



(22) Date de dépôt/Filing Date: 2010/06/18

(41) Mise à la disp. pub./Open to Public Insp.: 2011/12/18

(45) Date de délivrance/Issue Date: 2018/04/17

(51) Cl.Int./Int.Cl. *C08F 4/6592* (2006.01),
B01J 31/00 (2006.01), *C08F 10/00* (2006.01),
C08F 2/12 (2006.01), *C08F 4/02* (2006.01),
C08F 4/649 (2006.01)

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(54) Titre : CATALYSEURS DE CETIMIDE SUPPORTES DESTINES A AMELIORER LA CONTINUITE DU REACTEUR

(54) Title: SUPPORTED KETIMIDE CATALYSTS FOR IMPROVED REACTOR CONTINUITY

(57) Abrégé/Abstract:

Ketimide ligand containing catalyst/reactor continuity in a dispersed phase reaction in terms of initial activation and subsequent deactivation may be improved by treating the support with a metal salt. The activator and catalyst are then deposited on the treated support. The resulting catalyst has a lower consumption of ethylene during initiation and a lower rate of deactivation. Preferably the catalyst is used with an antistatic agent.

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SUPPORTED KETIMIDE CATALYSTS FOR IMPROVED REACTOR CONTINUITY

ABSTRACT OF THE DISCLOSURE

20 Ketimide ligand containing catalyst/reactor continuity in a dispersed phase
reaction in terms of initial activation and subsequent deactivation may be improved by
treating the support with a metal salt. The activator and catalyst are then deposited on
the treated support. The resulting catalyst has a lower consumption of ethylene during
initiation and a lower rate of deactivation. Preferably the catalyst is used with an
antistatic agent.

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SUPPORTED KETIMIDE CATALYSTS FOR IMPROVED REACTOR CONTINUITY

FIELD OF THE INVENTION

The present invention relates to improving the continuity of a ketimide ligand containing catalyst/reaction in a dispersed phase (i.e. gas phase, fluidized bed or stirred bed or slurry phase) olefin polymerization. There are a number of factors which impact on reactor continuity in a dispersed phase polymerization. Particularly there may be fouling which will decrease catalyst productivity and reactor operability. The decrease in catalyst productivity or activity is reflected by a decrease in ethylene uptake over time.

BACKGROUND OF THE INVENTION

Ketimide ligand containing catalysts for the polymerization of alpha olefins were introduced in U.S. patent 6,114,481 issued Sept 5, 2000 to McMeeking et al. assigned to NOVA Chemicals. These catalysts may be considered single site type catalysts. These catalysts are more active than the prior Ziegler Natta catalysts, which may lead to issues of polymer agglomeration. Additionally, static may contribute to the problem. As a result reactor continuity (e.g. fouling and also catalyst life time) may be a problem.

The kinetic profile of many single site catalysts starts off with a very high activity over a relatively short period of time, typically about the first five minutes of the reaction. The profile then goes through an inflection point and decreases rapidly for about the next five minutes and thereafter there is period of relative slower decline in the kinetic profile. This may be measured by the ethylene uptake, typically in standard liters of ethylene per minute in the reactor.

There is no prior art that the Applicant is aware of which expressly discloses a process to modify (improve) the kinetic profile of a catalyst containing a ketimide ligand.

There are a number of patents which teach modified porous inorganic supports for

polymerizations using single site catalysts. However, none of these patents expressly disclose that the kinetic profile of the resulting catalyst is modified.

United States patent 6,734,266 issued May 11, 2004 to Gao et al., assigned to NOVA Chemicals (International) S.A., teaches sulfating the surface of a porous
5 inorganic support with an acid, amide or simple salt such as an alkali or alkaline earth metal sulphate. The resulting treated support may be calcined. Aluminoxane and a single site catalyst, including a ketimide containing catalyst, are subsequently deposited on the support. The resulting catalyst shows improved activity. However, the patent fails to teach or suggest depositing zirconium sulphate on a silica support.

10 United States patent 7,001,962 issued Feb 21, 2006 to Gao et al., assigned to NOVA Chemicals (International) S.A., teaches treating a porous inorganic support with a zirconium compound including zirconium sulphate and an acid such as a fluorophosphoric acid, sulphonic acid, phosphoric acid and sulphuric acid. The support is dried and may be heated under air at 200°C and under nitrogen up to 600°C.
15 Subsequently a trialkyl aluminum compound (e.g. triethyl aluminum) or an alkoxy aluminum alkyl compound (e.g. diethyl aluminum ethoxide) and a single site catalyst, including a ketimide containing catalyst, are deposited on the support. The specification teaches away from using aluminoxane compounds. The activity of these supports is typically lower than the activity of the catalyst of U.S. patent 6,734,266
20 (compare Table 5 of U.S. patent 7,001,962 with Table 2 of U.S. patent 6,734,266). The present invention eliminates the required acid reagent that reacts with the zirconium compound.

Canadian Patent Application 2,683,019 filed Oct. 20, 2009 discloses a process to improve the dispersed phase reactor continuity of catalyst having a phosphinimine

ligand by supporting the catalyst on a support treated with a number of compounds including $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The support is also treated with MAO.

United States patent 7,273,912 issued Sept 25, 2007 to Jacobsen et al., assigned to Innovene Europe Limited, teaches a catalyst which is supported on a porous inorganic support which has been treated with a sulphate such as ammonium sulphate or an iron, copper, zinc, nickel or cobalt sulphate. The support may be calcined in an inert atmosphere at 200 to 850°C. The support is then activated with an ionic activator and then contacted with a single site catalyst. The patent fails to teach aluminoxane compounds and zirconium sulphate.

United States patent 7,005,400 issued Feb. 28, 2006 to Takahashi assigned to Polychem Corporation teaches a combined activator support comprising a metal oxide support and a surface coating of a group 2, 3, 4, 13 and 14 oxide or hydroxide different from the carrier. The support is intended to activate the carrier without the conventional "activators". However, in the examples the supported catalyst is used in combination with triethyl aluminum. The triethyl aluminum does not appear to be deposited on the support. Additionally the patent does not teach ketimide catalysts.

United States patent 7,442,750 issued Oct. 28, 2008 to Jacobsen et al., assigned to Innovene Europe Limited, teaches treating an inorganic metal oxide support typically with a transition metal salt, preferably a sulphate, of iron, copper, cobalt, nickel, and zinc. Then a single site catalyst, preferably a constrained geometry single site catalyst and an activator are deposited on the support. The activator is preferably a borate but may be an aluminoxane compound. The disclosure appears to be directed at reducing static in the reactor bed and product in the absence of a conventional antistatic agent such as STADIS®. The patent fails to teach or suggest a catalyst containing a ketimide ligand.

United States patent 6,653,416 issued Nov. 25, 2003 to McDaniel et al., assigned to Phillips Petroleum Company, discloses a fluoride silica-zirconia or titania porous support for a metallocene catalyst activated with an aluminum compound selected from the group consisting of alkyl aluminums, alkyl aluminum halides and alkyl aluminum alkoxides. Comparative examples 10 and 11 show the penetration of zirconium into silica to form a silica-zirconia support. However, the examples (Table 1) show the resulting catalyst has a lower activity than those when the supports were treated with fluoride.

Apart from U.S. 6,734,266 and 7,001,962 noted above none of the above art teaches catalyst containing a ketimide ligand.

The use of a salt of a carboxylic acids, especially aluminum stearate, as an antifouling additive to olefin polymerization catalyst compositions is disclosed in United States patent numbers 6,271,325 (McConville et al. to Univation) and 6,281,306 (Oskam et al. to Univation).

The preparation of supported catalysts using an amine antistatic agent, such as the fatty amine sold under the trademark KEMAMINE AS-990, is disclosed in U.S. patents 6,140,432 (Agapiou et al. to Exxon) and 6,117,955 (Agapiou et al. to Exxon).

Antistatic agents are commonly added to aviation fuels to prevent the buildup of static charges when the fuels are pumped at high flow rates. The use of these antistatic agents in olefin polymerizations is also known. For example, an aviation fuel antistatic agent sold under the trademark STADIS™ composition (which contains a "polysulfone" copolymer, a polymeric polyamine and an oil soluble sulfonic acid) was originally disclosed for use as an antistatic agent in olefin polymerizations in U.S. patent 4,182,810 (Wilcox to Phillips Petroleum). The examples of the Wilcox '810 patent illustrate the addition of the "polysulfone" antistatic agent to the isobutane diluent in a

commercial slurry polymerization process. This is somewhat different from the teachings of the earlier referenced patents - in the sense that the carboxylic acid salts or amine antistatics of the other patents were added to the catalyst instead of being added to a process stream.

5 The use of "polysulfone" antistatic compositions in olefin polymerizations is also subsequently disclosed in:

- 1) chromium catalyzed gas phase olefin polymerizations, in U.S. patent 6,639,028 (Heslop et al. assigned to BP Chemicals Ltd.);
- 2) Ziegler Natta catalyzed gas phase olefin polymerizations, in U.S. patent 10 6,646,074 (Herzog et al. assigned to BP Chemicals Ltd.); and
- 3) metallocene catalyzed olefin polymerizations, in U.S. patent 6,562,924 (Benazouzz et al. assigned to BP Chemicals Ltd.).

 The Benazouzz et al. patent does teach the addition of STADISTM antistat agent to the polymerization catalyst in small amounts (about 150 ppm by weight). However, 15 in each of the Heslop et al. '028, Herzog et al. '074 and Benazouzz et al. '924 patents listed above, it is expressly taught that it is preferred to add the STADISTM antistat directly to the polymerization zone (i.e. as opposed to being an admixture with the catalyst).

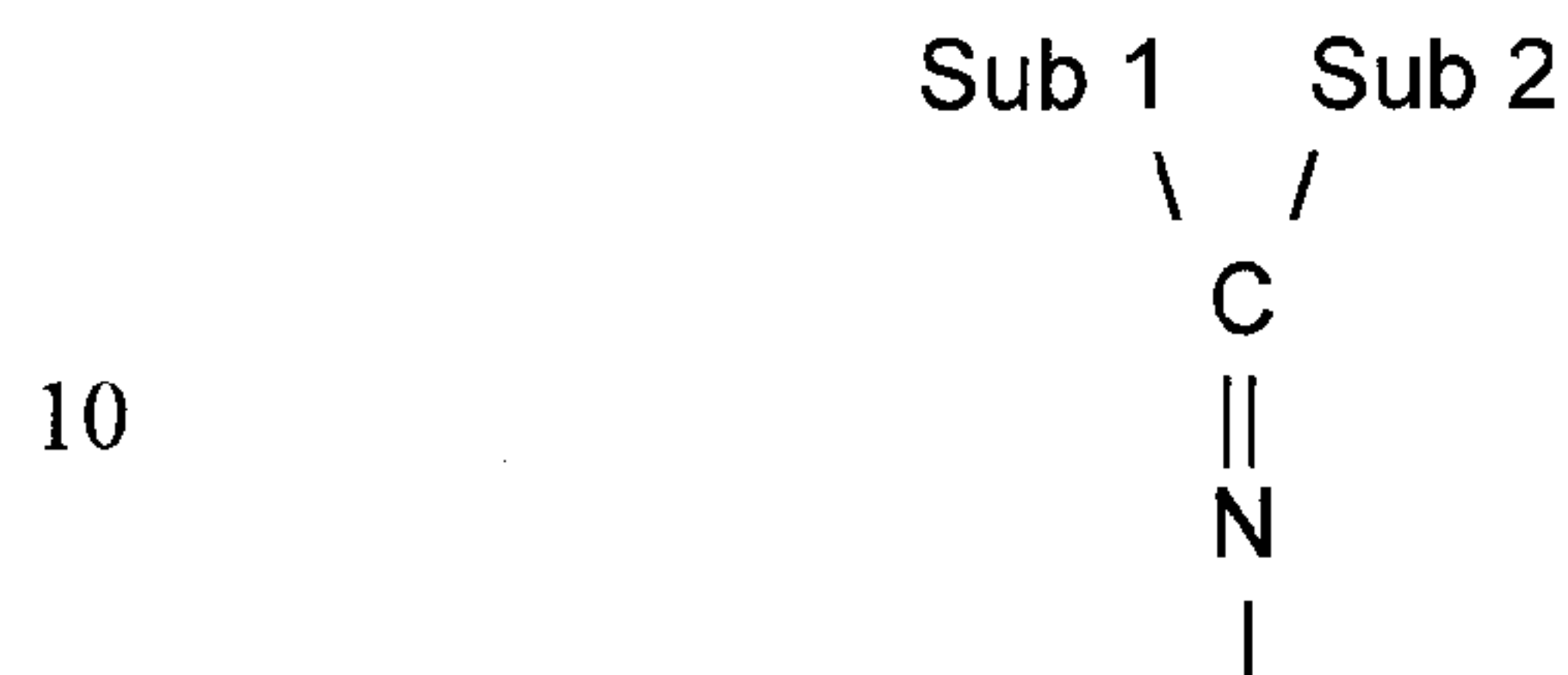
 None of the above art discusses polymerization catalysts containing a ketimide 20 ligand on a support which has been treated with $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, let alone the kinetic profile of such a catalyst system.

 The present invention seeks to provide a novel ketimide catalyst and support system suitable for use in a dispersed phase polymerization.

SUMMARY OF THE INVENTION

The present invention provides a catalyst comprising an organo group 4 metal complex containing a ketimide ligand and a calcined inorganic support impregnated with not less than 1 weight % of $Zr(SO_4)_2$ to provide from 0.010 to 0.50 mmol of Zr from the sulphate per gram of impregnated support.

In a further embodiment the ketimide has the formula:



wherein Sub 1 and Sub 2 are independently selected from the group consisting of C_{1-20} hydrocarbyl radicals which are unsubstituted or may be substituted by up to 4 hetero atoms selected from the group consisting of N, O, and S or up to three C_{1-9} straight chain, branched, cyclic or aromatic radicals which may be unsubstituted or substituted by a C_{1-6} alkyl radical or Sub 1 and Sub 2 taken together may form a saturated or unsaturated ring which may be substituted by up to 4 hetero atoms selected from the group consisting of N, O, and S and which ring may be further substituted by up to three C_{1-9} straight chain, branched, cyclic or aromatic radicals which may be unsubstituted or substituted by one or more C_{1-6} alkyl radicals.

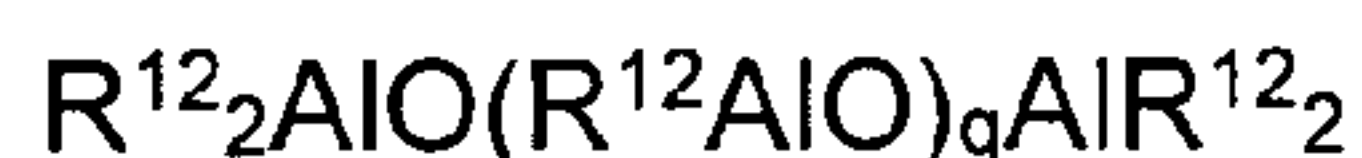
In a further embodiment the complex containing the ketimide ligand has the formula:



wherein M is a group 4 metal having an atomic number less than or equal to 72, L is a monoanionic ligand selected from the group consisting of a cyclopentadienyl-type ligand, K is a ketamide ligand, Y is independently selected from the group consisting of

activatable ligands, m is 0 or 1, n is 1 or 2, o is an integer and the sum of m+n+o equals the valence state of M.

In a further embodiment the support further comprises an activator of the formula



- 5 wherein each R^{12} is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and q is from 3 to 50 to provide from 50 to 500 parts by weight per part by weight of group 4 metal from the ketimide containing catalyst.

- In a further embodiment L is selected from the group consisting of a cyclopentadienyl radical, an indenyl radical and a fluorenyl radical which radicals are
10 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 more fluorine atoms.

In a further embodiment Y is selected from the group consisting of a chlorine atom, a methyl radical, an ethyl radical and a benzyl radical.

- 15 In a further embodiment in the activator R^{12} is a C_{1-4} alkyl radical and q is from 10 to 40.

In a further embodiment M is a group 4 metal.

In a further embodiment the catalyst comprises from 50 to 250 ppm based on the weight of the supported catalyst of an antistatic comprising:

- 20 (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 C_{6-20} α 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 C_{1-15} 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 anhydride;

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

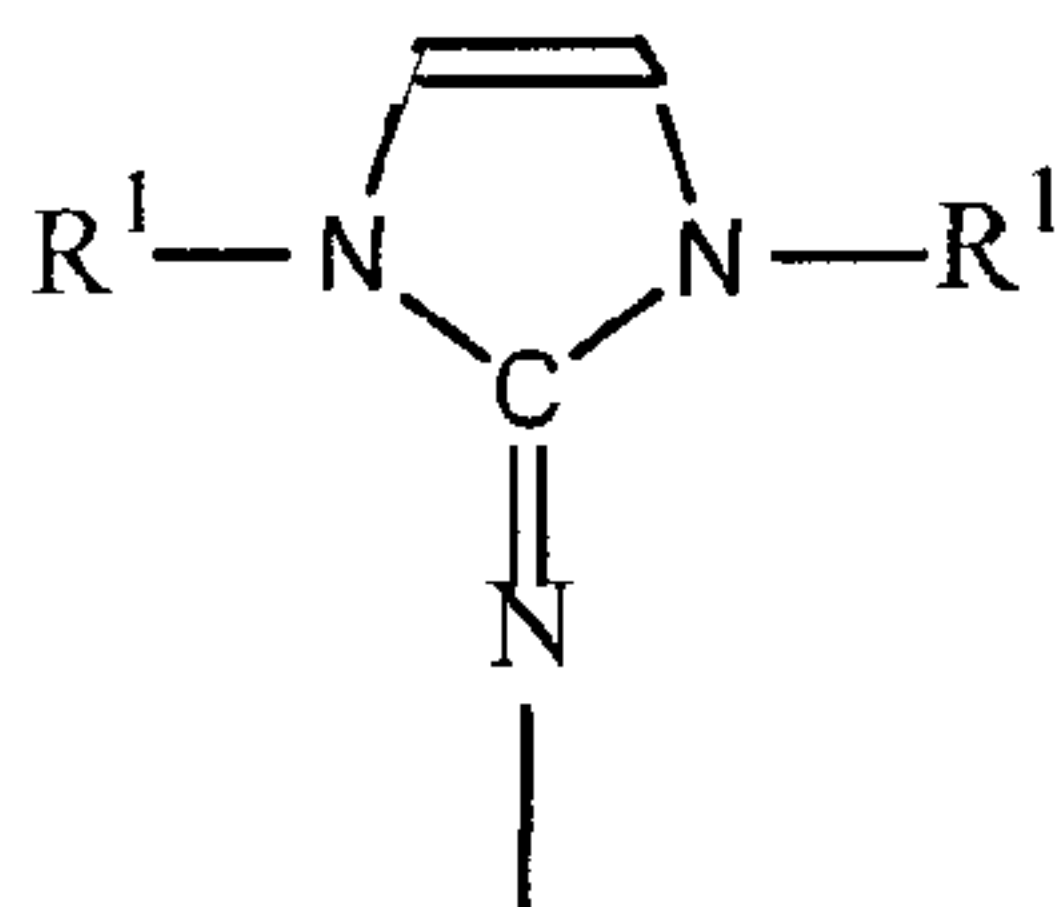


5 wherein R^1 is an aliphatic hydrocarbyl group of 8 to 24 carbon atoms; R^2 is an alkylene group of 2 to 6 carbon atoms, R^3 is the group R^2-HNR^1 ; R is R^1 or an N-aliphatic hydrocarbyl alkylene group having the formula R^1NHR^2 , a, b and c are integers from 0 to 20 and x is 1 or 2; with the proviso that when R is R^1 then a is greater than 2 and $b = c = 0$, and when R is R^1NHR^2 then a is 0 and the sum of $b+c$ is an integer from 2 to 20;

10 and

(iii) from 3 to 48 parts by weight of C_{10-20} alkyl or arylalkyl sulphonic acid.

In a further embodiment the ketimide ligand has the formula:



15 wherein each R^1 is independently selected from the group consisting of a phenyl radical which is unsubstituted or substituted by up to three C_{1-4} alkyl radicals.

In a further embodiment the catalyst may be prepared by:

- i) impregnating a porous particulate inorganic oxide support having an average particle size from 10 to 150 microns, a surface area greater than $100 \text{ m}^2/\text{g}$ and a pore volume greater than 0.3 ml./g with
- 20 (ii) an aqueous solution of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and hydrates thereof to provide not less than 1 weight % based on the weight of the support of said salt;

- (iii) calcining said impregnated support at a temperature from 300°C to 600°C for a time from 2 to 20 hours in an inert atmosphere;
- (iv) and either
- (a) contacting said calcined support with a hydrocarbyl solution containing at least 5 weight % of an aluminum activator compound of the formula $R^{12}_2AlO(R^{12}AlO)_qAlR^{12}_2$ wherein each R^{12} is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and q is from 3 to 50 to provide from 0.1 to 30 weight % of said aluminum compound based on the weight of said calcined support;
- optionally separating said activated support from said hydrocarbyl solution and contacting said activated support with a hydrocarbyl solution containing at least 5 weight % of a single site catalyst as set out below or
- (b) contacting said support with a hydrocarbyl solution containing at least 5 weight % of an aluminum activator compound of the formula $R^{12}_2AlO(R^{12}AlO)_qAlR^{12}_2$ wherein each R^{12} is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and q is from 3 to 50 and at least 5 weight % of the above ketamide; and
- (v) recovering and drying the catalyst.

A further embodiment comprises a disperse phase polymerization process comprising contacting one or more C_{2-8} alpha olefins with a ketimide catalyst, as described above, which does not have any anti static on the support and feeding to the reactor from 10 to 80 ppm based on the weight of the polymer produced of an antistatic 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 anhydride;
- (ii) from 3 to 48 parts by weight of one or more polymeric polyamines of the formula:
$$RN[(CH_2CHOHCH_2NR^1)_a-(CH_2CHOHCH_2NR^1-R^2-NH)_b-(CH_2CHOHCH_2NR^3)_c-H]_xH_{2-x}$$
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; and
- (iii) from 3 to 48 parts by weight of C₁₀₋₂₀ alkyl or arylalkyl sulphonic acid.

A further embodiment comprises a disperse phase polymerization process comprising contacting one or more C₂₋₈ alpha olefins with a ketimide catalyst, as described above, having an anti static agent on the support (or catalyst as the case may be).

Preferably the catalysts have an activity greater than 1350 g of polymer per gram of supported catalyst per hour normalized to 200 psig (1378 kPa) ethylene partial pressure and 90°C and having a kinetic profile for a plot of ethylene consumption in standard liters of ethylene per minute against time in minutes, at a reaction pressure of 1379 kPag (200psig) and 90°C, corrected for the volume of ethylene in the reactor prior to the commencement of the reaction, in a 2 liter reactor over a period of time from 0 to 60 minutes is such that the ratio of the maximum peak height over the first 10 minutes

to the average ethylene consumption from 10 to 60 minutes taken at not less than 40 data points, is less than 2.75.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is the kinetic profile of the catalysts run in example 1.

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DETAILED DESCRIPTION

As used in this specification dispersed phase polymerization means a polymerization in which the polymer is dispersed in a fluid polymerization medium. The fluid may be liquid in which case the polymerization would be a slurry phase polymerization or the fluid could be gaseous in which case the polymerization would be a gas phase polymerization, either fluidized bed or stirred bed.

10

As used in this specification kinetic profile means a plot of ethylene consumption in standard liters of ethylene per minute against time in minutes, corrected for the volume of ethylene in the reactor prior to the commencement of the reaction, in a 2 liter reactor over a period of time from 0 to 60 minutes.

15

As used in this specification gram of supported catalyst means a gram of the catalyst and activator on the support treated with $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$.

The Support

The support for the catalysts of the present invention comprises a silica oxide substrate having a pendant reactive moiety. The reactive moiety may be a siloxyl radical but more typically is a hydroxyl radical. 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 $100 \text{ m}^2/\text{g}$, preferably greater than about $250 \text{ m}^2/\text{g}$, most preferably from $300 \text{ m}^2/\text{g}$ to $1,000 \text{ m}^2/\text{g}$. 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.

25

Silica suitable for use as a support in the present invention is amorphous. For example, some commercially available silicas are marketed under the trademark of Sylopol[®] 958, 955 and 2408 by Davison Catalysts a Division of W. R. Grace and Company and ES70 and ES70W by Ineos Silica.

5 The resulting support is in the form of a free flowing dry powder.

Treatment of the Support

The support is treated with an aqueous solution of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The support need not be dried or calcined as it is contacted with an aqueous solution.

10 Generally a 2 to 50, typically a 5 to 15, preferably an 8 to 12, most preferably a 9 to 11 weight % aqueous solution of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is used to treat the support. The support is contacted with the solution of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ at a temperature from 10°C to 50°C, preferably from 20 to 30°C, for a time of not less than 30 minutes, typically from 1 to 10 hours, preferably from 1 to 4 hours, until the support is thoroughly impregnated with the solution.

15 The impregnated support is then recovered typically by drying at an elevated temperature from 100°C to 150°C, preferably from 120°C to 140°C, most preferably from 130°C to 140°C, for about 8 to 12 hours (e.g. overnight). Other recovery methods would be apparent to those skilled in the art.

20 The dried impregnated support is then calcined. It is important that the support be calcined prior to the initial reaction with an aluminum activator, catalyst or both. 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 600°C, preferably from 550°C to 600°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 of support.

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

The $\text{Zr}(\text{SO}_4)_2$ is substantially unchanged by calcining.

5 The resulting dried and calcined support is then contacted sequentially with the activator and the catalyst in an inert hydrocarbon diluent

The Activator

The activator is an aluminoxane compound of the formula $\text{R}^{12}_2\text{AlO}(\text{R}^{12}\text{AlO})_q\text{AlR}^{12}_2$ wherein each R^{12} is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and q is from 3 to 50. In the aluminum activator preferably R^{12} is a C_{1-4} alkyl radical, preferably a methyl radical and q is from 10 to 40. Optionally, a hindered phenol may be used in conjunction with the aluminoxane to provide a molar ratio of Al:hindered phenol from 2:1 to 5:1 if the hindered phenol is present. Generally, the molar ratio of Al:hindered phenol, if it is present, is from 3.25:1 to 4.50:1. Preferably
10 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 (aluminoxanes and optionally hindered phenol) are typically used as activators in substantial molar excess compared to the amount of transition metal (e.g. group 4 transition metal) in the catalyst. Aluminum:transition
20 metal (in the catalyst) molar ratios may range from 10:1 to 10,000:1, preferably 10:1 to 500:1, most preferably from 50:1 to 150:1, especially from 90:1 to 120:1.

Typically the loading of the alminoxane compound may range from 0.05 up to 30 weight % preferably from 0.1 to 2 weight %, most preferably from 0.15 to 1.75 weight % based on the weight of the calcined support impregnated with zirconium salt.

The aluminoxane is added to the support in the form of a hydrocarbyl solution, typically at a 5 to 30 weight % solution, preferably an 8 to 12 weight % solution, most preferably a 9 to 10 weight % solution. Suitable hydrocarbon solvents include C₅₋₁₂ hydrocarbons which may be unsubstituted or substituted by C₁₋₄ alkyl group such as
 5 pentane, hexane, heptane, octane, cyclohexane, methylcyclohexane, toluene, or hydrogenated naphtha. An additional solvent is Isopar ETM (C₈₋₁₂ aliphatic solvent, Exxon Chemical Co.).

The treated support may optionally be filtered and/or dried under an inert atmosphere (e.g. N₂) and optionally at reduced pressure, preferably at temperatures
 10 from room temperature up to about 80°C.

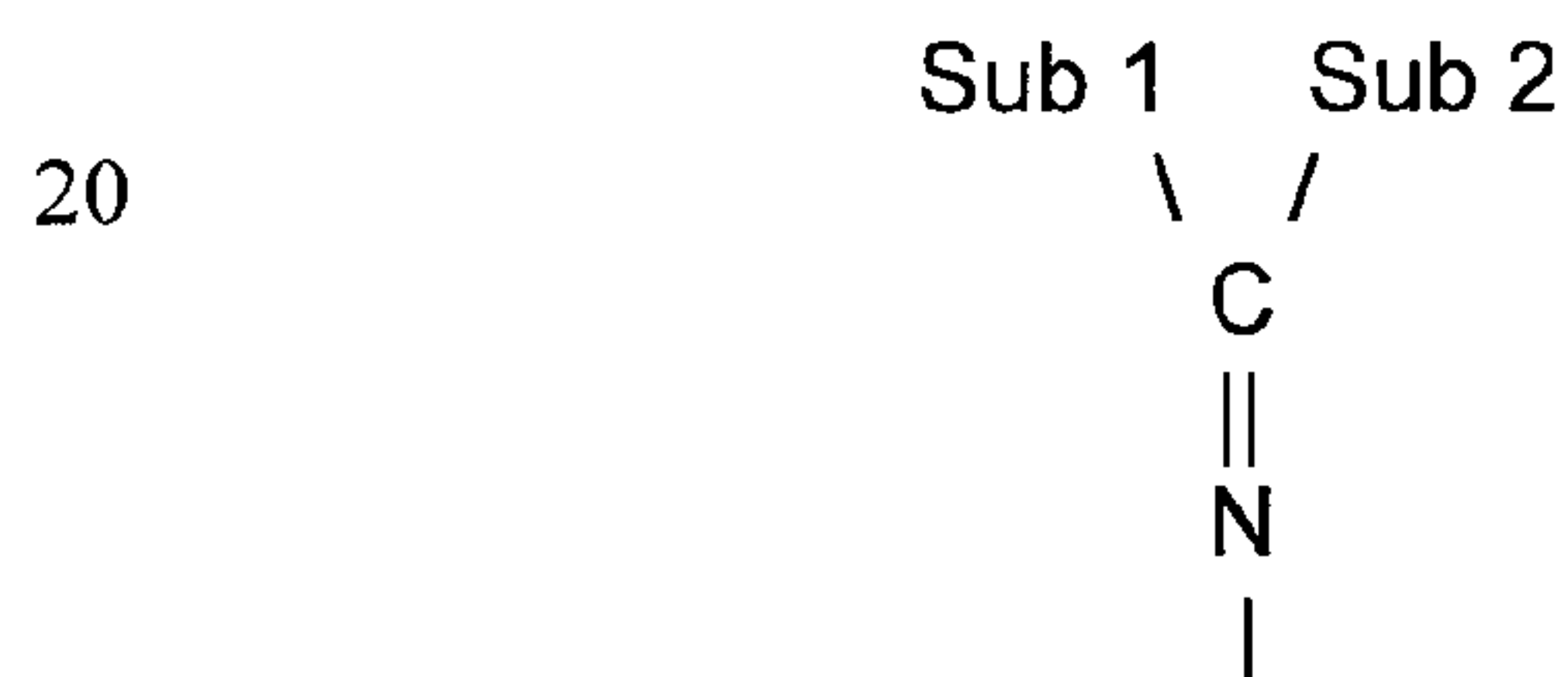
The optionally dried support with activator is then contacted with the complex containing the ketimide ligand (catalyst) again in a hydrocarbyl solution as noted above.

In an alternate embodiment the support could be treated with a combined solution of activator and catalyst.

15 The Complex Containing the Ketimide Ligand (Catalyst)

The catalyst comprises an organo group 4 metal complex containing a ketimide ligand. Preferably the group 4 metal has an atomic number not greater than 72.

The ketimide may have the formula:



25 wherein Sub 1 and Sub 2 are independently selected from the group consisting of C₁₋₂₀ hydrocarbyl radicals which are unsubstituted or may be substituted by up to 4 hetero atoms selected from the group consisting of N, O, and S or up to three C₁₋₉ straight

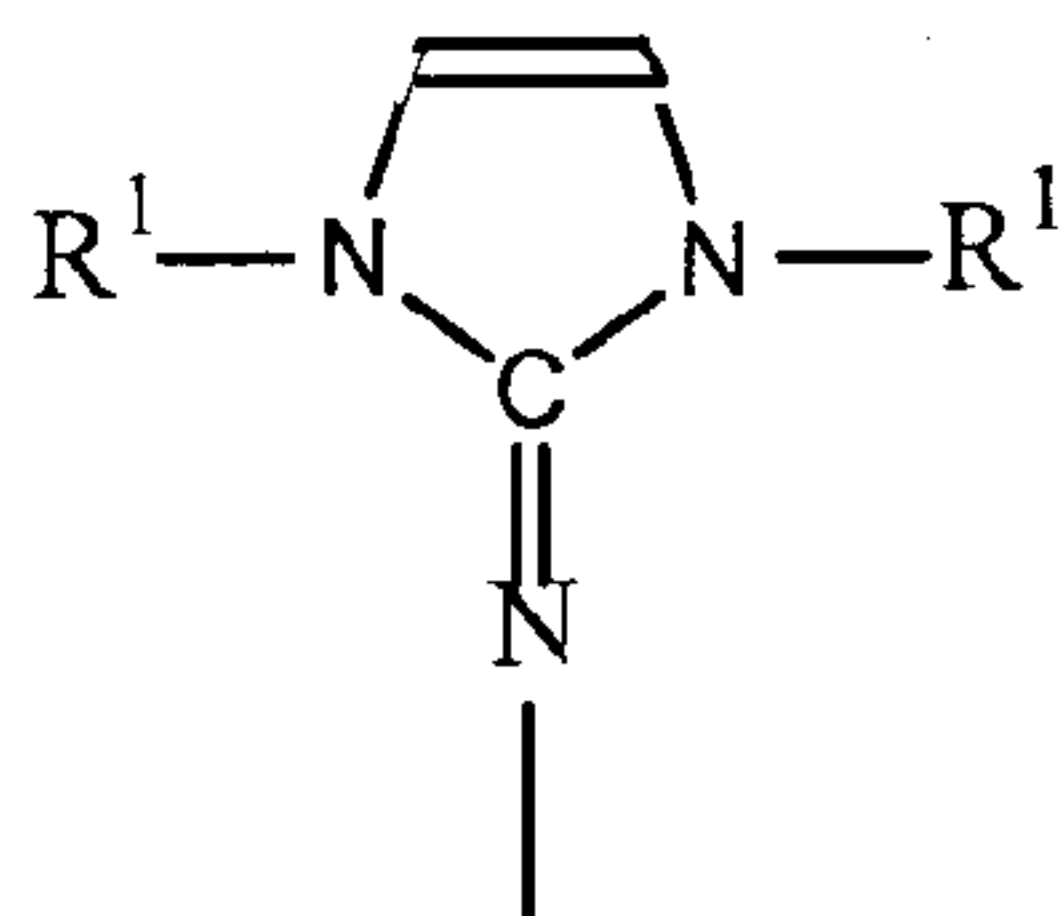
chain, branched, cyclic or aromatic radicals which may be unsubstituted or substituted by a C₁₋₆ alkyl radical or Sub 1 and Sub 2 taken together may form a saturated or unsaturated ring which may be unsubstituted or substituted by up to 4 hetero atoms selected from the group consisting of N, O, and S and which ring may be further substituted by up to three C₁₋₉ straight chain, branched, cyclic or aromatic radicals which may be unsubstituted or substituted by one or more C₁₋₆ alkyl radicals.

The complex containing the ketimide ligand may have the formula:



wherein M is a group 4 metal, most preferably Ti, having an atomic number not greater than 72 (e.g. less than or equal to 72), L is a monoanionic ligand selected from the group consisting of cyclopentadienyl-type ligands, K is a ketimide ligand, Y is independently selected from the group consisting of activatable ligands, m is 0 or 1, n is 1 or 2, o is an integer and the sum of m+n+o equals the valence state of M.

Preferred ketimide ligands have the formula



wherein each R¹ is independently selected from the group consisting of a phenyl radical which is unsubstituted or substituted by up to three C₁₋₄ alkyl radicals, preferably isopropyl radicals. A preferred ketimide is 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylideneamine.

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

transition metal, preferably group 4, (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 C₁₋₁₀ hydrocarbyl radicals which are unsubstituted or further substituted by one or more substituents selected from the group consisting of

5 a halogen atom; a C₁₋₄ alkyl radical; a halogen atom; a C₁₋₈ alkoxy radical; a C₆₋₁₀ aryl or aryloxy radical which is unsubstituted or may be up to fully substituted by one or more substituents selected from the group consisting of halogen atoms, preferably fluorine, C₁₋₄ alkyl radicals and a phenyl or benzyl radical which is unsubstituted or substituted by one or more fluorine atoms; an amido radical which is unsubstituted or

10 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, C₆₋₁₀ aryl or aryloxy radicals and germanyl radicals of the formula $\text{Ge}-(\text{R})_3$ wherein R is as defined above.

15 Preferably the cyclopentadienyl-type ligand is selected from the group consisting of a cyclopentadienyl radical, an indenyl radical and a fluorenyl radical which 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, C₁₋₄ alkyl radicals and a phenyl or benzyl radical which is unsubstituted or substituted by one or more fluorine atoms.

20 Activatable ligands Y may be selected from the group consisting of a halogen atom, C₁₋₄ alkyl radicals, C₆₋₂₀ aryl radicals, C₇₋₁₂ arylalkyl radicals, C₆₋₁₀ phenoxy radicals, amido radicals which may be substituted by up to two C₁₋₄ alkyl radicals and C₁₋₄ alkoxy radicals. Preferably, Y is selected from the group consisting of a chlorine atom, a methyl radical, an ethyl radical and a benzyl radical.

Suitable ketimide complexes (catalysts) are Group 4, preferably Ti, organometallic complexes which contain one or two, preferably one, ketimide ligands (as described above) and one or zero, preferably one, cyclopentadienyl-type (L) ligand and two activatable ligands.

- 5 The loading of the catalyst on the support should be such to provide from about 0.010 to 0.50, preferably from 0.015 to 0.40, most preferably from 0.015 to 0.035 mmol of group IV metal (e.g. Ti) from the ketimide complex (catalyst) per gram of support (support treated with $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) and calcined and treated with an activator).

- 10 The ketimide complex (catalyst) may be added to the support in a hydrocarbyl solvent such as those noted above. The concentration of ketimide complex (catalyst) in the solvent is not critical. Typically, it may be present in the solution in an amount from about 5 to 15 weight %.

- 15 The supported catalyst (e.g. support, $\text{Zr}(\text{SO}_4)_2$, activator and catalyst) typically has a reactivity in a dispersed phase reaction (e.g. gas or slurry phase) from 1350, preferably greater than 1400, g of polyethylene per gram of supported catalyst per hour normalized to an ethylene partial pressure of 200 psig (1379 kPa) and a temperature of 90°C.

- 20 The supported catalyst of the present invention may be used in dispersed phase polymerizations in conjunction with a scavenger such as an aluminum alkyl of the formula $\text{Al}(\text{R}^{30})_3$ wherein R^{30} is selected from the group consisting of C_{1-10} alkyl radicals, preferably C_{2-4} alkyl radicals. The scavenger may be used in an amount to provide a molar ratio of Al:Ti from 20 to 2000, preferably from 50 to 1000, most preferably 100:500. Generally, the scavenger is added to the reactor prior to the catalyst and in the absence of additional poisons over time declines to 0.

The supported catalyst will have a kinetic profile for a plot of ethylene consumption in standard liters of ethylene per minute against time in minutes, corrected for the volume of ethylene in the reactor prior to the commencement of the reaction, in a 2 liter reactor over a period of time from 0 to 60 minutes is such that the ratio of the maximum peak height over the first 10 minutes to the average ethylene consumption from 10 to 60 minutes taken at not less than 40, preferably greater than 60 most preferably from 120 to 300 data points, is less than 2.75, preferably less than 2, most preferably less than 1.75.

The supported catalyst may be used in conjunction with an antistatic agent. In one embodiment the antistatic is added directly to the supported catalyst. The antistatic may be added in an amount from 0 (e.g. optionally) up to 150,000 parts per million (ppm), preferably from 15,000 up to 120,000 ppm based on the weight of the supported catalyst.

In a further embodiment the antistatic may be added to the reactor in an amount from 0 to 100, preferably from 10 to 80 ppm based on the weight of the polymer produced (i.e. the weight of polymer in the fluidized bed or the weight of polymer dispersed in the slurry phase reactor). If present, the antistatic agent may be present in an amount from about 0 to 100, preferably from about 10 to 80 most preferably from 20 to 50 ppm based in the weight of polymer. From the productivity of the catalyst it is fairly routine to determine the feed rate of the antistatic to the reactor based on the catalyst feed rate.

Antistatic "Polysulfone" Additive

The antistatic polysulfone additive comprises at least one of the components selected from:

- (1) a polysulfone copolymer;

- (2) a polymeric polyamine; and
- (3) an oil-soluble sulfonic acid, and, in addition, a solvent for the polysulfone copolymer.

Preferably, the antistatic additive comprises at least two components selected from above components (1), (2) and (3). More preferably, the antistatic additive comprises a mixture of (1), (2) and (3).

According to the present invention, the polysulfone copolymer component of the antistatic additive (often designated as olefin-sulfur dioxide copolymer, olefin polysulfones, or poly(olefin sulfone)) is a polymer, preferably a linear polymer, wherein the structure is considered to be that of alternating copolymers of the olefins and sulfur dioxide, having a one-to-one molar ratio of the comonomers with the olefins in head to tail arrangement. Preferably, the polysulfone copolymer consists essentially of about 50 mole % of units of sulfur dioxide, about 40 to 50 mole % of units derived from one or more 1-alkenes each having from about 6 to 24 carbon atoms and from about 0 to 10 mole percent of units derived from an olefinic compound having the formula $ACH=CHB$ where A is a group having the formula $-(C_x H_{2x})-COOH$ wherein x is from 0 to about 17 and B is hydrogen or carboxyl, with the provision that when B is carboxyl, x is 0 and wherein A and B together can be a dicarboxylic anhydride group.

Preferably, the polysulfone copolymer employed in the present invention has a weight average molecular weight in the range 10,000 to 1,500,000, preferably in the range 50,000 to 900,000. The units derived from the one or more 1-alkenes are preferably derived from straight chain alkenes having 6-18 carbon atoms, for example 1-hexene, 1-heptene, 1-octene, 1-decene, 1-dodecene, 1-hexadecene and 1-octadecene. Examples of units derived from the one or more compounds having the formula $ACH=CHB$ are units derived from maleic acid, acrylic acid, 5-hexenoic acid.

A preferred polysulfone copolymer is 1-decene polysulfone 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 polymeric polyamines that can be suitably employed in the antistatic of the present invention are described in U.S. Patent 3,917,466, in particular at column 6 line 42 to column 9 line 29.

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 provision 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.

The polymeric polyamine may be prepared for example by heating an aliphatic primary monoamine or N-aliphatic hydrocarbyl alkylene diamine with epichlorohydrin in the molar proportion of from 1:1 to 1:1.5 at a temperature of 50°C to 100°C in the presence of a solvent, (e.g. a mixture of xylene and isopropanol) adding a strong base, (e.g. sodium hydroxide) and continuing the heating at 50 to 100°C for about 2 hours. The product containing the polymeric polyamine may then be separated by decanting and then flashing off the solvent.

The polymeric polyamine is preferably the product of reacting an N-aliphatic hydrocarbyl alkylene diamine or an aliphatic primary amine containing at least 8 carbon atoms and preferably at least 12 carbon atoms with epichlorohydrin. Examples of such aliphatic primary amines are those derived from tall oil, tallow, soy bean oil, coconut oil

and cotton seed oil. The polymeric polyamine derived from the reaction of tallowamine with epichlorohydrin is preferred. A method of preparing such a polyamine is disclosed in U.S. Patent 3,917,466, column 12, preparation B.1.0

5 The above-described reactions of epichlorohydrin with amines to form polymeric products are well known and find extensive use in epoxide resin technology.

A preferred polymeric polyamine is a 1:1.5 mole ratio reaction product of N-tallow-1,3-diaminopropane with epichlorohydrin. One such reaction product is "Polyflo™ 130" sold by Universal Oil Company.

10 According to the present invention, the oil-soluble sulfonic acid component of the antistatic is preferably any oil-soluble sulfonic acid such as an alkanesulfonic acid or an alkylarylsulfonic acid. A useful sulfonic acid is petroleum sulfonic acid resulting from treating oils with sulfuric acid.

Preferred oil-soluble sulfonic acids are dodecylbenzenesulfonic acid and dinonylnaphthylsulfonic acid.

15 The antistatic additive preferably comprises 1 to 25 weight % of the polysulfone copolymer, 1 to 25 weight % of the polymeric polyamine, 1 to 25 weight % of the oil-soluble sulfonic acid and 25 to 95 weight % of a solvent. Neglecting the solvent, the antistatic additive preferably comprises about 5 to 70 weight % polysulfone copolymer, 5 to 70 weight % polymeric polyamine and 5 to 70 weight % oil-soluble sulfonic acid
20 and the total of these three components is preferably 100%.

Suitable solvents include aromatic, paraffin and cycloparaffin compounds. The solvents are preferably selected from among benzene, toluene, xylene, cyclohexane, fuel oil, isobutane, kerosene and mixtures thereof.

According to a preferred embodiment of the present invention, the total weight of components (1), (2), (3) and the solvent represents essentially 100% of the weight of the antistatic additive.

One useful composition, for example, consists of 13.3 weight % 1:1 copolymer of
 5 1-decene and sulfur dioxide having an inherent viscosity of 0.05 determined as above,
 13.3 weight % of "Polyflo™ 130" (1:1.5 mole ratio reaction product of N-tallow-1,3-
 diaminopropane with epichlorohydrin), 7.4 weight % of either dodecylbenzylsulfonic
 acid or dinonylnaphthylsulfonic acid, and 66 weight % of an aromatic solvent which is
 preferably toluene or kerosene.

10 Another useful composition, for example, consists of 2 to 7 weight % 1:1
 copolymer of 1-decene and sulfur dioxide having an inherent viscosity of 0.05
 determined as above, 2 to 7 weight % of "Polyflo™ 130" (1:1.5 mole ratio reaction
 product of N-tallow-1,3-diaminopropane with epichlorohydrin), 2 to 8 weight % of either
 dodecylbenzylsulfonic acid or dinonylnaphthylsulfonic acid, and 78 to 94 weight % of an
 15 aromatic solvent which is preferably a mixture of 10 to 20 weight % toluene and 62 to
 77 weight % kerosene.

According to a preferred embodiment of the present invention, the antistatic is a
 material sold by Octel under the trade name STADIS™, preferably STADIS™ 450, more
 preferably STADIS™ 425.

20 Gas Phase Polymerization

Fluidized bed gas phase reactors to make polyethylene are generally operated
 at low temperatures from about 50°C up to about 120°C (provided the sticking
 temperature of the polymer is not exceeded) preferably from about 75°C to about
 110°C and at pressures typically not exceeding 3,447 kPa (about 500 psi) preferably
 25 not greater than about 2,414 kPa (about 350 psi).

Gas phase polymerization of olefins is well known. Typically, in the gas phase polymerization of olefins (such as ethylene) a gaseous feed stream comprising of at least about 80 weight % ethylene and the balance one or more C₃₋₆ copolymerizable monomers typically, 1-butene, or 1-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 and in some cases a condensable hydrocarbon (e.g. a C₄₋₆ alkane such as pentane). Typically, the feed stream passes through a distributor plate at the bottom of the reactor and vertically traverses a bed of polymer particles with active catalyst, typically a fluidized bed but the present invention also contemplates a stirred bed reactor. 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. If there is a condensable gas it is usually condensed and entrained in the recycle stream to remove heat of reaction by vaporization as it recycles through the fluidized bed.

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.

Slurry Polymerization

5 Slurry processes are conducted in the presence of a hydrocarbon diluent such as an alkane (including isoalkanes), an aromatic or a cycloalkane. The diluent may also be the alpha olefin comonomer used in copolymerizations. Preferred alkane diluents include propane, butanes, (i.e. normal butane and/or isobutane), pentanes, hexanes, heptanes and octanes. The monomers may be soluble in (or miscible with) 10 the diluent, but the polymer is not (under polymerization conditions). The polymerization temperature is preferably from about 5°C to about 200°C, most preferably less than about 110°C typically from about 10°C to 80°C. The reaction temperature is selected so that the ethylene copolymer is produced in the form of solid particles. The reaction pressure is influenced by the choice of diluent and reaction 15 temperature. For example, pressures may range from 15 to 45 atmospheres (about 220 to 660 psi or about 1500 to about 4600 kPa) when isobutane is used as diluent (see, for example, U.S. patent 4,325,849) to approximately twice that (i.e. from 30 to 90 atmospheres – about 440 to 1300 psi or about 3000 -9100 kPa) when propane is used (see U.S.patent 5,684,097). The pressure in a slurry process must be kept sufficiently 20 high to keep at least part of the ethylene monomer in the liquid phase.

The reaction typically takes place in a jacketed closed loop reactor having an internal stirrer (e.g. an impeller) and at least one settling leg. Catalyst, monomers and diluents are fed to the reactor as liquids or suspensions. The slurry circulates through the reactor and the jacket is used to control the temperature of the reactor. Through a 25 series of let down valves the slurry enters a settling leg and then is let down in pressure

to flash the diluent and unreacted monomers and recover the polymer generally in a cyclone. The diluent and unreacted monomers are recovered and recycled back to the reactor.

The Polymer

5 The resulting polymer may have a density from about 0.915 g/cc to about 0.960 g/cc. The resulting polymers may be used in a number of applications such as extrusion, and both injection and rotomolding applications. Typically the polymer may be compounded with the usual additives including heat and light stabilizers such as hindered phenols; ultra violet light stabilizers such as hindered amine stabilizers
10 (HALS); process aids such as fatty acids or their derivatives and fluoropolymers optionally in conjunction with low molecular weight esters of polyethylene glycol.

EXAMPLES

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

15 Experimental Procedure

The catalyst used in all experiments was a titanium (IV) complex having one Cp – C₆F₅ ligand, two chloride ligands and one ketimide ligand [C₆F₅Cp][1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-iminato]TiCl₂.

General Synthetic Methods

20 All reactions involving air and or moisture sensitive compounds were conducted under nitrogen using standard Schlenk or cannula techniques, or in a glovebox. Reaction solvents were purified either using the system described by Pangborn *et al.* in *Organometallics*, 1996, v15, p.1518 (toluene, heptanes) or distilled and stored over activated 4 Å sieves (tetrahydrofuran (THF)). Hexafluorobenzene was purchased from
25 Aldrich and stored over 4Å sieves in a glovebox. The following materials were

purchased from Aldrich and stored in an Innovative Technology™ glove box: K⁺OtBu, BuLi, NaCp, 1,2-Bis(2,6-Diisopropylphenylimino)ethane and TiCl₄. Trimethylsilylazide (TMSN₃) was purchased from Aldrich and used without further purification.

Zr(SO₄)₂·4H₂O (99.99+%) was used as received from Strem Chemicals. Deuterated solvents were purchased from Aldrich (toluene-d₈, THF-d₈) and were stored over 4Å sieves. NMR spectra were recorded using Bruker spectrometers (200, 300, 400 MHz for ¹H, 75.42 MHz for ¹³C, 121.42 MHz for ³¹P, 282.4 for ¹⁹F).

Molecule Preparation

1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene: This compound was prepared according to a published procedure of L. Jajapour, E.D.Stevens and S.P. Nolan *J. Organometallic Chem* 2000,606, 49-54.

¹H NMR (toluene-d₈, δ): 7.34-7.21 (m, 2H), 7.21-7.12 (m 4H), 6.65 (s, 2H), 3.06-2.81 (sept., 4H) and 1.38-1.1 (2d, 24H).

[1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-iminato]trimethylsilane: Solid 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene was dissolved in 20ml of toluene. To this solution was added batch-wise excess TMSN₃ (5.0ml, 38.0 mmol) as the solution was being heated to reflux. After all TMSN₃ was added the solution was refluxed at 125°C for 5 hours. All volatiles were pumped off leaving a yellow solid which was slurried in 20ml of toluene and hot (60°C) filtered. All toluene was pumped off leaving the product as a yellow solid, 4.9g (83%). ¹H NMR (toluene-d₈, δ): 7.32-7.04 (m, 6H), 5.96 (s, 2H), 3.28-3.01 (sep., 4H), 1.42-1.30 (d, 12H), 1.23-1.12 (d, 12H) and -0.24 (s, 9H).

[C₆F₅-Cp]TMS: To a Schlenk flask containing NaCp (2.0 M in THF, 160.0 mL, 320.0 mmol) was added a solution of hexafluorobenzene (29.8 g, 160.0 mmol) in 50 mL THF drop wise over 15 minutes. The purple solution was heated to 60°C for 3 hours.

ClSiMe₃ (30.0 mL, 225.0 mmol) was added via a dropping funnel over a period of 30 minutes, then stirred under nitrogen overnight. The volatiles were removed *in vacuo*, the solid was triturated 2 times with heptanes, filtered, and then washed with heptanes (5 x 10 mL). Heptanes were removed *in vacuo* yielding a brown/purple liquid, which
 5 was then distilled under full vacuum at 95°C. A clear, colorless liquid was obtained (21.8 g, 45%; 89% pure by GC/MS: M⁺ = 304 at 21.7 min).

Li(C₆F₅-CpTMS): BuLi (1.6 M in hexane, 49.4 mL, 79.0 mmol) was added to a solution of [C₆F₅CpTMS] (22.8 g, 75.0 mmol) in heptanes (300 mL) via a dropping funnel at room temperature over a period of 40 minutes. The reaction was stirred for 3
 10 days, filtered and the resulting white solid was washed with heptanes (3 x 5 mL) and isolated *in vacuo* (18.5 g, 60%). ¹H NMR (THF-*d*₈): δ 6.46 (m, 1H, CpH), 6.35 (m, 1H, CpH), 5.96 (m, 1H, CpH), 0.14 (s, 9H, SiCH₃). ¹⁹F NMR (THF-*d*₈): δ -145.8 (m, 2F), -168.6 (m, 2F), -172.7 (m, 1F).

[C₆F₅Cp]TiCl₃: [C₆F₅Cp]TMS (65.1 g, 214.0 mmol) was added drop-wise over
 15 20 minutes to neat titanium tetrachloride (49.1, 258.0 mmol) while stirring at 60°C. A dark red-brown solution resulted, which was subsequently stirred for 3 hours at 60°C. Heptane (100 mL) was then added to give a slurry, which was cooled by removing solvent under vacuum to half the initial volume. The solid product was isolated by filtration, washed with additional heptane and dried under vacuum to give an orange-
 20 brown solid (57.4 g, 70%). ¹H NMR (toluene-*d*₈): δ 6.67 (m, 2H), 6.09 (m, 2H). ¹⁹F NMR (toluene-*d*₈): δ -139.6 (m, 2F), -152.7 (t, *J* = 3.8 Hz, 1F), -163.0 (m, 2F).

[C₆F₅Cp][1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-iminato]TiCl₂: To a toluene solution of [C₆F₅Cp]TiCl₃ (0.2g, 0.4 mmol) was added [1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-iminato]trimethylsilane (0.2g,
 25 0.4mmol) at -40°C. The solution was then stirred for 16 hours while warming to room

temperature. All toluene was pumped off and the solid washed with pentane. The complex was precipitated from toluene:pentane (5:45ml), filtered and dried to give the product as a yellow solid, 0.2 g (64%). ^1H NMR (toluene- d_8 , δ): 7.35-6.88 (m, 6H), 6.65-6.47 (m, 2H), 5.81 (s, 2H), 5.72-5.65 (m, 2H), 3.03-2.76 (sep., 4H), 1.50-1.36 (d, 12H) and 1.12-0.99 (d, 12H).

The aluminoxane was a 10% MAO solution in toluene supplied by Albemarle.

The support was silica SYLOPOL 2408 obtained from W.R. Grace.

Preparation of the Support (apart from the control)

A 10 % aqueous solution of the $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ was prepared and impregnated into the support by incipient wetness impregnation procedure. The solid support was dried in air at about 135°C to produce a free flowing powder. The resulting powder was subsequently dried in air at 200°C for about 2 hours under air and then under nitrogen at 600°C for 6 hours.

NAA Characterization: A sample of $\text{Zr}(\text{SO}_4)_2$ treated SYLOPOL 2408 prepared as above was determined to have a sulfur:zirconium ratio of 0.703 by NAA analysis, which is consistent with the ratio expected for pure $\text{Zr}(\text{SO}_4)_2$.

XRD Analysis: A 1 gram sample of pure $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ was dehydrated in a muffle furnace at 600°C for 6 hours and the solid was analyzed by XRD analysis, which showed 100% of the $\text{Zr}(\text{SO}_4)_2$ remained.

The above shows that zirconia is not formed by the calcination process of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ at up to 600°C under nitrogen.

To a slurry of calcined support in toluene was added a toluene solution of 10 wt% MAO (4.5 wt% Al, purchased from Albemarle) plus rinsings (3 x 5 mL). The resultant slurry was mixed using a shaker for 1 hour at ambient temperature. The slurry was filtered, rinsed with toluene, pentane (2x), and dried to 400mTorr. To a slurry of

MAO-on-support is added a toluene solution of catalyst to give a molar ratio of Al:Ti of 120:1. After two hours of mixing at room temperature using a shaker, the slurry was filtered, yielding a colorless filtrate. The solid component was washed with toluene, and pentane (2x), then ~ 400 mTorr and sealed under nitrogen until use.

5 Polymerization

A 2L reactor fitted with a stirrer (~650 rpm) containing a NaCl seed bed (160g) (stored for at least 3 days at 130°C) was conditioned for 30 minutes at 105°C. An injection tube loaded in the glovebox containing the catalyst formulation was inserted into the reactor system, which was then purged 3 times with nitrogen and once with ethylene at 200 psi. Pressure and temperature were reduced in the reactor (below 2 psi and between 60 and 85°C) and TIBAL (500:1 Al:Ti) was injected *via* gastight syringe followed by a 2 mL precharge of 1-hexene. After the reactor reached 85°C the catalyst was injected via ethylene pressure and the reactor was pressurized to 200 psi total pressure with 1-hexene fed with a syringe pump at a mole ratio of 6.5% C₆/C₂ started 1 minute after catalyst injection. The temperature of reaction was controlled at 90°C for a total runtime of 60 minutes. Reaction was halted by stopping the ethylene flow and turning on reactor cooling water. The reactor was vented slowly to minimize loss of contents and the polymer / salt mixture was removed and allowed to air dry before being weighed. The results of the experiments are set forth in Table 1 below.

20

TABLE 1

Support	Al:Ti Molar ratio	Productivity gPE/g catalyst	Max C ₂ Flow	Time to Max Flow	Rate of Rise scLM/min	Max height 1-10 /Average C ₂ concentration
SYLOPOL 2408 – Zr(SO ₄) ₂	120:1	1467	1.16	3.02	0.38	1.73
SYLOPOL 2408	120:1	1313	1.64	4.56	0.36	2.99

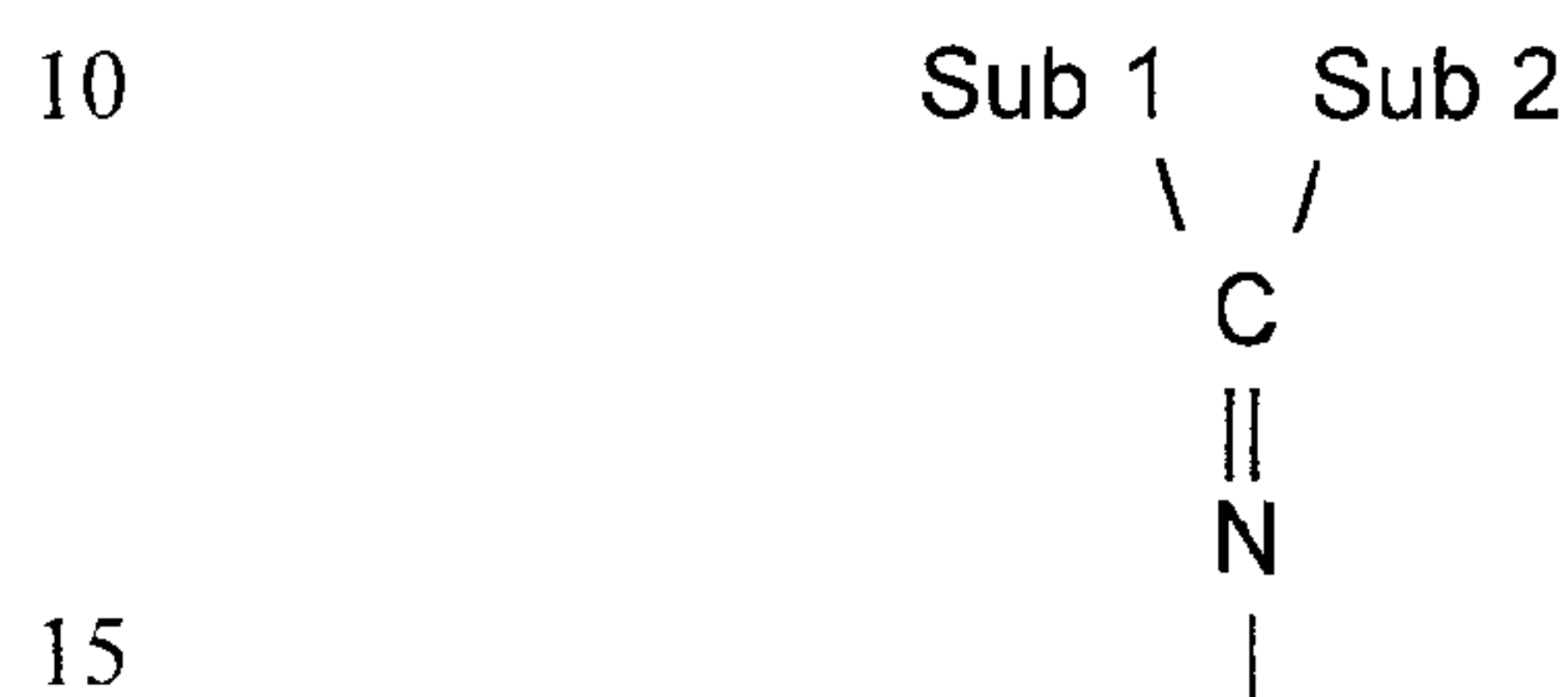
The results show an increased productivity of the catalyst on the support treated with $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The ratio of maximum peak height in the first 10 minutes to the average peak height for 10 to 60 minutes for the treated support was lower. There is a lower "light off" temperature even though it may have occurred earlier.

5

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A catalyst comprising an organo group 4 metal complex containing a ketimide ligand and a calcined silica support impregnated with not less than 1 weight % of Zr (SO₄)₂ to provide from 0.010 to 0.50 mmol of Zr from the sulphate per gram of impregnated support.

2. The catalyst according to claim 1, wherein the ketimide ligand has the formula:



wherein Sub 1 and Sub 2 are independently selected from the group consisting of C₁₋₂₀ hydrocarbyl radicals which are unsubstituted or may be substituted by up to 4 hetero atoms selected from the group consisting of N, O, and S or up to three C₁₋₉ straight chain, branched, cyclic or aromatic radicals which may be unsubstituted or substituted by a C₁₋₆ alkyl radical or Sub 1 and Sub 2 taken together may form a saturated or unsaturated ring which may be substituted by up to 4 hetero atoms selected from the group consisting of N, O, and S and which ring may be further substituted by up to three C₁₋₉ straight chain, branched, cyclic or aromatic radicals which may be unsubstituted or substituted by one or more C₁₋₆ alkyl radicals.

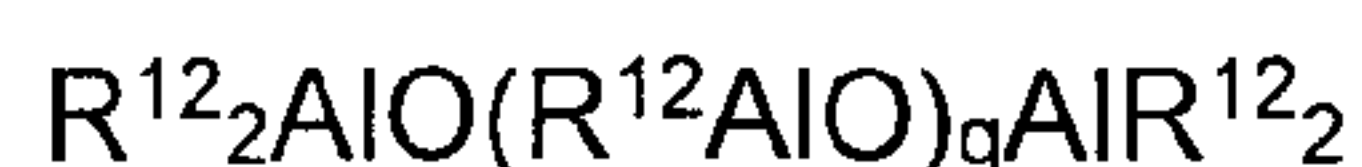
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3. The catalyst according to claim 2, wherein the organo group 4 metal complex has the the formula:



wherein M is a group 4 metal having an atomic number less than 72, L is a
monoanionic ligand selected from the group consisting of a cyclopentadienyl-type
ligand, K is the ketimide ligand, Y is independently selected from the group consisting
of activatable ligands, m is 0 or 1, n is 1 or 2, o is an integer and the sum of m+n+o
5 equals the valence state of M.

4. The catalyst according to claim 3, wherein the support further comprises an
activator of the formula:



10 wherein each R^{12} is independently selected from the group consisting of C_{1-20}
hydrocarbyl radicals and q is from 3 to 50 to provide from 50 to 500 parts by weight per
part by weight of group 4 metal from the ketimide containing catalyst.

5. The catalyst according to claim 4, wherein L is selected from the group
15 consisting of a cyclopentadienyl radical, an indenyl radical and a fluorenyl radical which
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
more fluorine atoms.

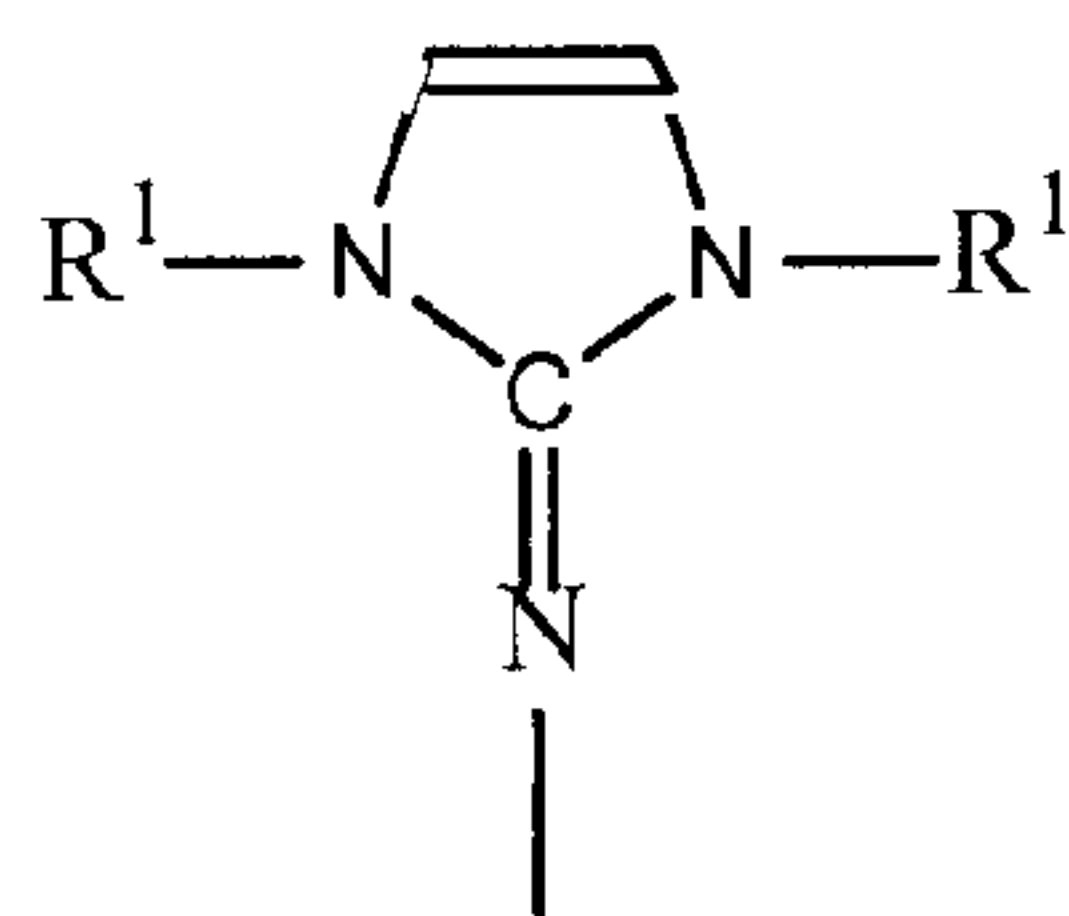
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6. The catalyst according to claim 5, wherein Y is selected from the group
consisting of consisting of a chlorine atom, a methyl radical, an ethyl radical and a
benzyl radical.

7. The catalyst according to claim 6, wherein in the activator R^{12} is a C_{1-4} alkyl radical and q is from 10 to 40.
8. The catalyst according to claim 7, wherein the molar ratio of aluminum from the activator to group 4 transition metal is from 10:1 to 500:1.
9. The catalyst according to claim 8, comprising from 50 to 250 ppm based on the weight of the supported catalyst of an antistatic 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 C_{6-20} α 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 C_{1-15} 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 anhydride;
 - (ii) from 3 to 48 parts by weight of one or more polymeric polyamines of the formula:

$$RN[(CH_2CHOHCH_2NR^1)_a-(CH_2CHOHCH_2NR^1-R^2-NH)_b-(CH_2CHOHCH_2NR^3)_c-H]_xH_{2-x}$$
 wherein R^1 is an aliphatic hydrocarbyl group of 8 to 24 carbon atoms; R^2 is an alkylene group of 2 to 6 carbon atoms; R^3 is the group R^2-HNR^1 ; R is R^1 or an N-aliphatic hydrocarbyl alkylene group having the formula R^1NHR^2 ; a, b and c are integers from 0 to 20 and x is 1 or 2; with the proviso that when R is R^1 then a is greater than 2 and $b = c = 0$, and when R is R^1NHR^2 then a is 0 and the sum of $b+c$ is an integer from 2 to 20; and
 - (iii) from 3 to 48 parts by weight of C_{10-20} alkyl or arylalkyl sulphonic acid.

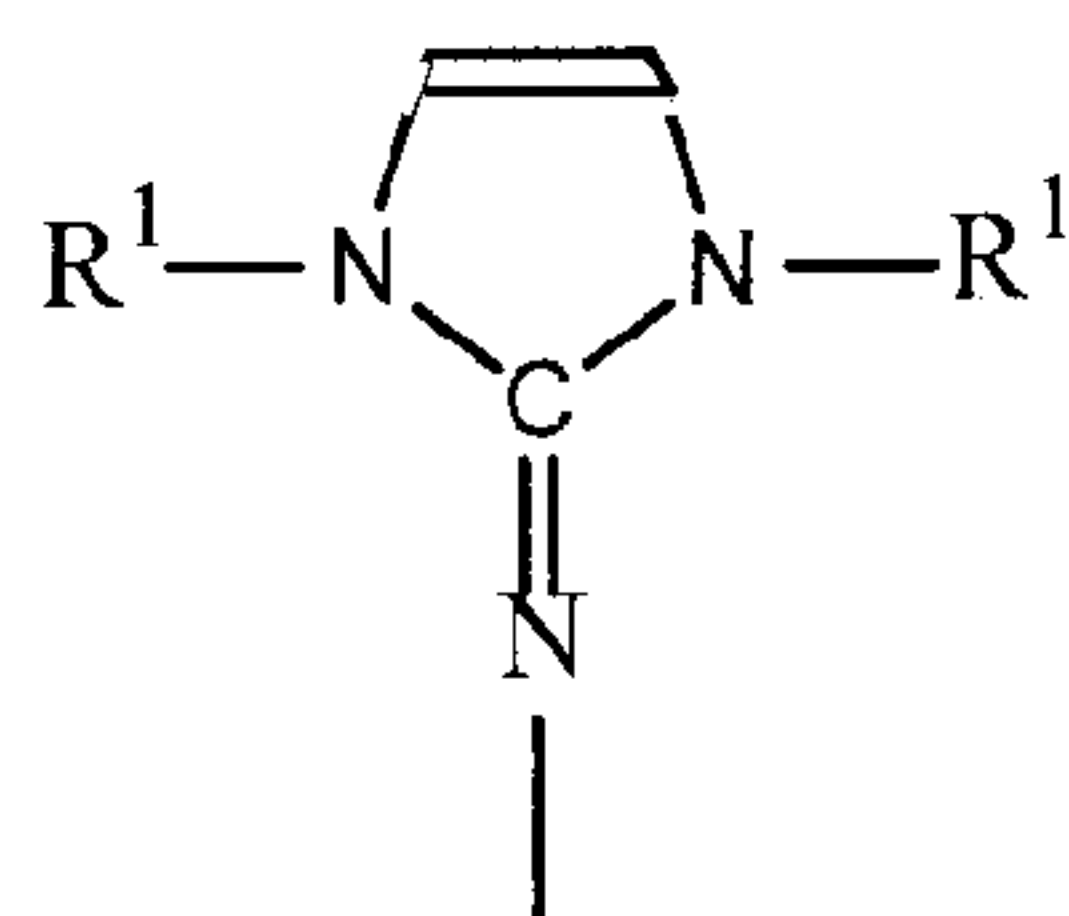
10. The catalyst according to claim 8, wherein the ketimide ligand has the formula:



wherein each R¹ is independently selected from the group consisting of a phenyl radical which is unsubstituted or substituted by up to three C₁₋₄ alkyl radicals

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11. The catalyst according to claim 9, wherein the ketimide ligand has the formula:



wherein each R¹ is independently selected from the group consisting of a phenyl radical which is unsubstituted or substituted by up to three C₁₋₄ alkyl radicals.

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12. A disperse phase polymerization process comprising contacting one or more C₂₋₈ alpha olefins with a catalyst according to claim 10 and feeding to a polymerization reactor from 10 to 80 ppm based on the weight of the polymer produced of an antistatic comprising:

- 15 (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 anhydride;

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



5 wherein R^1 is an aliphatic hydrocarbyl group of 8 to 24 carbon atoms; R^2 is an alkylene group of 2 to 6 carbon atoms; R^3 is the group R^2-HNR^1 ; R is R^1 or an N-aliphatic hydrocarbyl alkylene group having the formula R^1NHR^2 ; a, b and c are integers from 0 to 20 and x is 1 or 2; with the proviso that when R is R^1 then a is greater than 2 and b = c = 0, and when R is R^1NHR^2 then a is 0 and the sum of b+c is an integer from 2 to 20;

10 and

(iii) from 3 to 48 parts by weight of C_{10-20} alkyl or arylalkyl sulphonic acid.

13. A disperse phase polymerization process comprising contacting one or more C_{2-8} alpha olefins with a catalyst according to claim 10.

FIGURE 1

