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(54) Title: ADDITIVE FOR GAS PHASE POLYMERIZATION PROCESSES

(57) Abstract: A polymerization process including: polymerizing at least one olefin to form an olefin based polymer in a gas phase polymerization reactor; and feeding at least one polysulfone additive system to the polymerization reactor, wherein the polysulfone additive system includes a polysulfone copolymer, a polymeric polyamine, and an oil-soluble sulfonic acid.



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ADDITIVE FOR GAS PHASE POLYMERIZATION PROCESSES

CROSS REFERENCE TO RELATED CASE

[0001] This application claims the benefit of U.S. provisional application Serial No. 61/204,616, filed January 8, 2009, the disclosure of which is incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] Embodiments disclosed herein relate generally to the use of additives in polymerization processes. More specifically, embodiments disclosed herein relate to the use of additive systems comprising a polysulfone copolymer, a polymeric polyamine, and an oil-soluble sulfonic acid. The additive systems are suitable for use in the manufacture of ethylene-based and propylene-based polymers for food contact applications.

BACKGROUND

[0003] Metallocene catalysts allow the production of polyolefins with unique properties such as narrow molecular weight distribution. These properties in turn result in improved structural performance in products made with the polymers, such as greater impact strength and clarity in films. While metallocene catalysts have yielded polymers with improved characteristics, they have presented new challenges when used in traditional polymerization systems.

[0004] For example, when metallocene catalysts are used in fluidized bed reactors, "sheeting" and the related phenomena "drooling" may occur. See U.S. Patent Nos. 5,436,304 and 5,405,922. "Sheeting" is the adherence of fused catalyst and resin particles to the walls of the reactor. "Drooling" or dome sheeting occurs when sheets of molten polymer form on the reactor walls, usually in the expanded section or "dome" of the reactor, and flow along the walls of the reactor and accumulate at the base of the reactor. Dome sheets are typically formed much higher in the reactor, on the conical section of the dome, or on the hemi-spherical head on the top of the reactor.

[0005] Sheeting and drooling may be a problem in commercial gas phase polyolefin production reactors if the risk is not properly mitigated. The problem is characterized by the formation of large, solid masses of polymer on the walls of the reactor. These solid masses or polymer (the sheets) may eventually become dislodged from the walls and fall into the reaction section, where they may interfere with fluidization, block the product discharge port, and usually force a reactor shut-down for cleaning.

[0006] Various methods for controlling sheeting have been developed. These often involve monitoring the static charges near the reactor wall in regions where sheeting is known to

develop and introducing a static control agent into the reactor when the static levels fall outside a predetermined range. For example, U.S. Patent Nos. 4,803,251 and 5,391,657 disclose the use of various chemical additives in a fluidized bed reactor to control static charges in the reactor. A positive charge generating additive is used if the static charge is negative, and a negative charge generating additive is used if the static charge is positive.

[0007] U.S. Patent Nos. 4,803,251 and 5,391,657 disclose that static plays an important role in the sheeting process with Ziegler-Natta catalysts. When the static charge levels on the catalyst and resin particles exceed certain critical levels, the particles become attached by electrostatic forces to the grounded metal walls of the reactor. If allowed to reside long enough on the wall under a reactive environment, excess temperatures can result in particle sintering and melting, thus producing the sheets or drools.

[0008] U.S. Patent No. 4,532,311 discloses the use of a reactor static probe (the voltage probe) to obtain an indication of the degree of electrification of the fluid bed. U.S. Patent No. 4,855,370 combined the static probe with addition of water to the reactor (in the amount of 1 to 10 ppm of the ethylene feed) to control the level of static in the reactor. This process has proven effective for Ziegler-Natta catalysts, but has not been effective for metallocene catalysts.

[0009] For conventional catalyst systems such as traditional Ziegler-Natta catalysts or chromium-based catalysts, sheet formation usually occurs in the lower part of the fluidized bed. Formation of dome sheets rarely occurs with Ziegler-Natta catalysts. For this reason, the static probes or voltage indicators have traditionally been placed in the lower part on the reactor. For example, in U.S. Patent No. 5,391,657, the voltage indicator was placed near the reactor distributor plate. See also U.S. Patent No. 4,855,370. The indicators were also placed close to the reactor wall, normally less than 2 cm from the wall.

[0010] U.S. Patent No. 6,548,610 describes a method of preventing dome sheeting (or "drooling") by measuring the static charge with a Faraday drum and feeding static control agents to the reactor as required to maintain the measured charge within a predetermined range. Conventional static probes are described in U.S. Patent Nos. 6,008,662, 5,648,581, and 4,532,311. Other background references include WO 99/61485, WO 2005/068507, EP 0 811 638 A, EP 1 106 629 A, and U.S. Patent Application Publication Nos. 2002/103072 and 2008/027185.

[0011] As a result of the risks associated with reactor discontinuity problems when using metallocene catalysts, various techniques have been developed that are said to result in improved operability. For example, various supporting procedures or methods for producing a metallocene catalyst system with reduced tendencies for fouling and better operability have been discussed in

U.S. Patent No. 5,283,278, which discloses the prepolymerization of a metallocene catalyst. Other supporting methods are disclosed in U.S. Patent Nos. 5,332,706 and 5,473,028 5,427,991, 5,643,847 5,492,975, 5,661,095, and PCT publications WO 97/06186, WO 97/15602, and WO 97/27224.

[0012] Others have discussed different process modifications for improving reactor continuity with metallocene catalysts and conventional Ziegler-Natta catalysts. See, PCT publications WO 96/08520, WO 97/14721, U.S. Patent Nos. 5,627,243, 5,461,123, 5,066,736, 5,610,244, 5,126,414 and EP-A1 0 549 252. There are various other known methods for improving operability including coating the polymerization equipment, controlling the polymerization rate, particularly on start-up, and reconfiguring the reactor design and injecting various agents into the reactor.

[0013] With respect to injecting various agents into the reactor, antistatic agents and process “continuity additives” have been the subject of various publications. For example, EP 0 453116 discloses the introduction of antistatic agents to the reactor for reducing the amount of sheets and agglomerates. U.S. Patent No. 4,012,574 discloses adding a surface-active compound having a perfluorocarbon group to the reactor to reduce fouling. WO 96/11961, discloses an antistatic agent for reducing fouling and sheeting in a gas, slurry or liquid pool polymerization process as a component of a supported catalyst system. U.S. Patent Nos. 5,034,480 and 5,034,481 disclose a reaction product of a conventional Ziegler-Natta titanium catalyst with an antistatic agent to produce ultrahigh molecular weight ethylene polymers. For example, WO 97/46599 discloses the use of soluble metallocene catalysts in a gas phase process utilizing soluble metallocene catalysts that are fed into a lean zone in a polymerization reactor to produce stereoregular polymers. WO 97/46599 also discloses that the catalyst feedstream can contain antifoulants or antistatic agents such as ATMER 163 (commercially available from ICI Specialty Chemicals, Baltimore, Md.). Many of these references refer to anti-static agents but in most cases the static is never totally eliminated. Rather it is reduced to an acceptable level by generating a charge opposite that which currently exists in the polymerization system. In this sense, these “anti-static” agents are really “pro-static” agents that generate a countervailing charge that reduces the net static charge in the reactor. Herein we will refer to these compounds as static control agents.

[0014] Several of the above-mentioned references disclose the use of static control agents that, when introduced into a fluidized bed reactor, may influence or drive the static charge in the fluidized bed in a desired direction. Depending upon the static control agent used, the resulting static charge in the fluidized bed may be negative, positive, or a neutral charge. Static control

agents, for example, may include positive charge generating species such as MgO, ZnO, CuO, alcohols, oxygen, nitric oxide, and negative charge generating species such as V₂O₅, SiO₂, TiO₂, Fe₂O₃, water, and ketones. Other static control agents are also disclosed in EP 0229368 and U.S. Patent Nos. 5,283,278, 4,803,251, and 4,555,370, among others. As described in U.S. Patent Application Publication No. 2008/027185, aluminum stearate, aluminum distearate, ethoxylated amines, OCTASTAT 2000, a mixture of a polysulfone copolymer, polymeric polyamine, and oil-soluble sulfonic acid, as well as mixtures of carboxylated metal salts with amine-containing compounds, such as those sold under the trade names KEMAMINE and ATMER, may also be used to control static levels in a reactor. Various other static control agents are disclosed in U.S. Patent Application Publication No. 20050148742.

[0015] U.S. Patent No. 5,026,795, discloses the addition of an antistatic agent with a liquid carrier to the polymerization zone in a gas phase polymerization reactor. Preferably, the antistatic agent is mixed with a diluent and introduced into the reactor by a carrier comprising the comonomer. The preferred antistatic agent disclosed is a mixture, which was marketed under the trademark STADIS 450 by Octel Starreon (currently available as OCTASTAT 3000 from Innospec Inc.) and which contains a polysulfone, a polymeric polyamine, a sulfonic acid, and toluene. The amount of antistatic agent is disclosed to be very important. Specifically, there must be sufficient antistatic agent to avoid adhesion of the polymer to the reactor walls, but not so much that the catalyst is poisoned. U.S. Patent No. 5,026,795 also discloses that the amount of the preferred antistatic agent is in the range of about 0.2 to 5 parts per million by weight (ppmw) of polymer produced; however, no method for optimizing the level of antistatic agent is disclosed based on measurable reactor conditions. Various other references discussing use of OCTASTAT 2000, OCTASTAT 2500, and OCTASTAT 3000 (STADIS 425 and STADIS 450) may include U.S. Patent Nos. 7,205,363, 6,646,074, 6,894,127, 6,857,322, 6,639,028, 6,562,924, 6,518,385, 6,462,161, 6,998,440, 5,283,278, and 5,414,064, U.S. Patent Application Publication No. 2008/0161510, and PCT Publication Nos. WO2007/131646, WO2007/131645, and WO2007/137396.

[0016] Static control agents, including several of those described above, may result in reduced catalyst productivity. The reduced productivity may be as a result of residual moisture in the additive. Additionally, reduced productivity may result from interaction of the polymerization catalyst with the static control agent, such as reaction or complexation with hydroxyl groups in the static control agent compounds. Depending upon the static control agent used and the required amount of the static control agent to limit sheeting, loss in catalyst activities of 40% or more have been observed.

[0017] Additionally, continuity additives as formulated and as available, may include various components used as solvents or as residual components from production. For example, OCTASTAT 3000 (formerly STADIS 450) includes a polysulfone, a polymeric polyamine, a sulfonic acid, in a solvent / carrier fluid including toluene, light alcohols such as isopropanol and methanol, naphtha, and naphthalene. Such an admixture, however, does not meet regulatory approval for use in products that come into contact with food.

[0018] Changes in continuity additive formulation to meet food-grade regulatory requirements are possible, such as by changing solvents and carrier fluids. It cannot be predicted, however, if and how changes to the continuity additive formulation will affect various polymerization processes and catalysts. For example, although “active” ingredients in continuity additive formulations may remain similar, replacement of some compounds, including toluene and alcohols, which themselves may have a charge characteristic (antistatic effect), may result in an unpredictable change in how the continuity additive formulation impacts reactor performance. Changes in solvents and carrier fluids, for example, may inadvertently change the interaction of the continuity additive system, as a whole, with reactor components (metals and coatings) and with the polymers produced. With regard to fluidized bed gas-phase reactor performance, changing solvents and carrier fluids may additionally result in unpredictable changes to reactor operations, such as when operating in the condensed mode.

[0019] Further, it cannot be predicted how changes in the continuity additive formulation may result in increased interaction with various catalysts due to the presence of new compounds in the formulation or the absence of previously used compounds. For example, changing various compounds may unpredictably affect catalyst activity, productivity, and performance, especially for specialty catalysts, such as bimetallic catalysts.

[0020] Accordingly, there exists a need for additives suitable for contact with food and useful, for example, for the control of static levels, and thus sheeting, in a fluidized bed reactor, especially for use with, for example, bimetallic catalyst systems and for use in, for example, gas-phase polymerization processes operating in a condensed mode.

SUMMARY

[0021] Disclosed herein is a polymerization process that includes: polymerizing at least one olefin to form an olefin based polymer in a gas phase polymerization reactor and feeding at least one polysulfone additive system to the polymerization reactor, wherein the polysulfone additive system includes: a polysulfone copolymer; a polymeric polyamine; an oil-soluble sulfonic acid;

and a carrier fluid including at least one of pentane, hexane, heptane, and a food grade oil. The gas phase polymerization reactor may be operating in a condensed mode. The process may further comprise feeding a bimetallic catalyst to the polymerization reactor.

[0022] Also disclosed herein is a process for copolymerizing ethylene and one or more alpha olefins in a gas phase reactor, including: combining ethylene and one or more of 1-butene, 1-hexene, or 1-octene in the presence of a bimetallic catalyst comprising at least one metallocene, an activator and a support; monitoring static in said reactor by at least one recycle line static probe, at least one upper bed static probe, at least one annular disk static probe, or at least one distributor plate static probe; maintaining the static at a desired level by use of at least one polysulfone additive system including: a polysulfone copolymer; a polymeric polyamine; an oil-soluble sulfonic acid; and at least one of pentane, hexane, heptane, and a food grade oil, the polysulfone additive system being present in said reactor in the range from about 0.1 to about 50 ppm, based on the weight of polymer produced by said combining.

DETAILED DESCRIPTION

[0023] Before the present compounds, components, compositions, and/or methods are disclosed and described, it is to be understood that unless otherwise indicated this invention is not limited to specific compounds, components, compositions, reactants, reaction conditions, ligands, metallocene structures, or the like, as such may vary, unless otherwise specified. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

[0024] It must also be noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless otherwise specified.

[0025] Embodiments disclosed herein relate generally to use of polysulfone additive systems in polymerization processes, such as those for the production of ethylene-based and propylene-based polymers. More specifically, embodiments disclosed herein relate to the use of polysulfone additive systems comprising a polysulfone copolymer, a polymeric polyamine, and oil-soluble sulfonic acid suitable for use in the manufacture of ethylene-based and propylene-based polymers for food contact applications. Such additive systems may be useful, for example, where the polymerization is catalyzed by a metallocene catalyst or by a bimetallic catalyst and/or during polymerization in a condensed mode of operation. In some embodiments, the additive systems may be added to a polymerization reactor to control static levels in the reactor, preventing, reducing, or reversing sheeting, drooling and other discontinuity events resulting from excessive static levels.

Polysulfone Additive Systems for use in Food Contact Polymer Products

[0026] Polysulfone additive systems, suitable for use in the production of polymers for food contact applications and end products, may include compositions including a mixture of a polysulfone copolymer, a polymeric polyamine, and oil-soluble sulfonic acid, in a carrier fluid. The carrier fluid (solvent) may include a light hydrocarbon, such as pentane, hexane, or heptane, including the various isomers of each. Other compounds used in the carrier fluid may include various oils, such as those approved for food contact.

[0027] The polysulfone copolymer component of the additive system (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 percent (mol%) of units of sulfur dioxide, about 40 to 50 mol% of units derived from one or more 1-alkenes each having from about 6 to 24 carbon atoms, and from about 0 to 10 mol% of units derived from an olefinic compound having the formula $ACH=CHB$ where A is a group having the formula $-(C_xH_{2x})-COOH$ wherein x is from 0 to about 17, and B is hydrogen or carboxyl, with the proviso that when B is carboxyl, x is 0, and wherein A and B together can be a dicarboxylic anhydride group.

[0028] Preferably, the polysulfone copolymer has a weight average molecular weight in the range of 10,000 to 1,500,000, preferably in the range of 50,000 to 90,000. 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, and 5-hexenoic acid.

[0029] 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.

[0030] Further details of suitable polysulfones may be found in U.S. Patent Nos. 3,811,848, 3,917,466, 6,894,127, and 7,476,715, and in GB 1432265A and GB 1432266A.

[0031] The polymeric polyamine component of the additive system is preferably a polymeric polyamine having the general formula:



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 of 0-20 and x is 1 or 2, with the proviso that when R is R^1 then a is an integer of 2 to 20 and $b=c=0$, and when R is R^1NHR^2- then a is 0 and $b+c$ is an integer of 2 to 20.

[0032] Exemplary polymeric polyamine components are described in U.S. Patent No. 3,917,466, particularly at Column 6 Line 42 to Column 9 Line 29.

[0033] The polymeric polyamine component may be 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 preferred polymeric polyamine is a 1:1:5 mole ratio reaction product of N-tallow-1,3-diaminopropane with epichlorohydrin.

[0034] The oil-soluble sulfonic acid component of the additive system 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

[0035] Preferred oil-soluble sulfonic acids are dodecylbenzene-sulfonic acid and dinonylnaphthylsulfonic acid. In a preferred embodiment, the oil-soluble sulfonic acid component of the additive system is dodecylbenzene sulfonic acid.

[0036] The polysulfone additive system preferably comprises 1 to 25 wt% of the polysulfone copolymer, 1 to 25 wt% of the polymeric polyamine, 1 to 25 wt% of the oil-soluble sulfonic acid, and 25 to 95 wt% of the carrier fluid. In some embodiments, the additive system comprises from about 10 to about 30 wt% of the polysulfone copolymer, from about 1 to about 10 wt% of the polymeric polyamine, from about 5 to about 10 wt% of the oil-soluble sulfonic acid, and from about 30 to about 85 wt% of the carrier fluid.

[0037] In some embodiments, the polysulfone additive system may comprise 1 wt.% to 10 wt.% of the polymeric polyamine; 10 wt.% to 30 wt.% of the polysulfone copolymer; 5 wt.% to 10 wt.% of the oil-soluble sulfonic acid; and 40 wt.% to 80 wt.% of the at least one of pentane, hexane, and heptane. The polysulfone additive system may further comprises 1 wt.% to 10 wt.% of the food grade oil.

[0038] In some embodiments, the polysulfone additive system comprises, 12 to 25 wt% of the polysulfone copolymer, from about 2 to about 8 wt% of the polymeric polyamine, and from

about 5 to about 10 wt% of the oil-soluble sulfonic acid, and from about 35 wt% to about 85wt% of the light hydrocarbon, and from about 2 wt% to about 10 wt% of the food grade oil.

[0039] As used herein, “food grade oil” may refer to any oil, for example, a petroleum-derived mineral oil, that is intended for internal human consumption. It is used as a food additive and as a lubricant in enema preparations. In some embodiments, the sulphonic acid may include one or more of dodecylbenzene sulphonic acid (DDBSA) and dinonylnaphthylsulphonic acid (DINNSA).

[0040] In some embodiments, the polysulfone additive systems suitable for use in the production of polymers for food contact applications and end products may be essentially free of aromatic hydrocarbons, such as toluene, xylenes, and the like. Additionally, polysulfone additive systems suitable for use in the production of polymers for food contact applications and end products may be essentially free of alcohols, such as methanol, isopropanol, and other light (C_1 to C_6) alcohols. In some embodiments, polysulfone additive systems according to embodiments disclosed herein may contain less than 0.2 wt.% of a combined amount of toluene, xylenes, methanol, and isopropanol. In other embodiments, polysulfone additive systems according to embodiments disclosed herein may contain less than 0.1 wt.% of a combined amount of toluene, xylenes, methanol, and isopropanol; less than 0.05 wt.% in other embodiments; and less than 0.01 wt.% in yet other embodiments.

[0041] The polysulfone additive system may be fed to polymerization reactors as a solution or as a slurry, thus providing an effective transport medium. As formulated above, the additive system may be diluted in, for example, mineral oil or a light hydrocarbon, such as isopentane or heptane, prior to being fed to a polymerization reactor.

[0042] In some embodiments, the polysulfone additive system may comprises 1 to 10 wt% of the polymeric polyamine, 10 to 30 wt% of the polysulfone copolymer, 5 to 10 wt% of the oil-soluble sulfonic acid, 50 to 80 wt% of the light hydrocarbon, and from 1 to 10% of the food grade oil. The polymeric polyamine may be derived from a vegetable oil. The oil-soluble sulfonic acid may be dodecylbenzene sulphonic acid. The light hydrocarbon may be heptane. The polysulfone additive system may compress less than 0.1 wt% of toluene, and less than 0.1 wt% of iso-propanol, and less than 0.1 wt% of methanol.

[0043] The amount of polysulfone additive system added to the reactor system may depend upon the catalyst system used, as well as reactor pre-conditioning (such as coatings to control static buildup) and other factors known to those skilled in the art. In some embodiments, the polysulfone additive system may be added to the reactor in an amount ranging from 0.01 to 200 ppmw, based on polymer production rate. In other embodiments, the polysulfone additive

system may be added to the reactor in an amount ranging from 0.02 to 100 ppmw; or from 0.05 to 50 ppmw; or from 1 to 40 ppmw. In other embodiments, the polysulfone additive system may be added to the reactor in an amount of 2 ppmw or greater, based on polymer production rate. Other suitable ranges for the polysulfone additive system, based on the polymer production weight include lower limits of greater than or equal to 0.01, 0.02, 0.05, 0.1, 0.5, 1, 2, 3, 4, 5, 10, 12, 15, and upper limits of less than or equal to 200, 150, 100, 75, 50, 40, 30, 25, 20, where the ranges are bounded by any lower and upper limit described above.

[0044] In some embodiments, polysulfone additive systems may be used as or in a reactor coating emplaced during or prior to conducting polymerization reactions within the reactor. In other embodiments, the polysulfone additive system may interact with the particles and other components in the fluidized bed, reducing or neutralizing static charges related to frictional interaction of the catalyst, polymer particles, and reactor vessel.

Continuity Additives

[0045] In addition to the polysulfone additive systems described above, it may also be desired to additionally use one or more additional continuity additives to aid in regulating static levels in the reactor. "Continuity additives" as used herein also includes chemical compositions commonly referred to in the art as "static control agents." Such additional continuity additives, however, should be appropriately selected when used for the production of a product for food contact applications. Due to the enhanced performance of the reactor systems and catalysts that may result via use of a polysulfone additive system as described above, static control agents may be used at a lower concentration in polymerization reactors as compared to use of static control agents alone. Thus, the impact the static control agents have on catalyst productivity may not be as substantial when used in conjunction with polysulfone additive systems according to embodiments disclosed herein.

[0046] As used herein, a static control agent is a chemical composition which, when introduced into a fluidized bed reactor, may influence or drive the static charge (negatively, positively, or to zero) in the fluidized bed. The specific static control agent used may depend upon the nature of the static charge, and the choice of static control agent may vary dependent upon the polymer being produced and the catalyst being used. For example, the use of static control agents is disclosed in European Patent No. 0229368 and U.S. Patent No. 5,283,278.

[0047] For example, if the static charge is negative, then static control agents such as positive charge generating compounds may be used. Positive charge generating compounds may include

MgO, ZnO, Al₂O₃, and CuO, for example. In addition, alcohols, oxygen, and nitric oxide may also be used to control negative static charges. See, U.S. Patent Nos. 4,803,251 and 4,555,370.

[0048] For positive static charges, negative charge generating inorganic chemicals such as V₂O₅, SiO₂, TiO₂, and Fe₂O₃ may be used. In addition, water or ketones containing up to 7 carbon atoms may be used to reduce a positive charge.

[0049] In some embodiments, when catalysts such as, metallocene catalysts, are used in a circulating fluidized bed reactor, continuity additives such as aluminum stearate may also be employed. The continuity additive used may be selected for its ability to receive the static charge in the fluidized bed without adversely affecting productivity. Suitable static control agents may also include aluminum distearate and ethoxlated amines.

[0050] Any of the aforementioned continuity additives, as well as those described in, for example, WO 01/44322, listed under the heading Carboxylate Metal Salt and including those chemicals and compositions listed as antistatic agents may be employed either alone or in combination as an additional continuity additive. For example, the carboxylate metal salt may be combined with an amine containing control agent (*e.g.*, a carboxylate metal salt with any family member belonging to the KEMAMINE (available from Crompton Corporation) or ATMER (available from ICI Americas Inc.) family of products).

[0051] Other additional continuity additives useful in embodiments disclosed herein are well known to those in the art. Regardless of which continuity additives are used, care should be exercised in selecting appropriate continuity additives to avoid introduction of poisons into the reactor. In addition, in selected embodiments, the smallest amount of the continuity additives necessary to bring the static charge into alignment with the desired range should be used.

[0052] In some embodiments, continuity additives may be added to the reactor as a combination of two or more of the above listed continuity additives, or a combination of an continuity additive and a polysulfone additive system according to embodiments disclosed herein. In other embodiments, continuity additive(s) may be added to the reactor in the form of a solution or a slurry, and may be added to the reactor as an individual feed stream or may be combined with other feeds prior to addition to the reactor. For example, the continuity additives may be combined with the catalyst or catalyst slurry prior to feeding the combined catalyst-static control agent mixture to the reactor.

[0053] In some embodiments, continuity additives may be added to the reactor in an amount ranging from 0.05 to 200 ppmw, or from 2 to 100 ppmw or from 2 to 50 ppmw. In other embodiments, the static control agent may be added to the reactor in an amount of 2 ppmw or greater, based on polymer production rate.

Polymerization Process

[0054] Embodiments for producing polyolefin polymer disclosed herein may employ any suitable process for the polymerization of olefins, including any suspension, solution, slurry, or gas phase process, using known equipment and reaction conditions, and are not limited to any specific type of polymerization system. Generally, olefin polymerization temperatures may range from about 0 to about 300°C at atmospheric, sub-atmospheric, or super-atmospheric pressures. In particular, slurry or solution polymerization systems may employ sub-atmospheric, or alternatively, super-atmospheric pressures, and temperatures in the range of about 40 to about 300°C.

[0055] Liquid phase polymerization systems such as those described in U.S. Patent No. 3,324,095, may be used in some embodiments. Liquid phase polymerization systems generally comprise a reactor to which olefin monomers and catalyst compositions are added. The reactor contains a liquid reaction medium which may dissolve or suspend the polyolefin product. This liquid reaction medium may comprise an inert liquid hydrocarbon which is non-reactive under the polymerization conditions employed, the bulk liquid monomer, or a mixture thereof. Although such an inert liquid hydrocarbon may not function as a solvent for the catalyst composition or the polymer obtained by the process, it usually serves as solvent for the monomers used in the polymerization. Inert liquid hydrocarbons suitable for this purpose may include isobutane, isopentane, hexane, cyclohexane, heptane, octane, benzene, toluene, and mixtures and isomers thereof. Reactive contact between the olefin monomer and the catalyst composition may be maintained by constant stirring or agitation. The liquid reaction medium which contains the olefin polymer product and unreacted olefin monomer is withdrawn from the reactor continuously. The olefin polymer product is separated, and the unreacted olefin monomer and liquid reaction medium are typically recycled and fed back into the reactor.

[0056] Some embodiments of this disclosure may be especially useful with gas phase polymerization systems, at superatmospheric pressures in the range from 0.07 to 68.9 bar (1 to 1000 psig), from 3.45 to 27.6 bar (50 to 400 psig) in some embodiments, from 6.89 to 24.1 bar (100 to 350 psig) in other embodiments, and temperatures in the range from 30 to 130°C, or from 65 to 110°C, from 75 to 120°C in other embodiments, or from 80 to 120°C in other embodiments. In some embodiments, operating temperatures may be less than 112°C. Stirred or fluidized bed gas phase polymerization systems may be of use in embodiments.

[0057] Embodiments for producing polyolefin polymer disclosed herein may also employ a gas phase polymerization process utilizing a fluidized bed reactor. This type reactor, and means for operating the reactor, are well known and are described in, for example, U.S. Patent Nos.

3,709,853; 4,003,712; 4,011,382; 4,302,566; 4,543,399; 4,882,400; 5,352,749; 5,541,270; EP-A-0 802 202 and Belgian Patent No. 839,380. These patents disclose gas phase polymerization processes wherein the polymerization medium is either mechanically agitated or fluidized by the continuous flow of the gaseous monomer and diluent. As described above, the method and manner for measuring and controlling static charge levels may depend upon the type of reactor system employed.

[0058] Other gas phase processes contemplated include series or multistage polymerization processes. See U.S. Patent Nos. 5,627,242, 5,665,818 and 5,677,375, and European publications EP-A-0 794 200 EP-B1-0 649 992, EP-A-0 802 202 and EP-B-634 421.

[0059] In general, the polymerization process of the present invention may be a continuous gas phase process, such as a fluid bed process. A fluid bed reactor for use in the process of the present invention typically has a reaction zone and a so-called velocity reduction zone (disengagement zone). The reaction zone includes a bed of growing polymer particles, formed polymer particles and a minor amount of catalyst particles fluidized by the continuous flow of the gaseous monomer and diluent to remove heat of polymerization through the reaction zone. Optionally, some of the recirculated gases may be cooled and compressed to form liquids that increase the heat removal capacity of the circulating gas stream when readmitted to the reaction zone. A suitable rate of gas flow may be readily determined by simple experiment. Makeup of gaseous monomer to the circulating gas stream is at a rate equal to the rate at which particulate polymer product and monomer associated therewith is withdrawn from the reactor, and the composition of the gas passing through the reactor is adjusted to maintain an essentially steady state gaseous composition within the reaction zone. The gas leaving the reaction zone is passed to the velocity reduction zone where entrained particles are removed. Finer entrained particles and dust may be removed in a cyclone and/or fine filter. The gas is passed through a heat exchanger wherein the heat of polymerization is removed, compressed in a compressor and then returned to the reaction zone.

[0060] The process described herein is suitable for the production of homopolymers of olefins, including ethylene, and/or copolymers, terpolymers, and the like, of olefins, including polymers comprising ethylene and at least one or more other olefins. The olefins may be alpha-olefins. The olefins, for example, may contain from 2 to 16 carbon atoms in one embodiment. In other embodiments, ethylene and a comonomer comprising from 3 to 12 carbon atoms, or from 4 to 10 carbon atoms, or from 4 to 8 carbon atoms, may be used.

[0061] In embodiments, polyethylenes may be prepared by the process of the present invention. Such polyethylenes may include homopolymers of ethylene and interpolymers of ethylene and

at least one alpha-olefin wherein the ethylene content is at least about 50% by weight of the total monomers involved. Olefins that may be used herein include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 4-methylpent-1-ene, 1-decene, 1-dodecene, 1-hexadecene and the like. Also usable are polyenes such as 1,3-hexadiene, 1,4-hexadiene, cyclopentadiene, dicyclopentadiene, 4-vinylcyclohex-1-ene, 1,5-cyclooctadiene, 5-vinylidene-2-norbornene and 5-vinyl-2-norbornene, and olefins formed in situ in the polymerization medium. When olefins are formed in situ in the polymerization medium, the formation of polyolefins containing long chain branching may occur.

[0062] Other monomers useful in the process described herein include ethylenically unsaturated monomers, diolefins having 4 to 18 carbon atoms, conjugated or non-conjugated dienes, polyenes, vinyl monomers and cyclic olefins. Non-limiting monomers useful in the invention may include norbornene, norbornadiene, isobutylene, isoprene, vinylbenzocyclobutane, styrenes, alkyl substituted styrene, ethylidene norbornene, dicyclopentadiene and cyclopentene. In another embodiment of the process described herein, ethylene or propylene may be polymerized with at least two different comonomers, optionally one of which may be a diene, to form a terpolymer.

[0063] In one embodiment, the content of the alpha-olefin incorporated into the copolymer may be no greater than 30 mol % in total; from 3 to 20 mol % in other embodiments. The term "polyethylene" when used herein is used generically to refer to any or all of the polymers comprising ethylene described above.

[0064] In other embodiments, propylene-based polymers may be prepared by processes disclosed herein. Such propylene-based polymers may include homopolymers of propylene and interpolymers of propylene and at least one alpha-olefin wherein the propylene content is at least about 50% by weight of the total monomers involved. Comonomers that may be used may include ethylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 4-methylpentene-1, 1-decene, 1-dodecene, 1-hexadecene and the like. Also usable are polyenes such as 1,3-hexadiene, 1,4-hexadiene, cyclopentadiene, dicyclopentadiene, 4-vinylcyclohexene-1, 1,5-cyclooctadiene, 5-vinylidene-2-norbornene and 5-vinyl-2-norbornene, and olefins formed in situ in the polymerization medium. When olefins are formed *in situ* in the polymerization medium, the formation of polyolefins containing long chain branching may occur. In one embodiment, the content of the alpha-olefin comonomer incorporated into a propylene-based polymer may be no greater than 49 mol % in total; from 3 to 35 mol % in other embodiments.

[0065] Hydrogen gas is often used in olefin polymerization to control the final properties of the polyolefin. Increasing the concentration (partial pressure) of hydrogen may increase the melt flow index (MFI) and/or melt index (MI) of the polyolefin generated. The MFI or MI can thus

be influenced by the hydrogen concentration. The amount of hydrogen in the polymerization can be expressed as a mole ratio relative to the total polymerizable monomer, for example, ethylene, or a blend of ethylene and hexene or propylene. The amount of hydrogen used in the polymerization processes of the present invention is an amount necessary to achieve the desired MFI or MI of the final polyolefin resin. Melt flow rate for polypropylene may be measured according to ASTM D 1238 (230°C with 2.16 kg weight); melt index (I_2) for polyethylene may be measured according to ASTM D 1238 (190°C with 2.16 kg weight), for example.

[0066] Further, a staged reactor employing two or more reactors in series may be used, wherein one reactor may produce, for example, a high molecular weight component, and another reactor may produce a low molecular weight component. In one embodiment of the invention, the polyolefin is produced using a staged gas phase reactor. Such commercial polymerization systems are described in, for example, 2 METALLOCENE-BASED POLYOLEFINS 366-378 (John Scheirs & W. Kaminsky, eds. John Wiley & Sons, Ltd. 2000); U.S. Patent No. 5,665,818, U.S. Patent No. 5,677,375, and EP-A-0 794 200.

[0067] In one embodiment, the one or more reactors in a gas phase or fluidized bed polymerization process may have a pressure ranging from about 0.7 to about 70 bar (about 10 to 1000 psia), or from about 14 to about 42 bar (about 200 to about 600 psia). In one embodiment, the one or more reactors may have a temperature ranging from about 10°C to about 150°C, or from about 40°C to about 125°C. In one embodiment, the reactor temperature may be operated at the highest feasible temperature taking into account the sintering temperature of the polymer within the reactor. In one embodiment, the superficial gas velocity in the one or more reactors may range from about 0.2 to 1.1 meters/second (0.7 to 3.5 feet/second), or from about 0.3 to 0.8 meters/second (1.0 to 2.7 feet/second).

[0068] In one embodiment, the polymerization process is a continuous gas phase process that includes the steps of: (a) introducing a recycle stream (including ethylene and alpha olefin monomers) into the reactor; (b) introducing the supported catalyst system; (c) withdrawing the recycle stream from the reactor; (d) cooling the recycle stream; (e) introducing into the reactor additional monomer(s) to replace the monomer(s) polymerized; (f) reintroducing the recycle stream or a portion thereof into the reactor; and (g) withdrawing a polymer product from the reactor.

[0069] In embodiments, one or more olefins, C_2 to C_{30} olefins or alpha-olefins, including ethylene or propylene or combinations thereof, may be prepolymerized in the presence of the metallocene catalyst systems described above prior to the main polymerization. The prepolymerization may be carried out batch-wise or continuously in gas, solution or slurry

phase, including at elevated pressures. The prepolymerization can take place with any olefin monomer or combination and/or in the presence of any molecular weight controlling agent such as hydrogen. For examples of prepolymerization procedures, see U.S. Patent Nos. 4,748,221, 4,789,359, 4,923,833, 4,921,825, 5,283,278 and 5,705,578 and European publication EP-B-0279 863 and WO 97/44371 .

[0070] The present invention is not limited to any specific type of fluidized or gas phase polymerization reaction and can be carried out in a single reactor or multiple reactors such as two or more reactors in series. In embodiments, the present invention may be carried out in fluidized bed polymerizations (that may be mechanically stirred and/or gas fluidized), or with those utilizing a gas phase, similar to that as described above. In addition to well-known conventional gas phase polymerization processes, it is within the scope of the present invention that “condensing mode,” including the “induced condensing mode” and “liquid monomer” operation of a gas phase polymerization may be used.

[0071] Embodiments may employ a condensing mode polymerization, such as those disclosed in U.S. Patent Nos. 4,543,399; 4,588,790; 4,994,534; 5,352,749; 5,462,999; and 6,489,408. Condensing mode processes may be used to achieve higher cooling capacities and, hence, higher reactor productivity. In addition to condensable fluids of the polymerization process itself, other condensable fluids inert to the polymerization may be introduced to induce a condensing mode operation, such as by the processes described in U.S. Patent No. 5,436,304.

[0072] Other embodiments may also use a liquid monomer polymerization mode such as those disclosed in U.S. Patent No. 5,453,471; U.S. Ser. No. 08/510,375; PCT 95/09826 (US) and PCT 95/09827 (US). When operating in the liquid monomer mode, liquid can be present throughout the entire polymer bed provided that the liquid monomer present in the bed is adsorbed on or in solid particulate matter present in the bed, such as polymer being produced or inert particulate material (e.g., carbon black, silica, clay, talc, and mixtures thereof), so long as there is no substantial amount of free liquid monomer present. Operating in a liquid monomer mode may also make it possible to produce polymers in a gas phase reactor using monomers having condensation temperatures much higher than the temperatures at which conventional polyolefins are produced.

[0073] Any type of polymerization catalyst may be used, including liquid-form catalysts, solid catalysts, and heterogeneous or supported catalysts, among others, and may be fed to the reactor as a liquid, slurry (liquid/solid mixture), or as a solid (typically gas transported). Liquid-form catalysts useful in embodiments disclosed herein should be stable and sprayable or atomizable. These catalysts may be used alone or in various combinations or mixtures. For example, one or

more liquid catalysts, one or more solid catalysts, one or more supported catalysts, or a mixture of a liquid catalyst and/or a solid or supported catalyst, or a mixture of solid and supported catalysts may be used. These catalysts may be used with co-catalysts, activators, and/or promoters well known in the art. Examples of suitable catalysts include:

- A. Ziegler-Natta catalysts, including titanium based catalysts, such as those described in U.S. Patent Nos. 4,376,062 and 4,379,758. Ziegler-Natta catalysts are well known in the art, and typically are magnesium/titanium/electron donor complexes used in conjunction with an organoaluminum co-catalyst.
- B. Chromium based catalysts, such as those described in U.S. Patent Nos. 3,709,853; 3,709,954; and 4,077,904.
- C. Vanadium based catalysts, such as vanadium oxychloride and vanadium acetylacetonate, such as described in U.S. Patent No. 5,317,036.
- D. Metallocene catalysts, such as those described in U.S. Patent Nos. 6,933,258 and 6,894,131.
- E. Cationic forms of metal halides, such as aluminum trihalides.
- F. Cobalt catalysts and mixtures thereof, such as those described in U.S. Patent Nos. 4,472,559 and 4,182,814.
- G. Nickel catalysts and mixtures thereof, such as those described in U.S. Patent Nos. 4,155,880 and 4,102,817.
- H. Rare Earth metal catalysts, *i.e.*, those containing a metal having an atomic number in the Periodic Table of 57 to 103, such as compounds of cerium, lanthanum, praseodymium, gadolinium and neodymium. Especially useful are carboxylates, alcoholates, acetylacetonates, halides (including ether and alcohol complexes of neodymium trichloride), and allyl derivatives of such metals. In various embodiments, neodymium compounds, particularly neodymium neodecanoate, octanoate, and versatate, are particularly useful rare earth metal catalysts. Rare earth catalysts may be used, for example, to polymerize butadiene or isoprene.
- I. Any combination of one or more of the catalysts above.

[0074] The described catalyst compounds, activators and/or catalyst systems, as noted above, may also be combined with one or more support materials or carriers. For example, in some embodiments, the activator is contacted with a support to form a supported activator wherein the activator is deposited on, contacted with, vaporized with, bonded to, or incorporated within, adsorbed or absorbed in, or on, a support or carrier.

[0075] Support materials may include inorganic or organic support materials, such as a porous support material. Non-limiting examples of inorganic support materials include inorganic oxides and inorganic chlorides. Other carriers include resinous support materials such as polystyrene, functionalized or crosslinked organic supports, such as polystyrene divinyl benzene, polyolefins or polymeric compounds, or any other organic or inorganic support material and the like, or mixtures thereof.

[0076] The support materials may include inorganic oxides including Group 2, 3, 4, 5, 13 or 14 metal oxides, such as silica, fumed silica, alumina, silica-alumina and mixtures thereof. Other useful supports include magnesia, titania, zirconia, magnesium chloride, montmorillonite, phyllosilicate, zeolites, talc, clays, and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania and the like. Additional support materials may include those porous acrylic polymers described in EP 0 767 184. Other support materials include nanocomposites, as described in PCT WO 99/47598, aerogels, as described in WO 99/48605, spherulites, as described in U.S. Patent No. 5,972,510, and polymeric beads, as described in WO 99/50311.

[0077] Support material, such as inorganic oxides, may have a surface area in the range from about 10 to about 700 m²/g, a pore volume in the range from about 0.1 to about 4 cc/g, and an average particle size in the range from about 0.1 to about 1000 μm. In other embodiments, the surface area of the support may be in the range from about 50 to about 500 m²/g, the pore volume is from about 0.5 to about 3.5 cc/g, and the average particle size is from about 1 to about 500 μm. In yet other embodiments, the surface area of the support is in the range from about 100 to about 1000 m²/g, the pore volume is from about 0.8 to about 5.0 cc/g, and the average particle size is from about 1 to about 100 μm, or from about 1 to about 60 μm. The average pore size of the support material may be in the range from 10 to 1000 Å; or from about 50 to about 500 Å; or from about 75 to about 450 Å.

[0078] There are various methods known in the art for producing a supported activator or combining an activator with a support material. In an embodiment, the support material is chemically treated and/or dehydrated prior to combining with the catalyst compound, activator and/or catalyst system. In a family of embodiments, the support material may have various levels of dehydration, such as may be achieved by drying the support material at temperatures in the range from about 100°C to about 1000°C.

[0079] In some embodiments, dehydrated silica may be contacted with an organoaluminum or alumoxane compound. In the embodiment wherein an organoaluminum compound is used, the

activator is formed *in situ* in the support material as a result of the reaction of, for example, trimethylaluminum and water.

[0080] In yet other embodiments, Lewis base-containing support substrates will react with a Lewis acidic activator to form a support bonded Lewis acid compound. The Lewis base hydroxyl groups of silica are exemplary of metal/metalloid oxides where this method of bonding to a support occurs. These embodiments are described in, for example, U.S. Patent No. 6,147,173.

[0081] Other embodiments of supporting an activator are described in U.S. Patent No. 5,427,991, where supported non-coordinating anions derived from tris(perfluorophenyl) boron are described; U.S. Patent No. 5,643,847, discusses the reaction of Group 13 Lewis acid compounds with metal oxides such as silica and illustrates the reaction of tris(perfluorophenyl) boron with silanol groups (the hydroxyl groups of silicon) resulting in bound anions capable of protonating transition metal organometallic catalyst compounds to form catalytically active cations counter-balanced by the bound anions; immobilized Group IIIA Lewis acid catalysts suitable for carbocationic polymerizations are described in U.S. Patent No. 5,288,677; and James C. W. Chien, *Jour. Poly. Sci.: Pt A: Poly. Chem*, Vol. 29, 1603-1607 (1991), describes the olefin polymerization utility of methylalumoxane (MAO) reacted with silica (SiO_2) and metallocenes and describes a covalent bonding of the aluminum atom to the silica through an oxygen atom in the surface hydroxyl groups of the silica.

[0082] In some embodiments, the supported activator is formed by preparing, in an agitated, temperature and pressure controlled vessel, a solution of the activator and a suitable solvent, then adding the support material at temperatures from 0°C to 100°C, contacting the support with the activator solution for up to 24 hours, then using a combination of heat and pressure to remove the solvent to produce a free flowing powder. Temperatures can range from 40 to 120°C and pressures from 5 psia to 20 psia (34.5 to 138 kPa). An inert gas sweep can also be used to assist in removing solvent. Alternate orders of addition, such as slurring the support material in an appropriate solvent then adding the activator, can be used.

[0083] In an embodiment, the weight percent of the activator to the support material is in the range from about 10 weight percent to about 70 weight percent, or in the range from about 15 weight percent to about 60 weight percent, or in the range from about 20 weight percent to about 50 weight percent, or in the range from about 20 weight percent to about 40 weight percent in other embodiments.

[0084] Conventional supported catalysts system useful in embodiments disclosed herein include those supported catalyst systems that are formed by contacting a support material, an activator

and a catalyst compound in various ways under a variety of conditions outside of a catalyst feeder apparatus. Examples of conventional methods of supporting metallocene catalyst systems are described in U.S. Patent Nos. 4,701,432, 4,808,561, 4,912,075, 4,925,821, 4,937,217, 5,008,228, 5,238,892, 5,240,894, 5,332,706, 5,346,925, 5,422,325, 5,466,649, 5,466,766, 5,468,702, 5,529,965, 5,554,704, 5,629,253, 5,639,835, 5,625,015, 5,643,847, 5,665,665, 5,698,487, 5,714,424, 5,723,400, 5,723,402, 5,731,261, 5,759,940, 5,767,032, 5,770,664, 5,846,895, 5,939,348, 5,46,872, 6,090,740 and PCT publications WO 95/32995, WO 95/14044, WO 96/06187 and WO 97/02297, and EP-B1-0 685 494.

[0085] The catalyst components, for example a catalyst compound, activator and support, may be fed into the polymerization reactor as a mineral oil slurry. Solids concentrations in oil may range from about 1 to about 50 weight percent, or from about 10 to about 25 weight percent.

[0086] The catalyst compounds, activators and or optional supports used herein may also be spray dried separately or together prior to being injected into the reactor. The spray dried catalyst may be used as a powder or solid or may be placed in a diluent and slurried into the reactor. In other embodiments, the catalyst compounds and activators used herein are not supported.

[0087] Catalysts useful in various embodiments disclosed herein may include conventional Ziegler-Natta catalysts and chromium catalysts. Illustrative Ziegler-Natta catalyst compounds are disclosed in ZIEGLER CATALYSTS 363-386 (G. Fink, R. Mulhaupt and H. H. Brintzinger, eds., Springer-Verlag 1995); or in EP 103 120; EP 102 503; EP 0 231 102; EP 0 703 246; RE 33,683; U.S. Pat. Nos. 4,302,565; 5,518,973; 5,525,678; 5,288,933; 5,290,745; 5,093,415 and 6,562,905. Examples of such catalysts include those having Group 4, 5 or 6 transition metal oxides, alkoxides and halides, or oxides, alkoxides and halide compounds of titanium, zirconium or vanadium; optionally in combination with a magnesium compound, internal and/or external electron donors (alcohols, ethers, siloxanes, etc.), aluminum or boron alkyl and alkyl halides, and inorganic oxide supports.

[0088] In one or more embodiments, conventional-type transition metal catalysts can be used. Conventional type transition metal catalysts include traditional Ziegler-Natta catalysts in U.S. Pat. Nos. 4,115,639, 4,077,904, 4,482,687, 4,564,605, 4,721,763, 4,879,359 and 4,960,741. Conventional-type transition metal catalysts can be represented by the formula: MR_x , where M is a metal from Groups 3 to 17, or a metal from Groups 4 to 6, or a metal from Group 4, or titanium; R is a halogen or a hydrocarbyloxy group; and x is the valence of the metal M. Examples of R include alkoxy, phenoxy, bromide, chloride and fluoride. Preferred conventional-

type transition metal catalyst compounds include transition metal compounds from Groups 3 to 17, or Groups 4 to 12, or Groups 4 to 6.

[0089] Conventional-type transition metal catalyst compounds based on magnesium/titanium electron-donor complexes are described in, for example, U.S. Pat. Nos. 4,302,565 and 4,302,566. Catalysts derived from Mg/Ti/Cl/THF are also contemplated, which are well known to those of ordinary skill in the art.

[0090] Suitable chromium catalysts include di-substituted chromates, such as $\text{CrO}_2(\text{OR})_2$; where R is triphenylsilane or a tertiary polyalicyclic alkyl. The chromium catalyst system can further include CrO_3 , chromocene, silyl chromate, chromyl chloride (CrO_2Cl_2), chromium-2-ethylhexanoate, chromium acetylacetonate ($\text{Cr}(\text{AcAc})_3$), and the like. Illustrative chromium catalysts are further described in U.S. Pat. Nos. 3,709,853; 3,709,954; 3,231,550; 3,242,099; and 4,077,904.

[0091] Metallocenes are generally described throughout in, for example, 1 & 2 METALLOCENE-BASED POLYOLEFINS (John Scheirs & W. Kaminsky eds., John Wiley & Sons, Ltd. 2000); G. G. Hlatky in 181 COORDINATION CHEM. REV. 243-296 (1999) and in particular, for use in the synthesis of polyethylene in 1 METALLOCENE-BASED POLYOLEFINS 261-377 (2000). The metallocene catalyst compounds can include "half sandwich" and "full sandwich" compounds having one or more Cp ligands (cyclopentadienyl and ligands isolobal to cyclopentadienyl) bound to at least one Group 3 to Group 12 metal atom, and one or more leaving group(s) bound to the at least one metal atom. Hereinafter, these compounds will be referred to as "metallocenes" or "metallocene catalyst components."

[0092] The Cp ligands are one or more rings or ring system(s), at least a portion of which includes pi-bonded systems, such as cycloalkadienyl ligands and heterocyclic analogues. The ring(s) or ring system(s) typically include atoms selected from Groups 13 to 16 atoms, or the atoms that make up the Cp ligands can be selected from carbon, nitrogen, oxygen, silicon, sulfur, phosphorous, germanium, boron and aluminum and combinations thereof, wherein carbon makes up at least 50% of the ring members. Or, the Cp ligand(s) can be selected from substituted and unsubstituted cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl, non-limiting examples of which include cyclopentadienyl, indenyl, fluorenyl and other structures. Further non-limiting examples of such ligands include cyclopentadienyl, cyclopentaphenanthrenyl, indenyl, benzindenyl, fluorenyl, octahydrofluorenyl, cyclooctatetraenyl, cyclopentacyclododecene, phenanthrindenyl, 3,4-benzofluorenyl, 9-phenylfluorenyl, 8-H-cyclopent[a]acenaphthylenyl, 7H-dibenzofluorenyl, indeno[1,2-

9]anthrene, thiophenoindenyl, thiophenofluorenyl, hydrogenated versions thereof (e.g., 4,5,6,7-tetrahydroindenyl, or "H₄Ind"), substituted versions thereof, and heterocyclic versions thereof.

[0093] In one or more embodiments, a "mixed" catalyst system or "multi-catalyst" system may be used. A mixed catalyst system includes at least one metallocene catalyst component and at least one non-metallocene component. The mixed catalyst system may be described as a bimetallic catalyst composition or a multi-catalyst composition. As used herein, the terms "bimetallic catalyst composition" and "bimetallic catalyst" include any composition, mixture, or system that includes two or more different catalyst components, each having the same or different metal group but having at least one different catalyst component, for example, a different ligand or general catalyst structure. Examples of useful bimetallic catalysts are in U.S. Patent Nos. 6,271,325, 6,300,438, and 6,417,204. The terms "multi-catalyst composition" and "multi-catalyst" include any composition, mixture, or system that includes two or more different catalyst components regardless of the metals. Therefore, terms "bimetallic catalyst composition," "bimetallic catalyst," "multi-catalyst composition," and "multi-catalyst" will be collectively referred to herein as a "mixed catalyst system" unless specifically noted otherwise. Any one or more of the different catalyst components can be supported or non-supported.

[0094] Use of prior art continuity additives, in general, may enhance polymerization reactor operations by reducing the occurrence of sheeting and drooling. However, productivity of various catalysts may be adversely affected by use of such continuity additives. For example, it has been observed that for certain bimodal catalyst systems, use of various continuity additives may decrease catalyst productivity by up to 40% or more. Further, reactor operations may be sensitive when using such continuity additives, often requiring a continuous flow of continuity additive, and where a slight decrease in continuity additive concentration may result in immediate skin thermocouple excursions. In contrast, polysulfone additive systems according to embodiments disclosed herein may be used without significant detriment to catalyst productivity, including use with bimetallic catalysts and metallocene catalysts. Further, when using polysulfone additive systems according to embodiments disclosed herein, it may be possible to run a reactor for an extended time following loss or stoppage of additive flow to the reactor.

[0095] Processes disclosed herein may optionally use inert particulate materials as fluidization aids. These inert particulate materials can include carbon black, silica, talc, and clays, as well as inert polymeric materials. Carbon black, for example, has a primary particle size of about 10 to about 100 nanometers, an average size of aggregate of about 0.1 to about 30 microns, and a specific surface area from about 30 to about 1500 m²/g. Silica has a primary particle size of

about 5 to about 50 nanometers, an average size of aggregate of about 0.1 to about 30 microns, and a specific surface area from about 50 to about 500 m²/g. Clay, talc, and polymeric materials have an average particle size of about 0.01 to about 10 microns and a specific surface area of about 3 to 30 m²/g. These inert particulate materials may be used in amounts ranging from about 0.3 to about 80%, or from about 5 to about 50%, based on the weight of the final product. They are especially useful for the polymerization of sticky polymers as disclosed in U.S. Patent Nos. 4,994,534 and 5,304,588.

[0096] Chain transfer agents, promoters, scavenging agents and other additives may be, and often are, used in the polymerization processes disclosed herein. Chain transfer agents are often used to control polymer molecular weight. Examples of these compounds are hydrogen and metal alkyls of the general formula M_xR_y, where M is a Group 3-12 metal, x is the oxidation state of the metal, typically 1, 2, 3, 4, 5 or 6, each R is independently an alkyl or aryl, and y is 0, 1, 2, 3, 4, 5, or 6. In some embodiments, a zinc alkyl is used, such as diethyl zinc. Typical promoters may include halogenated hydrocarbons such as CHCl₃, CFC₃, CH₃-CCl₃, CF₂Cl-CCl₃, and ethyltrichloroacetate. Such promoters are well known to those skilled in the art and are disclosed in, for example, U.S. Patent No. 4,988,783. Other organometallic compounds such as scavenging agents for poisons may also be used to increase catalyst activity. Examples of these compounds include metal alkyls, such as aluminum alkyls, for example, triisobutylaluminum. Some compounds may be used to neutralize static in the fluidized-bed reactor, others known as drivers rather than antistatic agents, may consistently force the static from positive to negative or from negative to positive. The use of these additives is well within the skill of those skilled in the art. These additives may be added to the circulation loops, riser, and/or downer separately or independently from the liquid catalyst if they are solids, or as part of the catalyst provided they do not interfere with the desired atomization. To be part of the catalyst solution, the additives should be liquids or capable of being dissolved in the catalyst solution.

[0097] In one embodiment of the process of the invention, the gas phase process may be operated in the presence of a metallocene-type catalyst system and in the absence of, or essentially free of, any scavengers, such as triethylaluminum, trimethylaluminum, triisobutylaluminum and tri-n-hexylaluminum and diethyl aluminum chloride, dibutyl zinc, and the like. By “essentially free,” it is meant that these compounds are not deliberately added to the reactor or any reactor components, and if present, are present in the reactor at less than 1 ppm.

[0098] In some embodiments, one or more olefins, including ethylene or propylene or combinations thereof, may be prepolymerized in the presence of the catalyst systems described

above prior to the main polymerization within the reactors described herein. The prepolymerization may be carried out batch-wise or continuously in gas, solution, or slurry phase, including at elevated pressures. The prepolymerization can take place with any olefin monomer or combination and/or in the presence of any molecular weight controlling agent such as hydrogen. For examples of prepolymerization procedures, see U.S. Patent Nos. 4,748,221, 4,789,359, 4,923,833, 4,921,825, 5,283,278 and 5,705,578 and European publication EP-B-0279 863 and WO 97/44371.

[0099] In a family of embodiments, the reactors disclosed herein are capable of producing greater than 500 lbs of polymer per hour (227 Kg/hr) to about 300,000 lbs/hr (136,000 kg/hr) or higher of polymer, preferably greater than 1000 lbs/hr (455 kg/hr), more preferably greater than 10,000 lbs/hr (4540 kg/hr), even more preferably greater than 25,000 lbs/hr (11,300 kg/hr), still more preferably greater than 35,000 lbs/hr (15,900 kg/hr), still even more preferably greater than 50,000 lbs/hr (22,700 Kg/hr) and most preferably greater than 65,000 lbs/hr (29,000 kg/hr) to greater than 150,000 lbs/hr (68,100 kg/hr).

[0100] The polymers produced by the processes described herein can be used in a wide variety of products and end-use applications. The polymers produced may include linear low density polyethylene, elastomers, plastomers, high density polyethylenes, medium density polyethylenes, low density polyethylenes, polypropylene homopolymers and polypropylene copolymers, including random copolymers and impact copolymers.

[0101] The polymers, typically ethylene based polymers, have a density in the range of from 0.86 g/cc to 0.97 g/cc, preferably in the range of from 0.88 g/cc to 0.965 g/cc, and more preferably in the range of from 0.900 g/cc to 0.96 g/cc. Density is measured in accordance with ASTM-D-1238.

[0102] In yet another embodiment, propylene based polymers are produced. These polymers include atactic polypropylene, isotactic polypropylene, hemi-isotactic and syndiotactic polypropylene. Other propylene polymers include propylene block, random, or impact copolymers. Propylene polymers of these types are well known in the art, see for example U.S. Patent Nos. 4,794,096, 3,248,455, 4,376,851, 5,036,034 and 5,459,117.

[0103] The polymers may be blended and/or coextruded with any other polymer. Non-limiting examples of other polymers include linear low density polyethylenes produced via conventional Ziegler-Natta and/or bulky ligand metallocene catalysis, elastomers, plastomers, high pressure low density polyethylene, high density polyethylenes, polypropylenes, and the like.

[0104] Polymers produced by the processes disclosed herein and blends thereof are useful in such forming operations as film, sheet, and fiber extrusion and co-extrusion as well as blow

molding, injection molding and rotary molding. Films include blown or cast films formed by co-extrusion or by lamination useful as shrink film, cling film, stretch film, sealing films, oriented films, snack packaging, heavy duty bags, grocery sacks, baked and frozen food packaging, medical packaging, industrial liners, membranes, etc. in food-contact and non-food contact applications.

Condensed Mode of Operation

[00105] Embodiments of the processes disclosed herein may also be operated in a condensing mode, similar to those disclosed in U.S. Patent Nos. 4,543,399, 4,588,790, 4,994,534, 5,352,749, 5,462,999, and 6,489,408, and U.S. Patent Application Publication No. 20050137364. Condensing mode processes may be used to achieve higher cooling capacities and, hence, higher reactor productivity. In addition to condensable fluids of the polymerization process itself, including monomer(s) and co-monomer(s), other condensable fluids inert to the polymerization may be introduced to induce a condensing mode operation, such as by the processes described in U.S. Patent No. 5,436,304.

[00106] The condensing mode of operation in polymerization reactors may significantly increase the production rate or space time yield by providing extra heat-removal capacity through the evaporation of condensates in the cycle gas. Additional condensation is often promoted to extend the utility of condensed mode operation by adding an induced condensing agent ("ICA") into the reactor.

[00107] The amount of condensation of liquid in the circulating components can be maintained at up to about 90 percent by weight, for example. This degree of condensation is achieved by maintaining the outlet temperature from the heat exchange so as to achieve the required degree of cooling below the dew point of the mixture.

[00108] In general, it would be desirable to have a high proportion of the induced condensing agent in the gaseous stream, to enhance the heat-removal from the reactor. Within the polymer particles, there is dissolved ICA, comonomer(s), other hydrocarbon(s), and even monomer(s), with quantities depending on the types those species and the gas composition. Usually the amount of ICA in the circulating stream is one of the most important factors that affect the overall quantity of the dissolved species in the polymer. At certain levels of ICA, an excess amount of the ICA is dissolved into the polymer particles, making the polymer sticky. Therefore, the amount of the ICA that can be introduced into the reactor must be kept below the "stickiness limit" beyond which the circulating material becomes too sticky to discharge or to maintain the desired fluidization state. Each ICA has a different solubility in each specific

polymer product, and in general, it is desirable to utilize an ICA having relatively low solubility in the produced polymer, so that more of the ICA can be utilized in the gaseous stream before reaching the stickiness limit. For certain polymer products and certain ICAs, such a “stickiness limit” may not exist at all.

[00109] Suitable ICAs are materials having a low normal boiling point and/or a low solubility in polymers. For example, suitable ICAs may have a normal boiling point less than 25°C; or less than 20°C; or less than 15°C; or less than 10°C; or less than 0°C in some embodiments.

[00110] Suitable ICAs include those having a “typical solubility” less than 1.5 kg ICA per 100 kg of polyethylene in a reactor. In other embodiment, suitable ICAs include those having a typical solubility less than 1.25 kg ICA per 100 kg of polyethylene; or less than 1.0 kg ICA per 100 kg of polyethylene; or less than 0.8 kg ICA per 100 kg of polyethylene; or less than 0.5 kg ICA per 100 kg of polyethylene; or less than 0.3 kg ICA per 100 kg of polyethylene in yet other embodiments. “Typical solubility” is determined under 90°C reactor temperature and ICA partial pressure of 25 psi (1.72×10^5 Pa), for polyethylene with a melt index (I_2) = 1.0 dg/min and resin density = 918 kg/m³. In these embodiments, the melt index is determined using ASTM D1238.

[00111] In some embodiments, suitable ICAs include cyclobutane, neopentane, n-butane, isobutane, cyclopropane, propane, and mixtures thereof. It is recognized within the scope of embodiments disclosed herein that relatively volatile solvents such as propane, butane, isobutane or even isopentane can be matched against a heavier solvent or condensing agent such as isopentane, hexane, hexene, or heptane so that the volatility of the solvent is not so appreciably diminished in the circulation loops. Conversely, heavier solvents may also be used either to increase resin agglomeration or to control resin particle size.

[00112] As mentioned above, continuity additive formulations may have an unpredictable effect on polymerization reactor operability. Polysulfone additive systems according to embodiments disclosed herein may advantageously be used with gas phase polymerization reactors operating in a condensed mode. For example, the light hydrocarbons used as the carrier fluid may advantageously be used as an ICA component. Additionally, the high boiling point food grade oil may be recovered from the reactor along with the produced polymer. Additionally, the solubility of polysulfone additive systems according to embodiments disclosed herein in liquid hydrocarbons conventionally used as ICAs may allow for enhanced dispersal of the additive throughout the polymerization reactor system, thus improving control of static.

[00113] Additionally, with regard to liquid-phase reactor systems, it has been found that polysulfone additive systems according to embodiments disclosed herein may improve the

conductivity in liquids, acting in this sense as a true anti-static agent, allowing the charge to move more freely and discharge to the metal reactor wall.

Measurement and Control of Static

[00114] The entrainment zone is defined as any area in a reactor system above or below the dense phase zone of the reactor system. Fluidization vessel with a bubbling bed comprise two zones, a dense bubbling phase with an upper surface separating it from a lean or dispersed phase. The portion of the vessel between the (upper) surface of the dense bed and the exiting gas stream (to the recycle system) is called “freeboard.” Therefore, the entrainment zone comprises the freeboard, the cycle (recycle) gas system (including piping and compressors/coolers) and the bottom of the reactor up to the top of the distributor plate. Electrostatic activity measured anywhere in the entrainment zone is termed herein “carryover static,” and as such, is differentiated from the electrostatic activity measured by a conventional static probe or probes in the fluid bed.

[00115] The electrostatic activity (carryover or entrainment static) measured above the “at or near zero” level (as defined herein) on the carryover particles in the entrainment zone may correlate with sheeting, chunking or the onset of same in a polymer reaction system and may be a more reliable indicator of sheeting or a discontinuity event than electrostatic activity measured by one or more “conventional” static probes. In addition, monitoring electrostatic activity of the carryover particles in the entrainment zone may provide reactor parameters by which the amount of polysulfone additive and any additional continuity additive, if used, can be dynamically adjusted and an optimum level obtained to reduce or eliminate the discontinuity event.

[00116] If the level of electrostatic activity in the entrainment zone increases in magnitude during the course of the reaction, the amount of polysulfone additive in the reactor system may be adjusted accordingly as described further herein.

Static Probes

[00117] The static probes described herein as being in the entrainment zone include one or more of: at least one recycle line probe; at least one annular disk probe; at least one distributor plate static probe; or at least one upper reactor static probe, this latter will be outside or above the 1/4 to 3/4 reactor diameter height above the distributor plate of the conventional probe or probes. These probes may be used to determine entrainment static either individually or with one or more additional probes from each group mentioned above. The type and location of the static

probes may be, for example, as described in U.S. Patent Application Publication No. 20050148742.

[00118] Typical current levels measured with the conventional reactor probes range from ± 0.1 -10, or ± 0.1 -8, or ± 0.1 -6, or ± 0.1 -4, or ± 0.1 -2 nanoamps/cm². As with all current measurements discussed herein, these values will generally be averages over time periods, also these may represent root mean squared values (RMS), in which case they would all be positive values. However, most often, in reactors utilizing metallocene catalysts, the conventional reactor probes will register at or near zero during the beginning of or middle of a sheeting incident. By at or near zero, it is intended for either the conventional static reactor probe as well as the probes in the entrainment zone, to be a value of $\leq \pm 0.5$, or $\leq \pm 0.3$, or $\leq \pm 0.1$, or $\leq \pm 0.05$, or $\leq \pm 0.03$, or $\leq \pm 0.01$, or $\leq \pm 0.001$ or 0 nanoamps/cm². For example, a measured value of -0.4 would be "less than" " ± 0.5 ", as would a measured value of +0.4. When static is measured with a voltage probe, typical voltage levels measured may range from ± 0.1 -15,000, or ± 0.1 -10,000 volts. Use of polysulfone additives according to embodiments disclosed herein may result in measured voltage values of $\leq \pm 200$, or $\leq \pm 150$, or $\leq \pm 100$, or $\leq \pm 50$, or $\leq \pm 25$ volts.

[00119] The conventional static probe may register at or near zero static or current (as defined herein), while at least one other static probe in at least one location in the entrainment zone, may register static activity or current higher than that measured by the conventional static probe (this latter may most often be at or near zero with metallocene catalyst). In this event, where the difference between the current measured by conventional static probe and the current measured by one or more other (non-conventional static probes) is $\geq \pm 0.1$, or $\geq \pm 0.3$, or $\geq \pm 0.5$ nanoamps/cm², or greater, action will be taken to reduce or eliminate the static charge in being detected at one or more of the entrainment zone probes. Such action may be addition of at least one polysulfone additive according to embodiments disclosed herein (or a net increase in the presence in the reactor of at least one polysulfone additive according to embodiments disclosed herein), or a reduction in the catalyst feed rate, or a reduction in the gas throughput velocity, or combinations thereof. These actions constitute means for maintaining, reducing or eliminating carryover static and reactor static at or near zero.

[00120] When one or more of the static probes discussed above begin to register static activity above or below zero, (defined as being respectively above or below "at or near zero") measures should be taken to keep the level low or to return the level of static activity to at or near zero, which we have shown will prevent, reduce or eliminate reactor continuity events. The measures contemplated include addition of one or more polysulfone additives. Such addition may have

the effect of raising the level of polysulfone additive in the reactor if a certain level is already present.

[00121] The total amount of polysulfone additive or additives and any additional continuity additives or static control agents, if used, present in the reactor will generally not exceed 250, or 200, or 150, or 125, or 100 ppm (parts per million by weight of polymer being produced). The total amount of polysulfone additive and any additional continuity additives or static control agents, if used, will be greater than 0.01, or 1, or 5, or 10 ppm based on the weight of polymer being produced (usually expressed as pounds or kilograms per unit of time). Any of these lower limits are combinable with any upper limit given above. In some embodiments, the polysulfone additive system may be present in the reactor in the range from about 5 to about 50 ppmw by weight of polymer being produced. The polysulfone additive may be added directly to the reactor through a dedicated feed line, and/or added to any convenient feed stream, including the ethylene feed stream, the comonomer feed stream, the catalyst feed line, or the recycle line. If more than one polysulfone additive and additional continuity additive or static control agent is used, each one may be added to the reactor as separate feed streams, or as any combination of separate feed streams or mixtures. The manner in which the polysulfone additives are added to the reactor is not important, so long as the additive(s) are well dispersed within the fluidized bed, and that their feed rates (or concentrations) are regulated in a manner to provide minimum levels of carryover static.

[00122] The total amount of additive discussed immediately above may include polysulfone additive from any source, such as that added with the catalyst, added in a dedicated additive line, contained in any recycle material, or combinations thereof. In one embodiment, a portion of the polysulfone additive(s) would be added to the reactor as a preventative measure before any measurable electrostatic activity, in such case, when one or more static probes register static activity above the "at or near zero" level, the polysulfone additive will be increased to return the one or more probes registering static activity, back to at or near zero.

[00123] It is also within the scope of embodiments to introduce at least one polysulfone additive in the catalyst mixture, inject the catalyst mixture (containing at least one polysulfone additive) into the reactor system, and additionally or alternatively introduce at least one polysulfone additive into the reactor system via a dedicated additive feed line independent of the catalyst mixture, so that a sufficient concentration of the at least one additive is introduced into the reactor to prevent or eliminate a reactor discontinuity event. Either of these feed schemes or both together may be employed. The polysulfone additive in the catalyst/polysulfone additive

mixture and the polysulfone additive added via the separate additive feed line, may be the same or different.

[00124] Determination of optimal polysulfone additive feed rate to the reactor system is evidenced by a value of the carryover static at or near zero as defined herein. For example, after stabilizing the carryover static reading in the reactor, if additional (i.e. higher) levels of polysulfone additive are added, and if one or more static probes in the entrainment zone of the reactor shows an increase in magnitude of static reading, this is a qualitative indication that the optimum continuity level has been exceeded. In this event, the levels of polysulfone additive should be lowered until stability of the static activity (as indicated by relatively constant readings of static activity in the one or more static probes) is again achieved, or the static activity is lowered to near zero or regains zero. Thus, dynamically adjusting the amount of polysulfone additive to reach an optimum concentration range is desirable and is within the practice of embodiments of the present invention. By optimum concentration we intend herein an effective amount. Therefore, an effective amount of at least one polysulfone additive is that amount that reduces, eliminates or achieves stability in electrostatic charge as measured by one or more static probes. Thus, as noted herein, if too much polysulfone additive is added, electrostatic charge will reappear; such an amount of polysulfone additive will be defined as outside an effective amount.

EXAMPLES

[00125] It is to be understood that while the invention has been described in conjunction with the specific embodiments thereof, the foregoing description is intended to illustrate and not limit the scope of the invention. Other aspects, advantages and modifications will be apparent to those skilled in the art to which the invention pertains.

[00126] Therefore, the following examples are put forth so as to provide those skilled in the art with a complete disclosure and description and are not intended to limit the scope of that which the inventors regard as their invention.

[00127] Continuity additives used in the following Examples include:

aluminum distearate.

a mixture of aluminum distearate and an ethoxylated amine type compound (IRGASTAT AS-990, available from Huntsman (formerly Ciba Specialty Chemicals), referred to throughout the examples as a continuity additive mixture or CA-mixture.

STATSAFE: a mixture of a polysulphone copolymer, a polymeric polyamine derived from a vegetable amine, and dinonylnaphthylsulphonic acid as a solution in heptane, and a high boiling point food grade oil, where the solvents include less than 0.1 wt.% toluene and other aromatic compounds, less than 0.1 wt.% isopropanol, and less than 0.1 wt.% methanol, available from Innospec Inc.

[00128] Catalysts used in the following Examples are as follows:

XCAT EZ 100 Metallocene Catalyst: a metallocene catalyst available from Univation Technologies, LLC, Houston, Texas.

XCAT HP 100 Metallocene Catalyst: a metallocene catalyst available from Univation Technologies, LLC, Houston, Texas.

PRODIGY BMC-200 Catalyst: a bimodal catalyst available from Univation Technologies, LLC, Houston, Texas.

PRODIGY BMC-300 Catalyst: a bimodal catalyst available from Univation Technologies, LLC, Houston, Texas.

[00129] The polymerization reactions described in the following examples were conducted in a continuous pilot-scale gas phase fluidized bed reactor of 0.35 meters internal diameter and 2.3 meters in bed height. The fluidized bed was made up of polymer granules. The gaseous feed streams of ethylene and hydrogen together with liquid comonomer were introduced below the reactor bed into the recycle gas line. Hexene was used as comonomer. The individual flow rates of ethylene, hydrogen and comonomer were controlled to maintain fixed composition targets. The ethylene concentration was controlled to maintain a constant ethylene partial pressure. The hydrogen was controlled to maintain a constant hydrogen to ethylene mole ratio. The concentrations of all the gases were measured by an on-line gas chromatograph to ensure relatively constant composition in the recycle gas stream.

[00130] The solid catalyst XCAT EZ 100 Metallocene Catalyst was injected directly into the fluidized bed using purified nitrogen as a carrier. Its rate was adjusted to maintain a constant production rate. In the case of PRODIGY BMC-200 and BMC-300 Catalysts, the catalyst was injected directly into the reactor as a slurry in purified mineral oil and the rate of the slurry catalyst feed rate was adjusted to maintain a constant production rate of polymer. The reacting bed of growing polymer particles was maintained in a fluidized state by the continuous flow of the make up feed and recycle gas through the reaction zone. A superficial gas velocity of 0.6-0.9 meters/sec was used to achieve this. The reactor was operated at a total pressure of 2240

kPa. The reactor was operated at a constant reaction temperature of 85°C or 105°C, depending on desired product.

[00131] The fluidized bed was maintained at a constant height by withdrawing a portion of the bed at a rate equal to the rate of formation of particulate product. The rate of product formation (the polymer production rate) was in the range of 15-25 kg/hour. The product was removed semi-continuously via a series of valves into a fixed volume chamber. This product was purged to remove entrained hydrocarbons and treated with a small stream of humidified nitrogen to deactivate any trace quantities of residual catalyst.

Example 1

[00132] A test was carried out in the above mentioned polymerization reactor to evaluate the effect of STATS SAFE as a continuity additive. The reactor was operated to produce a film product of about 1.2 to 3.4 melt index and 0.925 density at the following reaction conditions using metallocene catalyst (XCAT EZ 100 Metallocene Catalyst): reaction temperature of 85°C, hexene-to-ethylene molar ratio of 0.009 and H₂ concentration of 835 ppm. Initially, the reactor was operating smoothly under the above conditions using aluminum distearate as continuity additive at about 23 ppmw based on production rate. The reactor was then transitioned to using STATS SAFE diluted in isopentane. As the feed of STATS SAFE was initiated, the reaction began to die and a skin thermocouple excursion occurred, indicating a possible discontinuity event. This excursion was attributed to residual oxygen in the new injection tube. The reaction was restabilized with continuous STATS SAFE solution feed at 60 ppmw and operation continued to be smooth for the next 38 hours. Minor broadening of bed static level and narrowing in entrainment static were observed. No sheeting was experienced.

[00133] Within 6 hours of stopping STATS SAFE feed, skin thermocouple excursions, especially in the expanded section were observed indicating onset of sheeting. STATS SAFE feed was re-established and operation continued to be smooth until the end of the experiment. Table 1 shows the effect of STATS SAFE compared to aluminum distearate as a continuity additive and operation with no continuity additive on XCAT EZ 100 Metallocene Catalyst productivity.

Table 1 - Effect of STATS SAFE on XCAT EZ 100 Metallocene Catalyst Productivity

Continuity Additive (CA)	Aluminum Distearate	STATSAFE	None
CA Level (ppmw)	23.2	60.4	0.0
Catalyst Productivity (material balance) (gm/gm)	6416	6162	6528

Example 2

[00134] Another test was carried out in the above mentioned polymerization reactor to evaluate another batch STATS SAFE as a continuity additive. In this test, an open reactor start-up was carried out where the reactor was charged with a fresh XCAT EZ 100 catalyzed seed bed and following standard drying to a residual moisture level of 6 ppmv purging with nitrogen, the seed bed was pretreated with 12 ppmw STATS SAFE based on bed weight while building monomer and comonomer concentration. The reactor was operated to produce a film product of about 1.2 to 2.4 melt index and 0.923-0.925 density at the following reaction conditions using metallocene catalyst (XCAT EZ 100 METALLOCENE CATALYST): reaction temperature of 85°C, hexene-to-ethylene molar ratio of 0.009 and H₂ concentration of 935 ppm. Initially, the reactor was operating smoothly under the above conditions while using STATS SAFE as a continuity additive at a continuous feed rate of 16 ppmw based on production rate. STATS SAFE was fed to the reactor as a solution in isopentane. The reactor was then transitioned to operation without any continuity additive for 12 hours before initiating STATS SAFE feed again at approximately 20 ppmw based on production rate.

[00135] Operation continued to be smooth until the end of the test (~ 8 bed turnovers (BTOs)). During this test, the bed static band was narrow with no skin thermocouple excursions or sheeting.

[00136] Based on analysis the effect of STATS SAFE on catalyst productivity is slightly lower than at operation with no additive at same reaction conditions and product conditions, as shown in Table 2.

Table 2 - Effect of STATS SAFE on XCAT EZ 100 Metallocene Catalyst Productivity

Continuity Additive (CA)	None	STATSAFE
CA Level, ppmw	0	19.86
Catalyst Productivity based on Zr measured by ICP (gm/gm)	7317	6818

Example 3

[00137] Samples from another batch of STATS SAFE were also evaluated in a single gas phase reactor while running with XCAT EZ 100 Metallocene Catalyst. During this evaluation, the reactor was initially stabilized using aluminum distearate co-feed as a continuity additive at a feed rate of 30 ppmw based on production rate. A switch was then made to feeding STATS SAFE diluted in isopentane. Three levels of STATS SAFE feed rates were tested, 10 ppmw, 20 ppmw and 30 ppmw based on production rate. The reactor operated smoothly with no sheeting or dome skin thermocouple excursions during this test. Other results from this evaluation showed that STATS SAFE drove the static level in the bed slightly positive with no impact on catalyst

productivity. It was also possible to manipulate the skin thermocouples in the reactor activities by the level of STATSAFE fed to the reactor.

Example 4

[00138] The following tests were carried out in a larger sized continuous pilot plant reactor with diameter of 0.57 meters and bed height of 3.8 meters with a production rate of 100-150 lb/hr. A test was carried out to evaluate the effect of STATSAFE on the static. The data shows that feeding STATSAFE to the reactor resulted in increasing the static level in a positive direction, demonstrating its ability to act as a static control agent.

[00139] The reactor was operated to produce a film product of 1.6 to 1.9 melt index and 0.921 density using the metallocene catalyst XCAT EZ-100. The reaction temperature was 84°C, the hexene-to-ethylene molar ratio was 0.008 and the H₂ molar concentration was 718 ppm. The entrainment and plate static levels were monitored. The plate static is a static probe connected to a cap on the distributor plate and represents the impact of high velocity gas-particle mixture as they enter the reaction section. This was compared to readings using aluminum distearate. Data are shown below in Table 3.

Table 3 - Effect of STATSAFE on XCAT EZ 100 Metallocene Catalyst Static

Continuity Additive	Aluminum Distearate	STATSAFE		
Continuity Additive Level (ppmw)	30	10	20	30
Entrainment Static (picoamp)	60	39	57	86
Plate Static (nanoamp)	15	-4	10	34

[00140] Data shows that as the level of STATSAFE is increased, the static level reading from both probes increased in a positive direction. For every 10 ppm increase in the level of STATSAFE, the entrainment static level increased approximately 25 picoamps and the plate static increased approximately 20 nanoamps.

Example 5

[00141] In this test, the PRODIGY BMC-200 Catalyst (spray dried) was fed to the reactor as a dry catalyst using purified nitrogen as a carrier. The catalyst feed rate was adjusted to maintain a constant production rate.

[00142] The reactor was initially operated in steady state while feeding CA-mixture as a continuity additive to produce a bimodal type product with 0.9 to 2.5 FI and a density of 0.945-0.946 gm/cc at the following reaction conditions: reaction temperature of 85°C, ethylene partial pressure of 210 psia, hexene-to-ethylene molar ratio of 0.003 and H₂-to-ethylene molar ratio of

0.0019. The CA-mixture feed rate was approximately 26.6 ppmw based on production rate. After operation for 8 bed turnovers (BTOs) at the above conditions, CA-mixture co-feed was stopped and a switch was made from co-feeding CA-mixture to STATS SAFE initially at 27.5 ppmw based on production rate and subsequently was reduced to 18.8 ppmw. The static activity spiking was eliminated and operation continued smoothly until the end of this part of test (~ 12 BTOs).

[00143] A retest of STATS SAFE was performed following a period of operation without any continuity additive co-feed (~ 9 BTOs). STATS SAFE feed was initiated at 18 ppm and only a slight broadening of static band was observed. No sheeting was experienced.

[00144] An increase in catalyst productivity was observed with STATS SAFE as compared with CA-mixture as shown in Table 4 below.

Table 4. Effect of STATS SAFE on Spray-Dried PRODIGY BMC-200 Catalyst Productivity compared to CA-mixture co-feed.

Continuity Additive (CA)	CA-mixture	STATSAFE (high)	STATSAFE (low)	No additive	STATSAFE (low)
CA level, ppmw	26.65	27.52	18.77	0	18.42
Catalyst Productivity based on residual Zr as measured by ICPEs (gm/gm)	5349	7302	6866	5897	6053

Example 6

[00145] In this test, the reactor was operated using PRODIGY BMC-200 Catalysts, where the catalyst was injected directly into the reactor as a slurry in purified mineral oil and the rate of the slurry catalyst feed rate was adjusted to maintain a constant production rate of polymer. Initially the reactor was running using CA-mixture as a continuity additive at 40 ppmw based on production rate to produce a bimodal product for pipe applications at a reaction temperature of 105°C. The reactor was transitioned to STATS SAFE feed at approximately 20 ppmw. The reactor ran smoothly using STATS SAFE for about two days before transitioning back to CA-mixture. The catalyst productivity based on material balance increased from 7900 gm/gm with CA-mixture as compared with 8900 gm/gm with STATS SAFE. There was no observable change in static or skin thermocouple activities during the test and no sheeting.

Example 7

[00146] Another experimental run was conducted to assess the effect of STATS SAFE on slurry-fed PRODIGY BMC-200 Catalyst activity and operability. The reactor was initially operated in steady state without feeding any continuity additive to produce a bimodal pipe type product with

6 to 7 FI and a density of 0.949 gm/cc at the following reaction conditions: reaction temperature of 100°C, ethylene partial pressure of 220 psia, hexene-to-ethylene molar ratio of 0.0055 and H₂-to-ethylene molar ratio of 0.0020.

[00147] STATS SAFE diluted in isopentane feed was initiated to the reactor at a feed rate to give approximately 40 ppmw based on production rate. A significant increase in the static level bandwidth was noted on the upper and lower reactor static probes. Nearly all the skin thermocouples showed some cold banding with the initiation of STATS SAFE feed.

[00148] The STATS SAFE feed rate was subsequently decreased to give an approximate concentration of 20 ppmw. The skin thermocouple signals returned to their normal values and the bandwidth of the signal from the lower static probe decreased.

[00149] The STATS SAFE feed rate was decreased further to give an approximate concentration of 10 ppmw. The bed static signal remained near the baseline and skin thermocouple activity remained stable. Operation continued on STATS SAFE with about 10 ppmw for approximately 7 BTOs.

[00150] Based on mass balance, the catalyst productivity decreased as shown in Table 5 with STATS SAFE concentration as compared with no continuity additive, however, at STATS SAFE concentration of 10 ppmw and 20 ppmw, the catalyst productivity was much higher than with CA-mixture.

[00151] In a subsequent portion of the experiment, the reactor was smoothly transitioned from feeding CA-mixture to STATS SAFE at a nominal feed rate of 20 ppmw. The operability performance with STATS SAFE during this repeat experiment was similar to that observed in the previous test mentioned above. However, the catalyst productivity was slightly higher at ~10,500 gm/gm based on mass balance. This is nominally the same productivity as observed without the use of continuity additive for this catalyst as shown in Table 5.

Table 5. Effect of STATS SAFE Level on Slurry-Fed PRODIGY BMC-200 Bimodal Catalyst Activity

	No Additive	CA-Mixture	STATS SAFE		
CA level, ppmw	0	36	46	20	10
Catalyst Productivity, (material balance) gm/gm	10518	7700	7306	8648	9083
Cat Productivity, (material balance) Repeat Test (gm/gm)	10691			10532	

Example 8: Evaluation of STATS SAFE - Co-fed with the catalyst

[00152] Another experimental run was conducted to assess the effect of pre-contacting of PRODIGY BMC-200 Catalyst with STATS SAFE before feeding to the reactor. In this test, STATS SAFE diluted in isopentane was fed to the reactor through the same PRODIGY BMC-200 Catalyst slurry feed line allowing for mixing of STATS SAFE with the slurry catalyst prior to feeding to the reactor. The reactor was initially operated in steady state without using as a continuity additive to produce a bimodal pipe type product with 5 to 6 dg/min glow index and a density of 0.949 gm/cc at the following reaction conditions: reaction temperature of 100°C, ethylene partial pressure of 220 psia, hexene-to-ethylene molar ratio of 0.0045 and H₂-to-ethylene molar ratio of 0.0020. Later on the test, STATS SAFE diluted in isopentane feed was initiated to catalyst injection line as mentioned above at a feed rate to give approximately 24 ppmw based on production rate. The static level remained low and the band narrow and no sheeting was experienced. There was a minor drop in catalyst productivity with pre-contacting STATS SAFE with the catalyst as shown in Table 6.

Table 6. Effect of Pre-contacting STATS SAFE with Slurry-Fed PRODIGY BMC-200 Catalyst on Catalyst Productivity

	No Additive	STATSAFE
CA level, ppmw	0	23.7
Catalyst Productivity, gm/gm (corrected) – ICP basis	11391	10123

[00153] The PRODIGY BMC-200 Catalyst productivity as measured using Zr ICP is corrected to account for the total amount of catalyst species present in the catalyst, not just those containing Zr.

[00154] As described above, embodiments disclosed herein may provide polysulfone additive systems comprising a polysulfone copolymer, a polymeric polyamine, and oil-soluble sulfonic acid, for use in polymerization reactors, such as a gas-phase reactor for the production of polyolefins, where the end-product may be used in food contact applications. Use of polysulfone additive systems according to embodiments disclosed herein may advantageously provide for prevention, reduction, or reversal of sheeting and other discontinuity events. Polysulfone additive systems according to embodiments disclosed herein may also provide for charge dissipation or neutralization without a negative effect on bimetallic catalyst activity, as is commonly found to occur with conventional static control agents. Additionally, polysulfone

additive systems according to embodiments disclosed herein may advantageously be used in condensed mode operations.

[00155] The phrases, unless otherwise specified, "consists essentially of" and "consisting essentially of" do not exclude the presence of other steps, elements, or materials, whether or not, specifically mentioned in this specification, so long as such steps, elements, or materials, do not affect the basic and novel characteristics of the invention, additionally, they do not exclude impurities and variances normally associated with the elements and materials used.

[00156] Only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited.

[00157] All documents cited are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted and to the extent such disclosure is consistent with the description of the present invention.

[00158] While the invention has been described with respect to a number of embodiments and examples, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope and spirit of the invention as disclosed herein.

CLAIMS

What is claimed is:

1. A polymerization process comprising:
polymerizing at least one olefin to form an olefin based polymer in a gas phase polymerization reactor; and
feeding at least one polysulfone additive system to the polymerization reactor, wherein the polysulfone additive system comprises:
a polysulfone copolymer;
a polymeric polyamine;
an oil-soluble sulfonic acid; and
a carrier fluid including at least one of pentane, hexane, heptane, and a food grade oil.
2. A process for copolymerizing ethylene and one or more alpha olefins in a gas phase reactor comprising:
combining ethylene and one or more of 1-butene, 1-hexene, or 1-octene in the presence of a bimetallic catalyst comprising at least one metallocene, an activator, and a support;
monitoring static in said reactor by at least one recycle line static probe, at least one upper bed static probe, at least one annular disk static probe, or at least one distributor plate static probe;
maintaining the static at a desired level by use of at least one polysulfone additive system comprising:
a polysulfone copolymer;
a polymeric polyamine;
an oil-soluble sulfonic acid; and
at least one of pentane, hexane, heptane, and a food grade oil;
wherein the polysulfone additive system is present in said reactor in the range from about 0.1 to about 50 ppm, based on the weight of polymer produced by said combining.
3. The polymerization process of claim 1 or 2, wherein the polysulfone additive system comprises:
1 wt.% to 10 wt.% of the polymeric polyamine;
10 wt.% to 30 wt.% of the polysulfone copolymer;

5 wt.% to 10 wt.% of the oil-soluble sulphonic acid; and
40 wt.% to 80 wt.% of the at least one of pentane, hexane, and heptane.

4. The polymerization process of claim 3, wherein the polysulfone additive system further comprises:

1 wt.% to 10 wt.% of the food grade oil.

5. The polymerization process of claim 1, wherein the polysulfone additive system is fed to the reactor in an amount ranging from 0.01 to 200 ppm, based on the weight of all feeds to the reactor, excluding recycle.

6. The polymerization process of claim 1 or 2, wherein the polysulfone additive system comprises less than 0.1 wt.% of a combined amount of toluene, xylenes, methanol, and isopropanol.

7. The polymerization process according to any of the previous claims, wherein the polymerization reactor comprises a fluidized bed reactor, an entrainment zone, a catalyst feed for introducing a catalyst system capable of producing the polymer, at least one polysulfone additive system feed for the feeding of the at least one polysulfone additive system independently of the catalyst mixture, the process comprising: (a) contacting the at least one olefin with the catalyst system under polymerization conditions in the fluidized bed reactor; and (b) introducing the at least one polysulfone additive system into the reactor system at anytime before, during, or after start of the polymerization reaction.

8. The polymerization process of claim 7, further comprising: (c) monitoring a level of electrostatic activity in the entrainment zone; and (d) adjusting the amount of the at least one polysulfone additive system introduced into the reactor system to maintain the levels of electrostatic activity in the entrainment zone at or near zero.

9. The polymerization process of claim 1, further comprising feeding a bimetallic catalyst system to the gas-phase polymerization reactor.

10. The polymerization process of claim 9, wherein the bimetallic catalyst system comprises at least one metallocene catalyst.

11. The polymerization process of claim 1, wherein the at least one olefin comprises at least one of ethylene and propylene.

12. The polymerization process of claim 11, wherein the at least one olefin further comprises at least one C₄ to C₈ alpha olefin.
13. The polymerization process of claim 1 or 2, wherein the polysulfone additive system is co-fed to the reactor with a polymerization catalyst.
14. The polymerization process of claim 1, further comprising operating the polymerization reactor in a condensed mode of operation.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/020313

A. CLASSIFICATION OF SUBJECT MATTER INV. C08F10/00 C08F2/00		
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) C08F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/68274 A1 (BP CHEM INT LTD [GB]; BP CHEMICALS SNC [FR]; BENAZOUZZ GACEM [FR]; CAM) 16 November 2000 (2000-11-16) page 5, line 24 - page 8, line 21 page 13, line 18 - line 24 claims	1-14
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 19 March 2010		Date of mailing of the international search report 15/04/2010
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Kaumann, Edgar

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/020313

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	WO 2005/068507 A1 (UNIVATION TECH LLC [US]; HAGERTY ROBERT O [US]; MUHLE MICHAEL E [US];) 28 July 2005 (2005-07-28) claims	1-14
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