligand single site catalysts having the formula



wherein M is selected from the group consisting of Ti, Zr, and Hf; L is a monoanionic ligand independently selected from the group consisting of cyclopentadienyl-type ligands, and a bulky heteroatom ligand containing not less than five atoms in total of which at least 20%, numerically are carbon atoms and further containing at least one heteroatom selected from the group consisting of boron, nitrogen, oxygen, phosphorus, sulfur and silicon, said bulky heteroatom ligand being sigma or pi-bonded to M, Y is independently selected for the group consisting of activatable ligands; 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.

19. The process according to claim 18, wherein the catalyst has the formula



wherein M is a transition metal selected from the group consisting of Ti, Hf and Zr; D is independently selected from the group consisting of a phosphinimine ligand and a ketamide ligand L is a monoanionic ligand selected from the group consisting of cyclopentadienyl-type ligands; D and L may optionally be joined by a bridging group; Y

is independently selected from the group consisting of activatable ligands; m is 1 or 2; n is 0, 1 or 2 and p is an integer and the sum of m+n+p equals the valence state of M, provided that when m is 2, D may be the same or different bulky heteroatom ligands and may optionally be bridged.

- 5 20. The process according to claim 19, further including an activator selected from the group consisting of:

(i) a complex aluminum compound of the formula $R^{12}_2AlO(R^{12}AlO)_mAlR^{12}_2$ wherein each R^{12} is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and m is from 3 to 50, and optionally a hindered phenol to provide
10 a molar ratio of Al:hindered phenol from 2:1 to 5:1 if the hindered phenol is present;

(ii) ionic activators selected from the group consisting of:

(A) compounds of the formula $[R^{13}]^+ [B(R^{14})_4]^-$ wherein B is a boron atom, R^{13} is a cyclic C_{5-7} aromatic cation or a triphenyl methyl cation and each R^{14} is independently selected from the group consisting of phenyl radicals which
15 are unsubstituted or substituted with 3 to 5 substituents selected from the group consisting of a fluorine atom, a C_{1-4} alkyl or alkoxy radical which is unsubstituted or substituted by a fluorine atom; and a silyl radical of the formula $-Si-(R^{15})_3$; wherein each R^{15} is independently selected from the group consisting of a hydrogen atom and a C_{1-4} alkyl radical; and

20 (B) compounds of the formula $[(R^{18})_t ZH]^+ [B(R^{14})_4]^-$ wherein B is a boron atom, H is a hydrogen atom, Z is a nitrogen atom or phosphorus atom, t is 2 or 3 and R^{18} is selected from the group consisting of C_{1-8} alkyl radicals, a phenyl radical which is unsubstituted or substituted by up to three C_{1-4} alkyl radicals, or one R^{18} taken together with the nitrogen atom may form an anilinium
25 radical and R^{14} is as defined above; and

(C) compounds of the formula $B(R^{14})_3$ wherein R^{14} is as defined above; and

(iii) mixtures of (i) and (ii).

21. The process according to claim 20, wherein clay is fed to the reactor.

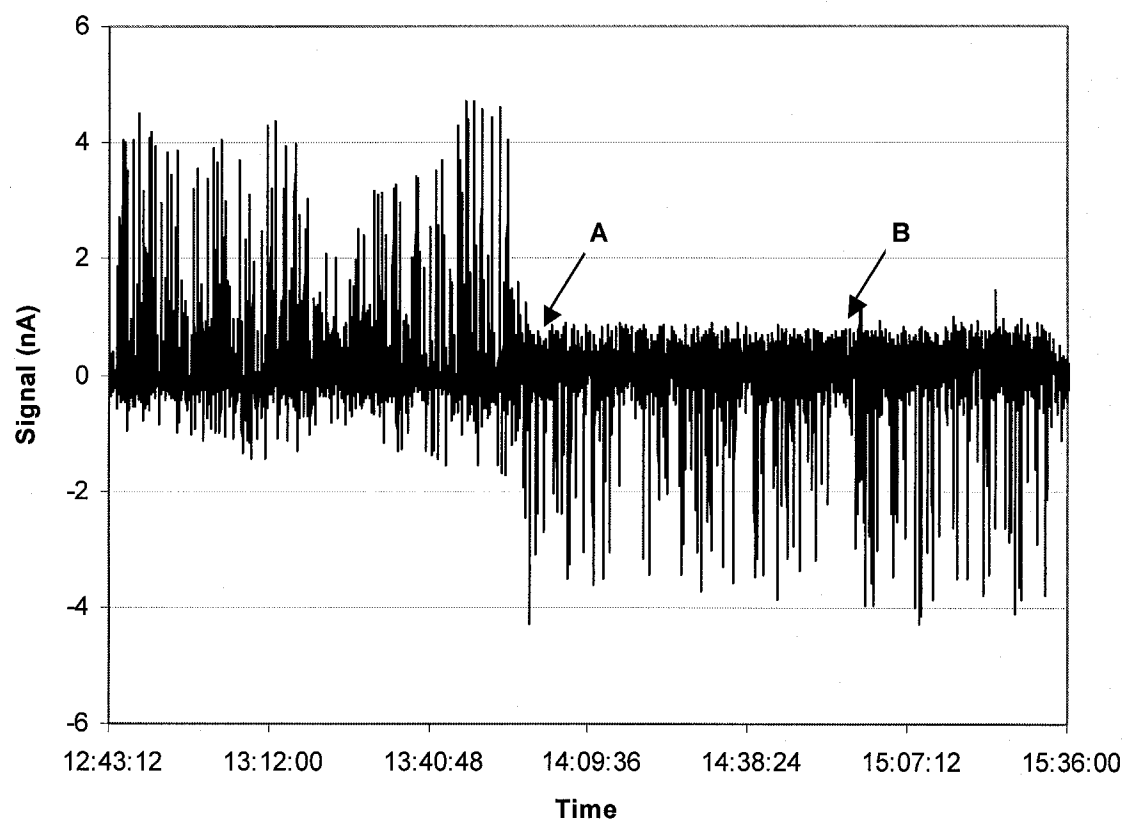
30 22. The process according to claim 20, wherein modified clay is fed to the reactor.

23. The process according to claim 21 or 22, wherein the clay is from the smectite group.

24. The process according to claim 21 or 22, wherein the clay is montmorillonite or bentonite.

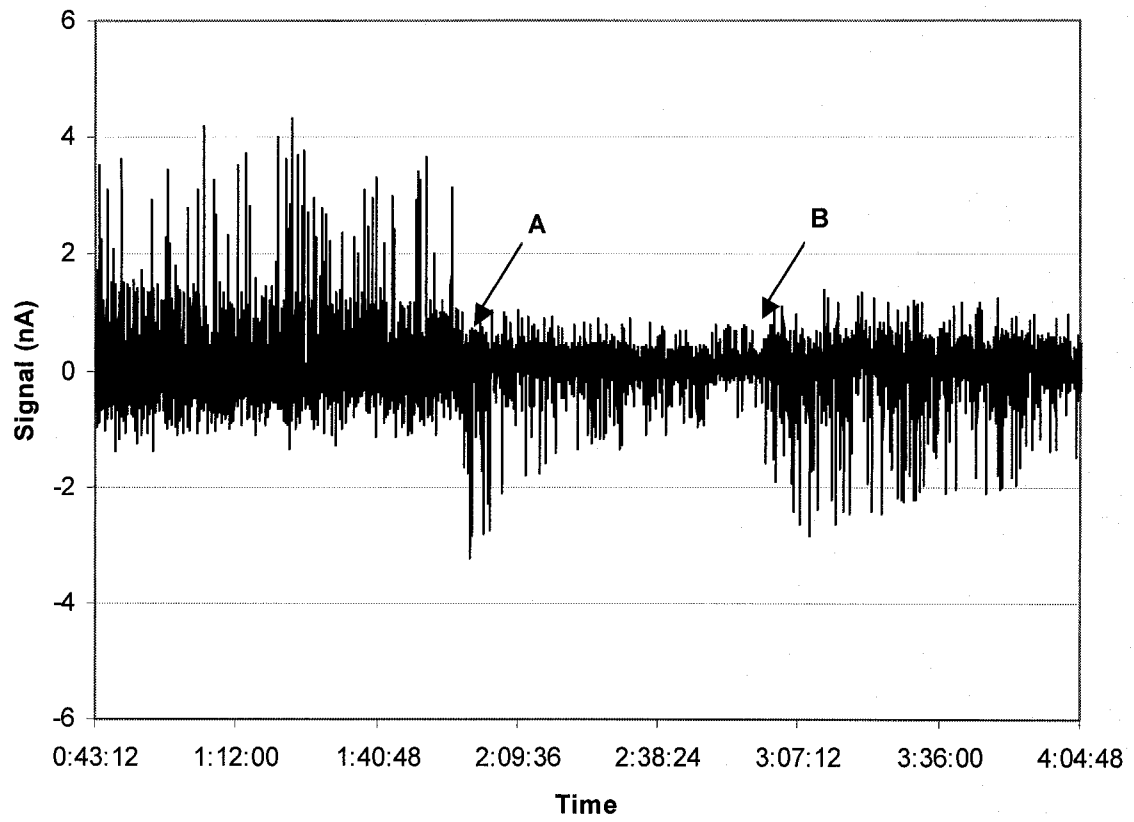
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Fig. 1



2/2

Fig. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2009/001584

A. CLASSIFICATION OF SUBJECT MATTER IPC: <i>C08F 2/01</i> (2006.01) , <i>C08F 10/00</i> (2006.01) , <i>C08F 2/34</i> (2006.01) , <i>C08F 4/24</i> (2006.01) , <i>C08F 4/6592</i> (2006.01) , <i>C08F 4/69</i> (2006.01), <i>C09K 3/16</i> (2006.01) 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) <i>C08F 2/01</i> (2006.01) , <i>C08F 10/00</i> (2006.01) , <i>C08F 2/34</i> (2006.01) , <i>C08F 4/24</i> (2006.01) , <i>C08F 4/6592</i> (2006.01) , <i>C08F 4/69</i> (2006.01), <i>C09K 3/16</i> (2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Keywords: clay, montmorillonite, bentonite, static, olefin, polymerization, fouling, gas phase and fluid bed and other related search terms Database: Canadian patent database, Questel Orbit, Scopus and Delphion																				
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>EP1270602 A1 (SATO, H. et al.) 02 January 2003 (02-01-2003) see whole document</td> <td>1-24</td> </tr> <tr> <td>A</td> <td>EP0881232 A1 (MAEHAMA, S. et al.) 02 December 1998 (02-12-1998) see whole document</td> <td>1-24</td> </tr> <tr> <td>A</td> <td>EP0811638 A2 (KIU, H.L. et al.) 10 December 1997 (10-12-1997) see whole document</td> <td>1-24</td> </tr> <tr> <td>A</td> <td>US6111034 A (GOODE, M.G. et al.) 29 August 2000 (28-08-2000) see whole document</td> <td>1-24</td> </tr> <tr> <td>A</td> <td>US6426394 B1 (ERICKSON, K.A. et al.) 30 July 2002 (30-07-2002) see whole document</td> <td>1-24</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	EP1270602 A1 (SATO, H. et al.) 02 January 2003 (02-01-2003) see whole document	1-24	A	EP0881232 A1 (MAEHAMA, S. et al.) 02 December 1998 (02-12-1998) see whole document	1-24	A	EP0811638 A2 (KIU, H.L. et al.) 10 December 1997 (10-12-1997) see whole document	1-24	A	US6111034 A (GOODE, M.G. et al.) 29 August 2000 (28-08-2000) see whole document	1-24	A	US6426394 B1 (ERICKSON, K.A. et al.) 30 July 2002 (30-07-2002) see whole document	1-24
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex. <table border="1"> <tbody> <tr> <td>* Special categories of cited documents :</td> <td>"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</td> </tr> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"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</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"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</td> </tr> <tr> <td>"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)</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </tbody> </table>			* Special categories of cited documents :	"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	"A" document defining the general state of the art which is not considered to be of particular relevance	"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	"E" earlier application or patent but published on or after the international filing date	"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	"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)	"&" document member of the same patent family	"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							
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Date of the actual completion of the international search 15 January 2010 (15-01-2010)		Date of mailing of the international search report 22 January 2010 (22-01-2010)																		
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476		Authorized officer Olivia Koentjoro (819) 994-1546																		

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2009/001584

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
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