

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
28 August 2008 (28.08.2008)

PCT

(10) International Publication Number
WO 2008/103145 A1

(51) International Patent Classification:
B01J 21/00 (2006.01)

(21) International Application Number:
PCT/US2007/004733

(22) International Filing Date:
22 February 2007 (22.02.2007)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant (for all designated States except US): **UNIVATION TECHNOLOGIES, LLC** [US/US]; 5555 San Felipe, Suite 1950, Houston, TX 77056-2746 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **PANNELL, Richard, B.** [US/US]; 3902 Hill Springs Drive, Kingwood, TX 77345 (US).

(74) Agents: **ARECHEDERRA, Leandro** et al.; UNIVATION TECHNOLOGIES, LLC, 5555 San Felipe, Suite 1950, Houston, TX 77056-2746 (US).

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

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

[Continued on next page]

(54) Title: SYSTEMS AND METHODS FOR MANUFACTURING A CATALYST AND MONITORING FABRICATION OF A CATALYST

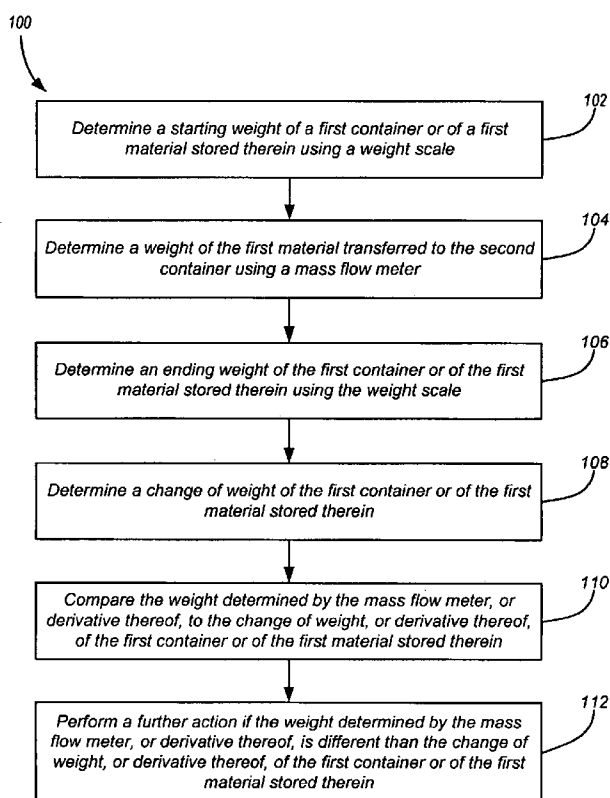


Figure 1

(57) Abstract: The present invention is directed to various methods and systems for manufacturing catalysts. In certain embodiments, the methods are performed in conjunction with one or more of a weight scale and a mass flow meter.

WO 2008/103145 A1



Published:

— *with international search report*

SYSTEMS AND METHODS FOR MANUFACTURING A CATALYST AND MONITORING FABRICATION OF A CATALYST

FIELD OF THE INVENTION

[0001] The present invention relates to catalyst manufacturing, and more particularly, this invention relates to systems and methods for monitoring and/or controlling catalyst manufacturing processes.

BACKGROUND OF THE INVENTION

[0002] In the gas phase process for production of polyolefins, such as polyethylene, monomers (e.g., ethylene), hydrogen, co-monomers (e.g., butene, hexene) and other raw materials are converted to polyolefin product. Generally, gas phase reactors include a fluidized bed reactor, a compressor, and a cooler. Typically, the reaction is maintained in a two-phase fluidized bed of granular polyethylene and gaseous reactants by the fluidizing gas which is passed through a distributor plate near the bottom of the reactor vessel. The reactor vessel may be constructed of carbon steel and rated for operation at pressures up to about 50 bars (or about 3.1 MPa). Catalyst is injected into the fluidized bed. Heat of reaction is transferred to the circulating gas stream. This gas stream is compressed and cooled in the external recycle line and then is reintroduced into the bottom of the reactor where it passes through a distributor plate. Make-up feedstreams are added to maintain the desired reactant concentrations.

[0003] Operation of most reactor systems is critically dependent at least in part, upon good mixing for uniform reactor conditions, heat removal, and effective catalyst. The process must be controllable and capable of a high production rate. Due in part to the high cost of catalyst and the need to control the rate of reaction, small amounts of catalyst are used to affect the polymerization process. Thus, the process is highly dependent upon the quality, for example, consistency from batch to batch, of the catalyst.

[0004] Further, because many reaction processes are steady state operations with catalyst and feedstock being continuously fed and product removed, it is desirable that the characteristics of any catalyst injected into the reaction chamber do not vary significantly over time. The characteristics and quality of a catalyst are greatly influenced by the process used to make the catalyst, and particularly, for example, consistent addition of raw materials. Thus, the catalyst manufacturing process should be controlled to maintain uniformity and consistency.

SUMMARY OF THE INVENTION

[0005] The present invention is broadly directed to various methods and systems for fabricating or manufacturing a catalyst. The invention is also broadly directed to various systems and methods that may be used in conjunction with systems for fabricating or manufacturing a catalyst.

[0006] A method for monitoring the manufacture or fabrication of a catalyst such as a metallocene catalyst, Ziegler-Natta catalyst, Cr-based catalyst, etc. according to a class of embodiments includes determining a starting weight of a first container or of a first material stored therein using a weight scale, the first material being a component used for catalyst manufacture. Upon transferring at least some of the first material to a second container, determining a weight of the first material transferred to the second container using a mass flow meter. An ending weight of the first container or of the first material stored therein is determined using the weight scale. A change of weight of the first container or of the first material stored therein is determined. The weight determined by the mass flow meter, or derivative thereof, is compared to the change of weight, or derivative thereof, of the first container or of the first material stored therein. A further action is performed if the weight determined by the mass flow meter, or derivative thereof, is different than the change of weight, or derivative thereof, of the first container or of the first material stored therein.

[0007] Further embodiments include the following steps: determining a starting weight of a third container or of a second material stored therein using a second

weight scale, the second material being a component used for the catalyst manufacture; transferring the second material to the second container; determining a weight of the second material transferred to the second container using a second mass flow meter; determining an ending weight of the third container or of the second material stored therein using the second weight scale; determining a change of weight of the third container or of the second material stored therein; comparing the weight determined by the second mass flow meter, or derivative thereof, to the change of weight, or derivative thereof, of the third container or of the second material stored therein; and performing a further action if the weight determined by the second mass flow meter, or derivative thereof, is different than the change of weight, or derivative thereof, of the third container or of the second material stored therein.

[0008] A method for monitoring the manufacture of a catalyst according to other embodiments includes determining a starting weight of a second container using a weight scale; transferring at least some of a first material from a first container to the second container, the first material being a component used for catalyst manufacture; determining a weight of the first material transferred to the second container using a mass flow meter; determining an ending weight of the second container using the weight scale; determining a change of weight of the second container; comparing the weight determined by the mass flow meter, or derivative thereof, to the change of weight, or derivative thereof, of the second container; and performing a further action if the weight determined by the mass flow meter, or derivative thereof, is different than the change of weight of the second container, or derivative thereof.

[0009] A method for monitoring the manufacture of a catalyst according to yet another embodiment includes determining a change in weight, or derivative thereof, of a first container or of a first material stored therein using a weight scale, the first material being a component used for catalyst manufacture; transferring at least some of a first material from a first container to a second container, determining a volume of the first material in the first container; calculating a weight, or derivative thereof, of the first material in the first

container based on the volume; comparing the change in weight, or derivative thereof, to the calculated weight, or derivative thereof; and performing a further action if the change in weight, or derivative thereof, is different than the calculated weight, or derivative thereof.

[0010] A method for monitoring the manufacture of a catalyst according to yet another embodiment includes determining a weight, or derivative thereof, of the first material transferred to the second container using a mass flow meter, the first material being a component used for catalyst manufacture; determining a volume of the first material in one of the containers; calculating a weight, or derivative thereof, of the first material in the one of the containers based on the volume; comparing the weight determined using the mass flow meter, or derivative thereof, to the calculated weight, or derivative thereof; and performing a further action if the weight determined using the mass flow meter, or derivative thereof, is different than the calculated weight, or derivative thereof.

[0011] A method for the manufacture a metallocene catalyst according to an embodiment of the present invention includes adding a solid material to a reaction vessel, the solid material being a component used for metallocene catalyst manufacture; adding a first liquid to the reaction vessel, the first liquid being another component used for the metallocene catalyst manufacture; and determining an amount of the first liquid added to the reaction vessel using at least one of a mass flow meter and a weight scale.

[0012] An amount of the first liquid added to the reaction vessel may be determined using both a mass flow meter and a weight scale, wherein a further action is performed if the amount determined by the flow meter is different than the amount determined by the weight scale. An amount of the first liquid added to the reaction vessel may be determined, for example, as a function of time using both the mass flow meter and the weight scale. A flow rate of the first liquid may be adjusted for altering a reaction condition in the reaction vessel based on the amount of first liquid added as a function of time. A flow rate of a second material into the reaction vessel may also be adjusted for altering a reaction

condition in the reaction vessel based on the amount of first material added as a function of time.

[0013] A system for manufacturing a catalyst according to one embodiment includes a first container containing a first material, the first material being a component used for catalyst manufacture; a reaction vessel for receiving the first material; a mass flow meter for determining a weight of the first material transferred to the reaction vessel; and at least one weight scale for selectively determining a weight of at least one of: the first container, the first material stored in the first container, the reaction vessel, and materials stored in the reaction vessel.

[0014] A processing unit for comparing a reading of the mass flow meter to a reading of the at least one weight scale. A processing unit may also be provided. The processing unit may perform one or more of the following functions: determining an amount of the first material added to the reaction vessel as a function of time using both the mass flow meter and the at least one weight scale, adjusting a flow rate of the first material into the reaction vessel for altering a reaction condition in the reaction vessel based on the amount of first material added as a function of time, and adjusting a flow rate of a second material into the reaction vessel for altering a reaction condition in the reaction vessel based on the amount of first material added as a function of time.

[0015] A method for manufacturing a metallocene catalyst according to a further embodiment of the present invention includes determining a starting weight of a first container or of a first material stored therein using a weight scale, the first material being a raw material used in metallocene catalyst manufacture; transferring at least some of the first material to a second container; determining an ending weight of the first container or of the first material stored therein using the weight scale; determining a change of weight of the first container or of the first material stored therein; comparing the weight determined by the weight scale, or derivative thereof, to a predefined weight, or derivative thereof; and performing

a further action if the change in weight determined by the weight scale, or derivative thereof, is different than the predefined weight, or derivative thereof.

[0016] A method for manufacturing a metallocene catalyst according to a further embodiment of the present invention includes transferring a first material to a container, the first material being a raw material used in metallocene catalyst manufacture; determining a weight of the first material transferred to the container using a mass flow meter; comparing the weight determined by the mass flow meter, or derivative thereof, to a predefined weight, or derivative thereof; and performing a further action if the weight determined by the mass flow meter, or derivative thereof, is different than the predefined weight, or derivative thereof.

[0017] A method for monitoring the manufacture of a catalyst according to yet another embodiment includes determining a weight of a first container or of a first material stored therein, or derivative thereof, transferring at least some of the first material to the second container, the first material being a component used for catalyst manufacture; comparing the weight determined using the weight scale, or derivative thereof and performing a further action if the weight determined using the weight scale, or derivative thereof, is different than a predefined weight, or derivative thereof.

[0018] A method for monitoring the manufacture of a catalyst according to yet another embodiment includes transferring at least some of a first material contained in a first container to the second container using a mass flow meter, the first material being a component used for catalyst manufacture; comparing the weight determined using the mass flow meter, or derivative thereof and performing a further action if the weight determined using the mass flow meter, or derivative thereof, is different than a predefined weight, or derivative thereof.

[0019] A method for monitoring the manufacture of a catalyst according to yet another embodiment includes determining a weight of a first container or of a first material stored therein, or derivative thereof, transferring at least some of the first material to the second container, the first material being a component used for catalyst manufacture; comparing the weight determined using the weight scale, or

derivative thereof and performing a further action if the weight determined using the weight scale, or derivative thereof, is different than a predefined weight, or derivative thereof.

[0020] A method for monitoring the manufacture of a catalyst according to yet another embodiment includes transferring at least some of a first material contained in a first container to the second container using a volumetric flow meter, the first material being a component used for catalyst manufacture; comparing the weight determined using the volumetric flow meter and density of the first material, or derivative thereof and performing a further action if the weight determined using the volumetric flow meter, or derivative thereof, is different than a predefined weight, or derivative thereof.

[0021] A method for monitoring the manufacture of a catalyst according to yet another embodiment includes transferring at least some of a first material contained in a first container to the second container using a level indicator attached to the first container, the first material being a component used for catalyst manufacture; comparing the weight determined using the level indicator, dimensions of the container and density of the first material, or derivative thereof and performing a further action if the weight determined using the volumetric flow meter, or derivative thereof, is different than a predefined weight, or derivative thereof.

[0022] In the various embodiments above, illustrative first materials include toluene, methyl alumoxane (MAO), at least one catalyst, such as, at least one metallocene, etc. The first material may also be a mixture of at least two materials.

[0023] The further action may include such actions, for example, as adding an additional amount of the first material to the second container, analyzing a composition of any materials in the second container, adding an amount of a second material to the second container to obtain a predetermined ratio of the first material to the second material, etc.

[0024] The second container may be, for example, a reaction vessel, a premix vessel for preparation of a batch charge, etc.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] Figure 1 is a schematic representation of the general methods, systems and/or apparatus of certain embodiments of the invention.

[0026] Figure 2 is a schematic representation of the general methods, systems and/or apparatus of certain embodiments of the invention.

[0027] Figure 3 is a schematic representation of the general methods, systems and/or apparatus of certain embodiments of the invention.

[0028] Figure 4 is a schematic representation of the general methods, systems and/or apparatus of certain embodiments of the invention illustrating implementation in a catalyst fabrication system.

[0029] Figure 5 is a schematic representation of the general methods, systems and/or apparatus of certain embodiments of the invention illustrating implementation in a catalyst fabrication system.

Detailed Description

[0030] The present invention is generally directed toward systems and methods for fabricating a catalyst and systems and methods for monitoring fabrication of a catalyst. Catalysts prepared in conjunction with the following systems, methods, and their equivalents are more consistent, for example, from batch to batch, which promotes stability of the reaction process in which the catalyst is ultimately used.

[0031] In a class of embodiments, a general method 100 of the invention can be described, for example, with reference to Figure 1, in which a starting weight of a first container or of a first material stored therein is determined in operation 102 using a weight scale, the first material being a component used for catalyst fabrication. In operation 104, after at least some of the first material is transferred

to a second container, a weight of the first material transferred to the second container is determined using a mass flow meter. In operation 106, an ending weight of the first container or of the first material stored therein is determined using the weight scale. In operation 108, a change of weight of the first container or of the first material stored therein is determined. In operation 110, the weight determined by the mass flow meter, or derivative thereof, is compared to the change of weight, or derivative thereof, of the first container or of the first material stored therein. In operation 112, a further action is performed if the weight determined by the mass flow meter, or derivative thereof, is different than the change of weight, or derivative thereof, of the first container or of the first material stored therein.

[0032] Further details of catalyst fabrication systems and methods, including specific apparatuses adapted therefore, are described below, and each of the below-described details are specifically considered in various combination with these and other embodiments described herein.

[0033] In another class of embodiments, with reference to the method 200 and Figure 2, a starting weight of a second container is determined using a weight scale in operation 202. In operation 204, after at least some of a first material is transferred from a first container to the second container, the first material being a component used for catalyst fabrication, a weight of the first material transferred to the second container is determined using a mass flow meter. In operation 206, an ending weight of the second container is determined using the weight scale. In operation 208, a change of weight of the second container is determined. In operation 210, the weight determined by the mass flow meter, or derivative thereof, is compared to the change of weight, or derivative thereof, of the second container. In operation 212, a further action is performed if the weight determined by the mass flow meter, or derivative thereof, is different than the change of weight of the second container, or derivative thereof.

[0034] In another class of embodiments, with reference to the method 300 and Figure 3, a solid material is added to a reaction vessel in operation 302, the solid

material being a component used for metallocene catalyst fabrication. In operation 304, a first liquid material is added to the reaction vessel, the first liquid material being another component used for the metallocene catalyst fabrication. In operation 306, an amount of the first liquid material added to the reaction vessel is determined using a mass flow meter during the adding of the first liquid material to the reaction vessel. In alternative operation 308, an amount of the first liquid material added to the reaction vessel is determined using a weight scale. In optional operation 310, a further action is performed if the amount determined by the flow meter is different than the amount determined by the weight scale, if the amount determined by the flow meter is different than a predetermined amount, and/or if the amount determined by the weight scale is different than a predetermined amount.

[0035] The present invention also includes devices and systems effective for fabricating a catalyst according to the aforementioned methods. In general, such devices are systems or apparatus that comprise a reaction vessel, one or more source containers, one or more weight scales, and one or more mass flow meters.

[0036] For example, a preferred general system 400 of the invention, shown in Figure 4, may comprise a first container 402 containing a first material 404 where the first material 404 is a component used for catalyst fabrication, a reaction vessel 406 for receiving the first material 404, a mass flow meter 408 for determining a weight of the first material 404 transferred to the reaction vessel 406, and at least one weight scale 410 for selectively determining a weight of: the first container 402, the first material 404 stored in the first container 402, the reaction vessel 406, and/or materials stored in the reaction vessel 406.

[0037] While the present invention is applicable to liquid/solid-based catalyst production, the broad concepts and teachings herein also have applicability to many types of processes, including but not limited to, gas phase, gas/solid phase, liquid/solid phase, gas/liquid phase, and gas/liquid/solid phase catalyst reactor systems including polymerized catalyst reactor systems; gas phase, gas/solid

phase, liquid/solid phase, gas/liquid phase, and gas/liquid/solid phase batch charge preparation systems, etc.

[0038] For ease of understanding of the reader, as well as to place the various embodiments of the invention in a context, much of the following description shall be presented, for illustration, in terms of a commercial, metallocene catalyst production system. It should be kept in mind that this is done by way of non-limiting example only.

[0039] Using the methods and systems as described herein results in, for example, a simple, commercially useful and cost effective catalyst which is consistent from batch to batch. Further, any deviations from optimal material transfer can be detected early on, resulting in the ability to adjust the fabrication process to account for the deviation, as well as terminate fabrication early in the process if an unrecoverable error occurs.

[0040] The catalysts creatable using the systems and methods described herein are useful in any reaction process, including polymerization processes, such as solution, slurry, and gas phase processes. In a class of embodiments, the invention in one aspect creates a polymerization catalyst that results in better reactor operability by ensuring the composition and quality of the particular catalyst.

Catalyst Fabrication – General Considerations

[0041] A catalyst is fabricated according to a recipe. A recipe specifies the amounts of the materials used in the fabrication of the catalyst. A recipe pre-defines the weights (or mass, which for purposes of the present disclosure is understood to be equivalent to “weight”) and/or volumes of materials used in catalyst fabrication. The recipe also specifies temperatures and/or pressures to be used during catalyst fabrication as well as times for material additions, reactions, drying, etc. Materials may be solids, liquids, solutions of solids in a suitable solvent or suspensions of solids in a suitable liquid.

[0042] Addition of known amounts of materials used in catalyst fabrication as specified in a catalyst recipe is important in obtaining catalyst batches that are consistent. Measurement of the amounts of materials used in catalyst fabrication can be performed using numerous techniques. These techniques include determining the quantities of materials used in catalyst fabrication by one or more of weight, volume, level or derivatives thereof. Such derivatives may include volumetric flow rate, mass flow rate or the like. Such derivatives may also include processing an addition measurement technique of a material addition time period to determine quantities of materials added for catalyst fabrication.

[0043] Addition measurement techniques are used for determining the quantity of material used in catalyst fabrication. Non-limiting examples include a weight scale, a mass flow meter, a volumetric flow meter, a level indicator or the like. For weight determination a volumetric flow meter and the density or a level indicator and the density and the container volume/height relationship may be used. The use of a mass flow meter, a volumetric flow meter and a level indicator are typically used for measurement of liquids. An addition measurement technique for determining the weight of solid material is typically the use of a weight scale.

[0044] Addition measurement techniques used for determining the volume of liquid material may similarly be measured using the same general techniques. Non-limiting examples include a weight scale and liquid density and container volume/height relationship, mass flow meter and liquid density, volumetric flow meter or level indicator and container volume/height relationship.

[0045] Materials used in catalyst fabrication are generally supplied in a container. Materials used in catalyst fabrication are typically transferred from a supply container to a fabrication container. The fabrication container may be a reactor for preparing the catalyst or an intermediate container to mix materials prior to addition to a reactor for catalyst fabrication.

[0046] Non-limiting examples of the use of measurement techniques include: determining the quantity of material addition by change of weight of a container

with materials for catalyst fabrication; determining the quantity of material addition by change of volume of material in a container with materials for catalyst fabrication; determining the quantity of material addition using a mass flow meter; determination of the quantity of material addition using a volumetric flow meter. Addition measurement using flow meters may require a derivative processing step to determine the total quantity of material over the time period of flow.

[0047] At least one addition measurement technique is used to determine the quantity of a material used in catalyst fabrication. However, more than one measurement technique may be used to determine the quantity of a material used in catalyst fabrication.

[0048] A method for monitoring fabrication of a catalyst such as a metallocene catalyst, Ziegler-Natta catalyst, Cr-based catalyst, Fe-based catalyst, and mixtures thereof, etc. according to one embodiment includes transferring a least some of a first material from a first container to a second container. The first material being a component used for catalyst fabrication and determining the quantity of the first material transferred using an addition measurement technique.

[0049] Also in the various embodiments herein, flush materials may be used to flush piping or other types of lines used to transfer the materials used for catalyst fabrication. The use of a flush material helps ensure that little or no materials used for catalyst fabrication remain in the transfer piping or lines. Suitable flush materials include gases and liquids, and are preferably compatible with the catalyst fabrication materials.

[0050] In each of the aforementioned generally preferred approaches and/or embodiments, the weight scale(s) and/or mass flow meter(s) can be employed for monitoring a variety of materials and processes, including but not limited to, gas phase, gas/solid phase, liquid/solid phase, gas/liquid phase, and gas/liquid/solid phase catalyst reactor systems including polymerized catalyst reactor systems; gas phase, gas/solid phase, liquid/solid phase, gas/liquid phase, and gas/liquid/solid phase batch charge preparation systems; etc.

Catalyst Fabrication System

[0051] In each of the aforementioned approaches and/or embodiments, a catalyst fabrication system can include a reaction vessel and one or more containers holding the various raw materials of the catalyst. Figure 4, discussed above, illustrates one approach.

[0052] With reference to Figure 5, a system 500 for fabricating a catalyst according to one embodiment of the invention includes a series of first containers 402. In a catalyst fabrication system, each first container may contain a raw material used to fabricate a catalyst, such as methyl alumoxane (MAO) and/a non-coordinating anions (NCAs), toluene, metallocene, and/or other known materials. A premix vessel 405 may receive the materials from the first containers 402, or the materials may be transported directly to the reaction vessel 406. A mass flow meter 408 may be associated with each first container 402 for determining a weight of the material transferred to the premix vessel 405 or reaction vessel 406. Alternatively, the flows from various first containers 402 may be directed through a single a mass flow meter 408.

[0053] A weight scale 410 may be associated with one or more of the first containers 402, premix vessel 405, reaction vessel 406, etc. for selectively determining a weight of: the associated container or vessel and material(s) stored therein, or the material(s) stored in the associated container or vessel [as where the weight scale is tared to the weight of the vessel or container].

[0054] The flow meters 408 and weight scales 410 may each be operatively coupled to a processing unit 412 via wired link, wireless link, etc., collectively represented by the reference symbol "A" in Figure 5. Operation of various components of the system 500 are set forth in more detail below.

Catalyst Reaction Vessels

[0055] The catalyst reaction typically takes place in an agitated vessel. Illustrative reaction vessels of this type include a conical screw blender (CSB), a catalyst mix vessel (CMV), or other type. An illustrative CSB has both an orbit arm and a screw for mixing. An illustrative CMV contains a double-helical ribbon blender, paddle or other type of agitator. The reaction vessel is typically a closed vessel. In a closed vessel, one or more fluids, gasses and/or solids are generally bounded by a barrier so that the fluids and particles are contained. Any of these may be associated with various residential, commercial, and/or industrial applications.

Weight Scales

[0056] With reference to Figures 4-5, the weight scales 410 may be any type of monitoring devices capable of providing an indication of a weight of a container and/or solid, liquid and/or gas material exerting forces due to gravity. The weight scale may be capable of taking single measurements at a time, periodic measurements, continuous measurements as a function of time, or combinations thereof.

[0057] In one approach, a container rests on the weight scale. In such embodiments, the weight scale may weigh the container at any desired time. Alternatively, the weight scale may be tared to the weight of the container, thereby providing an indication of the amount of material found therein.

[0058] In another approach, the container is integral to the weight scale, or vice versa.

[0059] Illustrative weight scales include floor scales, crane scales, platform scales, surface acoustic wave scales, and other types also known in the art. Suppliers of such scales include ARLYN SCALES, East Rockaway, NY; METTLER-TOLEDO, INC., Columbus, OH; etc.

Mass Flow Meters

[0060] With reference to Figures 4-5, the mass flow meters 408 may be any type of monitoring devices capable of providing an indication of an amount of a solid, liquid and/or gas material moving through a pipe, tube, through a trough, along a belt, etc. The indication of the amount of a material may be based on a mass of the material flowing by the sensor of the mass flow meter, a volume of the material of known density flowing by the sensor, etc. The mass flow meters may be capable of taking single measurements at a time, periodic measurements, continuous measurements as a function of time, or combinations thereof.

[0061] Illustrative mass flow meters include orifice, turbine, positive displacement, vortex shedding, rotameter, venturi, and Coriolis type flow meters known in the art. Illustrative Coriolis flow meters include the ACM series of Coriolis type flow meters from the AW COMPANY, Franksville, WI; the MICRO MOTION series Coriolis flow meters from EMERSON PROCESS MANAGEMENT, St. Louis, Missouri; etc.

Processing Unit

[0062] With reference to Figure 5, the processing unit 412 is coupled to the weight scales and the mass flow meters. The processing unit may be a simple monitoring device. Illustrative processing units include an application specific integrated circuit (ASIC), reconfigurable logic, or the like, and associated user interfaces. More complex processing units are also contemplated, such as computerized systems. The processing unit may be coupled to other system components such as process controllers.

[0063] In preferred embodiments, one or more circuit modules of the processing unit can be implemented and realized as an ASIC. Portions of the processing can also be performed in software in conjunction with appropriate circuitry and/or a host computing system.

[0064] The processing unit also preferably includes memory circuitry for storing various measurements for purposes including but not limited to logging,

measuring the amounts of materials added, comparing amounts of materials added to pre-determined batch material charges, controlling the amounts of added and controlling amounts of materials added at specified addition rates.

[0065] As mentioned above, while the weight meters and mass flow meters are described above and below in terms of being coupled to an external processing unit, the circuitry may also be implemented with a weight meter or mass flow meter in a single standalone unit. As an example, the weight scale may comprise a weight meter, a signal processing circuit, and/or a data retrieval circuit (e.g., comprising data memory circuitry, perhaps adapted for recording raw data received from the weight meter and, possibly, the mass flow meter).

Catalyst Fabrication Process Monitoring— General Considerations

[0066] In one approach, before transfer of a material from a source container to a destination container, the processing unit takes a reading from a weight scale weighing the source container. During transfer of the material from the source container to the destination container, the processing unit takes a series of readings from the mass flow meter to calculate the quantity of material transferred. Upon completion of the transfer, the processing unit takes another reading from the weight scale weighing the source container. The processing unit then compares the change in weight of the source container to the measured or calculated weight from the mass flow meter for various purposes, such as one or more of to verify that the proper weight of material has been added, to double check the reading of the mass flow meter against a weight difference of a source container, etc. If the difference in values is greater than a predetermined tolerance, the processing unit performs an action, such as outputting an alert or initiating remedial action. The predetermined tolerance may be, for example, within about 10.0% on a weight basis, preferably within about 5.0% on a weight, and ideally within less than about 2.0% on a weight basis. Illustrative alerts may include or result in: output of data for display to a user, sending of an electronic message (email, text message, etc.), sounding of an alarm, etc. Remedial action may include such actions as addition or removal of the subject material, addition or removal of one or more other materials to obtain a predetermined ratio of the

various materials, increase or decrease in flow rates of various materials, e.g., as in a continuous process, calibrating the weight scale and/or mass flow meter, etc. The further action may also include analyzing a composition of materials in the destination container, and possibly taking further steps.

[0067] In another approach, before transfer of a material from a source container to a destination container, the processing unit takes a reading from a weight scale weighing the destination container. During transfer of the material from the source container to the destination container, the processing unit takes a reading from the mass flow meter. Upon completion of the transfer, the processing unit takes another reading from the weight scale weighing the destination container. The processing unit then compares the change in weight of the destination container to the measured or calculated weight from the mass flow meter. If a discrepancy is found, the processing unit performs an action, such as outputting an alert or initiating remedial action.

[0068] In one approach, during transfer of a material from a source container to a destination container, the processing unit monitors a signal from the mass flow meter and a signal from a weight scale weighing the source or destination container. The processing unit continuously compares the change in weight of the subject container to the measured or calculated weight from the mass flow meter. If a discrepancy arises, the processing unit performs an action, such as outputting an alert or initiating remedial action.

[0069] In yet another approach, a mass derived from a volumetric measurement is compared to one or more weight-based values, e.g., a change in weight of a container, weight determined by a mass flow meter, derivatives thereof, etc. The mass may be derived from a volumetric measurement by multiplying the volume of the material transferred by the density of the material. The volumetric measurement can be taken or derived from the full volume of a container, the partial volume of a container, a reading from a volumetric flow meter, etc.

[0070] In any of the various approaches herein, various steps may be performed by a user as opposed to a processing unit, or they may work in conjunction with each other.

[0071] Illustrative processes for catalyst fabrication are provided by way of example below.

Catalyst Components and Catalyst Systems

[0072] Illustrative catalysts according to the present invention may include metallocene catalysts, Ziegler-Natta catalysts, and Cr-based catalysts, Fe-based catalysts, Ni-based catalysts, Pd-based catalysts, Pt-based catalysts, Ti-based catalysts, and mixtures thereof.

[0073] Chromium catalysts are generally obtained by calcining a chromium compound carried on an inorganic oxide carrier in a non-reducing atmosphere to activate it such that at least a portion of the carried chromium atoms is converted to hexavalent chromium atoms (Cr^{+6}) commonly referred to in the art as the Phillips catalyst.

[0074] Ziegler-Natta catalysts are typically based on titanium chlorides, magnesium chlorides and organometallic alkyl aluminum compounds.

[0075] Preferred catalysts of the invention, for example, are typically metal complexes derivable from the formula: $\{[(\text{L}^p)_m\text{M}(\text{A}^q)_n]^{+k}\}h[\text{B}'^{-j}]_i$ where L is a ligand bonded to M, p is the anionic charge of L and m is the number of L ligands and m is 1, 2 or 3; A is a ligand bonded to M and capable of inserting an olefin between the M-A bond, q is the anionic charge of A and n is the number of A ligands and n is 1, 2, 3 or 4, M is a metal, preferably a transition metal, and $(p \times m) + (q \times n) + k$ corresponds to the formal oxidation state of the metal center; where k is the charge on the cation and k is 1, 2, 3 or 4, and B' is a chemically stable, non-nucleophilic anionic complex, preferably having a molecular diameter of 4 Å or greater and j is the anionic charge on B', h is the number of cations of charge k, and i the number of anions of charge j such that $h \times k = j \times i$.

[0076] Any two L and/or A ligands may be bridged to each other. The catalyst compound may be "full-sandwich" compounds having two or more ligands L, which may be cyclopentadienyl ligands or substituted cyclopentadienyl ligands, or "half-sandwich" compounds having one ligand L, which is a cyclopentadienyl ligand or heteroatom substituted cyclopentadienyl ligand or hydrocarbyl substituted cyclopentadienyl ligand such as an indenyl ligand, a benzoindenyl ligand or a fluorenyl ligand and the like or any other ligand capable of η -5 bonding to a transition metal atom. One or more of these bulky ligands is π -bonded to the transition metal atom. Each L can be substituted with a combination of substituents, which can be the same or different. Non-limiting examples of substituents include hydrogen or a linear, branched or cyclic alkyl, alkenyl or aryl radical or combination thereof having from 1 to 30 carbon atoms or silyl containing radicals. The substituent can also be substituted with hydrogen or a linear, branched or cyclic alkyl, alkenyl or aryl radical having from 1 to 30 carbon atoms.

[0077] L may also be other types of ligands including but not limited to bulky amides, phosphides, alkoxides, aryloxides, imides, carbolides, borollides, porphyrins, phthalocyanines, corrins and other polyazomacrocycles. The metal atom may be a Group 4, 5 or 6 transition metal or a metal from the lanthanide and actinide series, preferably the transition metal is of Group 4. Other ligands may be bonded to the transition metal, such as a leaving group, such as but not limited to weak bases such as amines, phosphines, ether and the like. In addition to the transition metal, these ligands may be optionally bonded to A or L. Non-limiting examples of catalyst components and catalyst systems are discussed in for example, U.S. Patent Nos. 4,530,914, 4,871,705, 4,937,299, 5,124,418, 5,017,714, 5,120,867, 5,278,264, 5,278,119, 5,304,614, 5,324,800, 5,347,025, 5,350,723, 5,391,790, 5,391,789, EP-A-0591756, EP-A-0520732, EP-A-0420436, WO 91/104257, WO 92/00333, WO 93/08221, WO 93/08199 and WO 94/01471.

[0078] In a class of embodiments, the activated catalyst of the invention is formed from a catalyst compound represented by the general formula: $(L^p)_m M(A^q)_n (E^r)_o$ where L, M, A, and p, m, q and n are as defined above and E is an anionic leaving

group such as but not limited to hydrocarbyl, hydrogen, halide or any other anionic ligands; r is the anionic charge of E and o is the number of E ligands and o is 1, 2, 3 or 4 such that $(p \times m) + (q \times n) + (r \times o)$ is equal to the formal oxidation state of the metal center, and an aluminum alkyl, alumoxane, modified alumoxane or any other oxy- containing organometallic compound or non-coordinating ionic activators, or a combination thereof

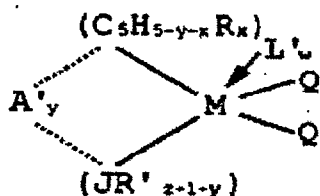
[0079] Further, the catalyst component of the invention may include monocyclopentadienyl heteroatom containing compounds. This heteroatom is activated by either an alumoxane, modified alumoxane, a non-coordinating ionic activator, a Lewis acid or a combination thereof to form an active polymerization catalyst system. These types of catalyst systems are described in, for example, WO 92/100333, WO 94/07928, WO 91/04257, WO 94/03506, U.S. Patent Nos. 5,057,475, 5,096,867, 5,055,438, 5,198,401, 5,227,440, 5,264,405, and EP-A-0420436. Additionally it is within the scope of this invention that the metallocene catalysts and catalyst systems may be those described in U. S. Patent Nos. 5,064,802, 5,145,819, 5,149,819, 5,243,001, 5,239,022, 5,276,208, 5,296,434, 5,321,106, 5,329,031, 5,304,614, WO 93/108221, WO 93/108199, WO 95/07140, EP-A-0578838, and EP-A-0638595.

[0080] The preferred transition metal component of the catalyst of the invention is a Group 4 metal, particularly, titanium, zirconium and hafnium. The transition metal may be in any formal oxidation state, preferably +2, +3 or +4 or a mixture thereof, preferably +4.

[0081] In another embodiment the catalyst may be represented by one of the formula (I): $(C_5H_{5-d-f}R''_d)_eR'''_fMQ_{g-e}$ wherein M is a Group 4, 5, 6 transition metal, at least one $(C_5H_{5-d-f}R''_d)$ is an unsubstituted or substituted cyclopentadienyl ligand bonded to M , each W , which can be the same or different is hydrogen or a substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, R is one or more or a combination of carbon, germanium, silicon,

phosphorous or nitrogen atoms containing radical bridging two $(C_5H_{5-d-f}R''_d)$ rings, or bridging one $(C_5H_{5-d-f}R''_d)$ ring to M; each Q which can be the same or different is a hydride, substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides or any other univalent anionic ligand or combination thereof; two Q can be an alkylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anion chelating ligand having from 1 to 30 carbon atoms, where g is an integer corresponding to the formal oxidation state of M, d is 0, 1, 2, 3, 4 or 5, f is 0 or 1 and e is 1, 2 or 3.

[0082] In another preferred embodiment of this invention the catalyst may be represented by the formula (II):



wherein M is Ti, Zr or Hf, $(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring which is substituted with from 0 to 5 substituent groups R, "x" is 0, 1, 2, 3, 4 or 5 denoting the degree of substitution, and each substituent group R is, independently, a radical selected from a group consisting of C_1 - C_{20} hydrocarbyl radicals, substituted C_1 - C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, C_1 - C_{20} hydrocarbyl-substituted metalloids wherein the metalloid is selected from the Group 14 of the Periodic Table of Elements, and halogen radicals or $(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring in which two adjacent R-groups are joined forming C_4 - C_{20} ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand such as indenyl, tetrahydroindenyl, fluorenyl or octahydrofluorenyl; (JR'_{z-1-y}) is a heteroatom ligand in which J is an element with a coordination number of three from Group 15 or an element with a coordination number of two from Group 16 of the Periodic Table of Elements, preferably nitrogen, phosphorus, oxygen or sulfur with nitrogen being preferred, and each R' is, independently, a radical selected from a group consisting of C_1 - C_{20} hydrocarbyl radicals wherein one or more

hydrogen atoms is replaced by a halogen atom, y is 0 or 1, and " z " is the coordination number of the element J ; each Q is, independently any univalent anionic ligand such as halogen, hydride, or substituted or unsubstituted C_1 - C_{30} hydrocarbyl, alkoxide, aryloxy, amide or phosphide, provided that two Q may be an alkylidene, a cyclometallated hydrocarbyl or any other divalent anionic chelating ligand; A is a covalent bridging group containing a Group 15 or 14 element such as, but not limited to, a dialkyl, alkylaryl or diaryl silicon or germanium radical, alkyl or aryl phosphine or amine radical, or a hydrocarbyl radical such as methylene, ethylene and the like; L' is a Lewis base such as diethylether, tetraethylammonium chloride, tetrahydrofuran, dimethylaniline, aniline, trimethylphosphine, n -butylamine, and the like; and w is a number from 0 to 3. Additionally, L' may be bonded to any of R , R' or Q .

[0083] For the purposes of this patent specification and appended claims, the terms "cocatalysts" and "activators" are used interchangeably and are defined to be any compound or component which can activate a catalyst, for example, a metallocene catalyst. Examples include a Lewis acid or a non-coordinating ionic activator or ionizing activator or any other compound that can convert a neutral metallocene catalyst component to a metallocene cation. It is within the scope of this invention to use alumoxane as an activator, and/or to also use preferably, compatible ionizing activators, neutral or ionic, such as tri(n -butyl) ammonium tetrakis(pentafluorophenyl) boron or a tris(perfluorophenyl) boron metalloid precursor which ionize the neutral metallocene compound and stabilize its resulting metallocene cation.

[0084] There are a variety of methods for preparing alumoxane and modified alumoxanes, non-limiting examples of which are described in U. S. Patent No. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031, 5,278,119, 5,391,793, 5,391,529, EP-A-0561476, EP-B1-0279586, EP-A-0594218 and WO 94/10180.

[0085] Ionizing compounds may contain an active proton, or some other cation associated with but not coordinated or only loosely coordinated to the remaining ion of the ionizing compound. Such compounds and the like are described in, for example, EP-A-0570982, EP-A-0520732, EP-A-0495375, EP-A-0426637, EP-A-500944, EP-A-0277003, EP-A-0277004, U. S. Patent Nos. 5,153,157, 5,198,401, 5,066,741, 5,206,197, 5,241,025, 5,387,568 and 5,384,299, and U.S. Patent Application Serial No. 08/285,380, filed August 3, 1994. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations, see for example, WO 94/07928, U.S. Application Serial No. 08/155,313 filed November 19, 1993, and U.S. Patent No. 5,153,157. In an embodiment of the invention two or more metallocenes as described above can be combined to form a catalyst system, see for example, those mixed catalysts described in U.S. Patent No. 5,281,679 and U.S. Application Serial No. 138,818, filed October 14, 1993. In another embodiment of the catalyst system of the invention combinations of one or more of catalyst components of general formula (I) and/or (H) are contemplated. In one embodiment, metallocene catalyst components can be combined to form blend compositions as described in, for example, WO 90/03414. In yet another embodiment, mixed metallocenes as described in, for example, U.S. Patent Nos. 4,937,299 and 4,935,474, may be used to produce polymers having a broad molecular weight distribution and/or a multimodal molecular weight distribution.

[0086] In another embodiment of the invention, at least one metallocene catalyst can be combined with a non-metallocene, including nitrogen containing tridentate compounds or traditional Ziegler-Natta catalysts, non-limiting examples are described in U.S. Patent Nos. 4,701,432, 5,124,418, 5,077,255, 5,183,867, 5,391,660 and 5,395,810.

[0087] For purposes of this patent specification the terms "carrier" or "support" are interchangeable and can be any support material, preferably a porous support material, such as for example, talc, inorganic oxides, inorganic chlorides, for example magnesium chloride, and resinous support materials such as polystyrene or polystyrene divinyl benzene polyolefins or polymeric compounds or any other

organic or inorganic support material and the like, or mixtures thereof. The preferred support materials are inorganic oxide materials, which include those of Groups 2, 3, 4, 5, 13 or 14 metal oxides. In a preferred embodiment, the catalyst support materials include silica, alumina, silica-alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina, or silica-alumina, magnesia, titania, zirconia, and the like.

[0088] It is preferred that the carrier of the catalyst of this invention has a surface area in the range of from about 10 to about 700 m²/g, pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from about 1 to about 500 μm. More preferably, the surface area is in the range of from about 50 to about 500 m²/g, pore volume of from about 0.5 to about 3.5 cc/g and average particle size of from about 1 to about 200 μm. Most preferably the surface area range is from about 100 to about 400 m²/g, pore volume from about 0.8 to about 3.0 cc/g and average particle size is from about .1 to about 100 μm. The average pore size of the carrier of the invention typically has pore size in the range of from 10 to 1000Å, preferably 50 to about 500Å, and most preferably 75 to about 350Å.

Catalyst Fabrication Methodology

[0089] The following process descriptions apply to production of catalysts. The following process descriptions are particularly useful for fabricating polymerization catalysts. The following presentation of process steps may be used for various catalyst grades; however, steps may be added or omitted for any reason without straying from the spirit and scope of the present invention. The quantities of raw materials added may vary by grade or type of catalyst. Further, steps from the various processes may be combined and/or substituted in each of the various possible permutations.

[0090] Chromium catalysts are generally obtained by calcining a chromium compound carried on an inorganic oxide carrier in a non-reducing atmosphere to activate it such that at least a portion of the carried chromium atoms is converted

to hexavalent chromium atoms (Cr^{+6}) commonly referred to in the art as the Phillips catalyst. The respective material is disposed onto silica, fluidized and heated in the presence of oxygen to about 250°C – 860°C , converting chromium from the $+3$ oxidation state to the $+6$ oxidation state.

[0091] There are a variety of methods for preparing metallocene and other catalysts, non-limiting examples of which are described in WO 96/34020, WO 96/39450, WO 97/06187, WO 97/24375, WO 97/29134, WO 97/31035, WO 97/48735, WO 98/13393, WO 98/44011, WO 98/55518, WO 99/26989, WO 99/29737, WO 99/51648, and WO 99/61486.

[0092] In a class of embodiments, the invention provides for a batch process for fabricating a metallocene catalyst, with a batch size, for example, of approximately 1,200 lbs of finished catalyst. Reference is also made to Figure 5. The catalyst process in this example may be divided into the following general steps:

1. Silica Dehydration
2. Premix Preparation
3. Premix/Silica Reaction
4. Additive B Addition and Mixing
5. Catalyst Drying Under Vacuum

Silica Dehydration

[0093] Granular silica is dehydrated at high temperature, e.g., $>500^{\circ}\text{C}$ for a period of time, generally ranging from a few hours to an entire day or more.

Premix Preparation

[0094] Based on the catalyst grade, the recipe quantities of the aromatic solvent, for example, toluene, the co-catalyst, for example, methyl alumoxane (MAO), and metallocene solutions are transferred from first containers 402 and mixed in a

premix vessel 405. To ensure that the proper quantities of each component are added to the premix vessel 405, the starting weight of the source container 402 or of the liquid stored therein may be obtained using a weight scale 410 of a type known in the art. During the transfer, the amount of component added to the premix vessel 405 can be measured using a mass flow meter 408 of a type known in the art. After the transfer, the ending weight of the source container 402 or of the liquid stored therein is obtained using the weight scale 410. The change of weight of the source container 402 or the liquid therein is then determined and compared to the weight determined by the mass flow meter 408, or a derivative thereof (e.g., weight of the component of interest in solution, a voltage level indicating the current or last weight measurement, a digital signal indicating a weight, etc.), or calculated from a reading thereof.

[0095] If the weight determined by the mass flow meter 408, or derivative thereof, is different than the change of weight, or derivative thereof, of the source container 402 or of the component stored therein, then a further action is performed. The further action may be taken by a user, by a processing unit in conjunction with the appropriate equipment, or combination thereof. The further action may be a remedial action, such as addition or removal of the subject component, addition or removal of one or more other components to obtain a predetermined ratio of the various components, calibrating the weight scale 410 and/or mass flow meter 408, etc. The further action may include analyzing a composition of materials in the premix vessel 405, and possibly taking further steps. Yet another action may include discarding the materials in the premix vessel 405 and starting over.

[0096] If the weight determined by the mass flow meter 408, or derivative thereof, is about the same as the change of weight, or derivative thereof, of the source container 402 or of the liquid stored therein, i.e., within acceptable tolerances, the producer can be confident that the proper amount of the component has been added, and the process proceeds.

[0097] It also bears mention that just because a further action is to be taken does not mean that the production process is stopped. On the contrary, the process may continue, the further action being performed concurrently therewith or as a portion thereof.

[0098] Thus, the amounts of one or more of the components added to the premix vessel 405 can be verified by comparing the change in weight of the source container 402 and the mass flow meter 408 reading. In this example, for instance, the source container 402 containing toluene can be weighed prior to transferring the toluene to the premix vessel 405. As the toluene, for example, is being transferred, a mass flow meter 408 may be used to determine the amount of the toluene added to the premix vessel 405. If the two measurements vary by greater than a predetermined tolerance (determined by producer), an additional action can be performed.

[0099] In a variation, the weight of the premix vessel 405 both prior to addition of one or more components and thereafter is determined rather than, or in addition to, the weight of the source container 402. The change in weight, or derivative thereof, is then compared to a mass flow meter 408 reading of the amount of the one or more components added to the premix vessel 405. If the weight determined by the mass flow meter 408, or derivative thereof, is different than the change of weight, or derivative thereof, of the premix vessel 405, then a further action can be performed. If the change in weight, or derivative thereof, is about the same as the weight determined from the mass flow meter 408, or derivative thereof, then process proceeds.

[0100] In a further variation, the change in weight of the source container 402, or derivative thereof, is compared to the change in weight, or derivative thereof, of the premix vessel 405 and the weight from the mass flow meter 408 reading, or derivative thereof. If the various weights, or derivatives thereof, do not match, a further action can be performed. If the change in weight, or derivative thereof, is about the same as the weight determined from the mass flow meter 408, or derivative thereof, then process proceeds.

[0101] In a variation, an estimated weight transferred from the first container 402 to the premix vessel 405, or derivative thereof, may be determined by a mass flow meter 408 or weight scale 410, and compared to a predetermined desired weight, e.g., recipe weight, of material that should have been added to the premix vessel 405. If the weight determined by the mass flow meter 408 or mass scale is different than the predefined value, a further action can be performed.

[0102] Following the addition of these raw materials, the source containers 402 are rinsed with a specified amount of toluene, for example, to flush residual material into the premix vessel 405. The change in weight of the rinse fluid source container 402, or derivative thereof, may be compared to a weight obtained or derived from a mass flow meter 408 monitoring the addition of the rinse fluid to the reaction system. In another approach, the change in weight of the premix vessel 405, or derivative thereof, may be compared to a weight obtained or derived from a mass flow meter 408 monitoring the addition of the rinse fluid to the reaction system. Additional rinses may be performed throughout the process, and the amount of material added thereby may be monitored in a similar manner.

[0103] The solution in the premix vessel 405 is mixed at ambient temperature for 30-120 minutes, for example. The premix vessel 405 allows for catalyst to be prepared, preferably using a liquids-to-solids method (i.e., premix is added on top of silica which is already located in the catalyst reactor).

[0104] The premix vessel 405 can be bypassed if direct addition of the raw materials to the reaction vessel 406 is desired for any catalyst. In such an embodiment, the change in weights of the source containers 402, or derivatives thereof, may be compared to the weights obtained or derived from mass flow meter 408s monitoring the addition of the various components to the reaction vessel 406.

Premix/Silica Reaction

[0105] In this example, 850 lbs of dehydrated silica is added to the catalyst reaction vessel 406, which may be a CSB, a CMV, or other type. The premix solution is transferred into the reactor (liquids-to-solids addition) and mixed with the silica for 30-120 minutes.

[0106] To ensure that the proper amount of premix has been added to the reaction vessel 406, the change in weight of the premix vessel 405 and/or reaction vessel 406, or derivative thereof, can be compared to each other and/or a mass flow meter 408 reading of the transferred premix. Again, if the various values match within a predefined tolerance, the process continues. If the various values do not match within the predefined tolerance, a further action may be taken.

[0107] An amount of one or more of the various components added to the reaction vessel 406 may also be determined as a function of time using both a mass flow meter 408 on the material transfer line and a weight scale 410 on the source container 402/premix vessel 405 and/or the reaction vessel 406. This allows, for example, control of compositions within the catalyst preparation vessel by adjusting feed flow rate(s) of the various components to control the rates of reaction and/or to obtain desired reaction products.

[0108] A toluene rinse, for example, of the premix vessel 405 is performed and sent to the catalyst reactor. Both the CMV and CSB may be jacketed vessels. Thus, the vessel temperature may be controlled by a tempered water system that may include both a steam heater and cooling water cooler.

Additive B Addition and Mixing

[0109] Once the premix/silica reaction is complete, Additive B solution is charged to the catalyst reactor based on the recipe value. Additive B may be, a continuity additive, such as, for example, Atmer AS-990 in an aromatic solvent, such as, toluene, containing 5.3 pounds (2.4 kg) of contained Atmer AS-990 (available from CIBA SPECIALTY CHEMICALS CORPORATION, Houston, TX).

[0110] To ensure that the proper amount of Additive B has been added to the reaction vessel 406, the change in weight of the source container 402 and/or reaction vessel 406, or derivative thereof, can be compared to each other and/or a mass flow meter 408 reading of the transferred Additive B. Again, if the various values match within a predefined tolerance, the process continues. If the various values do not match within the predefined tolerance, a further action may be taken.

[0111] Following the Additive B addition, a toluene rinse is performed on the Additive B line and the rinse is sent to the catalyst reactor. The contents of the catalyst reactor are mixed for 10-120 minutes.

Catalyst Drying Under Vacuum

[0112] After the catalyst has finished mixing, the temperature of the catalyst reactor is increased by circulating tempered water through the vessel jacket. The toluene is removed from the catalyst by pulling a vacuum on the catalyst reaction vessel 406. During drying, a small amount of nitrogen is sparged through the vessel to aid in removal of toluene. As the toluene vaporizes, it passed through an overhead filter to prevent catalyst particles from entering the recovery system. The vapor stream is condensed in an overhead condenser and recovered in a toluene accumulator. The typical drying time for a batch of catalyst is 8-24 hours. When the batch is finished drying, it may be cooled to <100°F (for safety) and transferred while optionally screening the catalyst through screener into a catalyst storage vessel.

[0113] It should also be kept in mind that various steps performed in the methodology presented herein may be performed in any combination in each of the various combinations and permutations of the present invention.

Operating Conditions

[0114] The operating conditions of the reactor and other systems should not be narrowly construed. While general operating conditions have been provided

above for polymerization reactor systems, other systems, in addition to those listed above, have widely varying process conditions, such as temperature, pressure, fluid flowrate, *etc.* but may also be applied.

EXAMPLES

[0115] Several illustrative methods of fabricating catalysts are presented below. In each of the following examples, the amounts of materials added from vessel to vessel may be measured using weight scales and/or mass flow meters as set forth above. Thus, the change in weight of a source vessel and/or a destination vessel, or derivative thereof, can be compared to each other and/or a mass flow meter reading for the material being transferred. Again, if the various values do not match within a predefined tolerance, a further action may be taken.

[0116] Example 1: The supported catalyst of this example was prepared from 800 lbs (364 kg) of silica (Davison 948 available from W.R. GRACE, DAVISON CHEMICAL DIVISION, Baltimore, Maryland) dehydrated at 600°C. The catalyst was prepared in a mixing vessel with an agitator. An initial charge of 1156 pounds (525 kg) toluene was added to the mixer. This was followed by mixing 925 pounds (420 kg) of 30 percent by weight methyl alumoxane (MAO) in toluene (available from ALBERMARLE CORPORATION, Baton Rouge, Louisiana). This was followed with 100 pounds (46 kg) of 20 percent by weight bis(1,3-methyl-n-butyl cyclopentadienyl) zirconium dichloride in toluene (20.4 pounds (9.3 kg) of contained metallocene)). An additional 144 pounds (66 kg) of toluene was added to the mixer to rinse the metallocene feed cylinder and allowed to mix for 30 minutes at ambient conditions. The above mixture was added to the silica after which 54.3 pounds (25 kg) of a Atmer AS-990 in toluene solution, containing 5.3 pounds (2.4 kg) of contained Atmer AS-990 (available from CIBA SPECIALTY CHEMICALS CORPORATION, Houston, TX). An additional 100 pounds (46Kg) of toluene rinsed the surface modifier container and was added to the mixer. The total liquid volume was equivalent to 2.4 cc/cc pore volume of the silica. The resulting slurry was vacuum dried at 3.2 psia (22 kPa) at 175°F (79°C) to a free flowing powder. The final catalyst weight was 1093 pounds (497 kg).

The catalyst had a final zirconium loading of 0.40 weight percent and an aluminum loading of 12.0 weight percent.

[0117] Example 2: The metallocene catalyst was prepared from 600°C silica having a water content of 1.3 weight percent (Davison 948 silica, available from W. R. GRACE, DAVISON CHEMICAL DIVISION, Baltimore, Maryland). This catalyst was prepared by mixing 850 pounds (386 kg) of silica with 340 pounds (154 kg) of a catalyst precursor. The catalyst precursor was separately prepared by mixing together 82 pounds (37 kg) of a 28 weight percent solution of bis(1-methyl-3-n-butylcyclopentadienyl) zirconium dichloride in toluene with 1060 pounds (481 kg) of a 30 percent by weight solution of methylalumoxane available from ALBEMARLE CORPORATION, Baton Rouge, Louisiana). An additional 1300 pounds (590 kg) of toluene were added and the mixture held at 80°F (27°C) for 1 hour after which 6 pounds (3 kg) of (Atmer AS-990 available from CIBA SPECIALTY CHEMICALS CORPORATION, Houston, TX) was added and allowed to mix for one hour. A vacuum was applied and the catalyst was allowed to dry for fifteen hours. It was then dried at 175°F (79°C) to a free flowing powder. The final catalyst weight was 1216 pounds (552 kg). The final catalyst had a zirconium loading of 0.40 % and aluminum loading of 12.5%.

[0118] Example 3: The metallocene catalyst was prepared from 850 lbs (385.9 kg) of silica (Davison 948 available from W. R. GRACE, DAVISON CHEMICAL DIVISION, Baltimore, Maryland) dehydrated at 600°C. The catalyst was prepared in a mixing vessel with an agitator. An initial charge of 1325 lbs (601.6 kgs) toluene was added to the mixer. This was followed by mixing 1050 lbs (476.7 kgs) of 30 percent by weight methyl alumoxane (MAO) in toluene (available from ALBERMARLE CORPORATION, Baton Rouge, Louisiana). This was followed with 92 lbs (41.8 kgs) of 20 percent by weight bis(1-methyl, 3-n-butyl cyclopentadienyl) zirconium dichloride in toluene (18.4 lbs (8.3 5 kgs) of contained metallocene)). An additional 500 lbs (227 kgs) of toluene were added to the mixer to rinse the metallocene feed cylinder and allowed to mix for 30 minutes at ambient conditions. The above mixture was added to the silica after which 60 lbs (27.2 kgs) of a Atmer AS-990 in toluene solution, containing 6 lbs

(2.7 kgs) of contained Atmer AS-990 (available from CIBA SPECIALTY CHEMICALS CORPORATION, Houston, TX) was added. An additional 100 lbs (46 kgs) of toluene rinsed the surface modifier container and was added to the mixer. The total liquid volume was equivalent to 2.58 cc/cc pore volume of the silica. The resulting slurry was vacuum dried at 3.2 psia (22 kPa) at 175°F (79°C) to a free flowing powder. The final catalyst weight was 1190 lbs (540 kgs). The catalyst had a final zirconium loading of approximately 0.40 weight percent and an aluminum loading of approximately 12.0 weight percent.

[0119] Example 4: The metallocene catalyst was prepared from 600°C silica having a water content of 1.3 weight percent (Davison 948 silica, available from W.R. GRACE, DAVISON CHEMICAL DIVISION, Baltimore, Maryland). This catalyst was prepared by mixing 850 pounds (386 kg) of silica with 340 pounds (154 kg) of a catalyst precursor. The catalyst precursor was separately prepared by mixing together 82 pounds (37 kg) of a 28 weight percent solution of bis(1-methyl-3-n-butyl-cyclo pentadienyl) zirconium dichloride in toluene with 1060 pounds (481 kg) of a 30 percent by weight solution of methylalumoxane available from ALBERMARLE CORPORATION (Baton Rouge, Louisiana). An additional 1300 pounds (590 kg) of toluene were added and the mixture held at 80°F (27 °C) for 1 hour after which 6 pounds (3 kg) of a surface modifier (Atmer AS-990 available from CIBA SPECIALTY CHEMICALS CORPORATION, Houston, TX) was added and allowed to mix for one hour. Vacuum was applied and the catalyst was allowed to dry for fifteen hours. It was then dried at 175 °F (79°C) to a free flowing powder. The final catalyst weight was 1216 pounds (552 kg). The final catalyst had a zirconium loading of 0.40% and aluminum loading of 12.5%

[0120] Example 5: The metallocene-type catalyst compound used in this Example 5 was a dimethylsilyl-bis(tetrahydroindenyl)zirconium dichloride ($\text{Me}_2\text{Si}(\text{H}_4\text{Ind})_2\text{ZrCl}_2$) available from ALBEMARLE CORPORATION, Baton Rouge, Louisiana. The ($\text{Me}_2\text{Si}(\text{H}_4\text{Ind})_2\text{ZrCl}_2$) catalyst compound was prepared on Crosfield ES-70 grade silica which is dehydrated at 600°C having an approximately a 1.0 weight percent water content. The Crosfield ES-70 grade

silica having an Average Particle Size of 40 microns is available from Crosfield, Manchester, England. The first step in the manufacture of the supported metallocene-type catalyst above involves forming a precursor solution. 460 lbs (209 kg) of sparged and dried toluene is added to an agitated reactor after which 1060 lbs (482 kg) of a weight percent methylaluminoxane (ALBEMARLE CORP., Baton Rouge, LA.) is added. 947 lbs (430 kg) of a 2 weight percent toluene solution of a dimethyl silylbis(tetrahydroindenyl)zirconium dichloride catalyst compound and 600 lbs (272 kg) of additional toluene are introduced into the reactor. The precursor solution is then stirred at 80°F to 100°F (26.7 to 37.8°C) for one hour. While stirring the precursor solution above, 850 lbs (386 kg) of 600°C dehydrated silica as described above is added slowly to the precursor solution and the mixture agitated for 30 min at 80°F to 100°F (26.7 to 37.8°C). At the end of the 30 min agitation of the mixture, 240 lbs (109kg) of a 10 weight percent toluene solution of AS-990 (N,N-bis(2-hydroxyethyl)octadecylamine ($C_{18}H_{37}N(CH_2CH_2OH)_2$) available as Atmer AS-990 CIBA SPECIALTY CHEMICALS CORPORATION, Houston, TX, is added together with an additional 110 lbs (50 kg) of a toluene rinse and the reactor contents then mixed for 30 min while heating to 175°F (79°C). After 30 min, vacuum is applied and the catalyst mixture dried at 175°F (79°C) for about 15 hours to a free flowing powder. The final catalyst weight was 1200 lbs (544 kg) and had a Zr wt% of 0.35 and an Al wt% of 12.0.

CLAIMS

What is claimed is:

1. A method for monitoring the manufacture of a catalyst, comprising:

determining a starting weight of a first container or of a first material stored therein using a weight scale, the first material being a component used for catalyst manufacture;

after at least some of the first material is transferred to a second container, determining a weight of the first material transferred to the second container using a mass flow meter;

determining an ending weight of the first container or of the first material stored therein using the weight scale;

determining a change of weight of the first container or of the first material stored therein;

comparing the weight determined by the mass flow meter, or derivative thereof, to the change of weight, or derivative thereof, of the first container or of the first material stored therein; and

performing a further action if the weight determined by the mass flow meter, or derivative thereof, is different than the change of weight, or derivative thereof, of the first container or of the first material stored therein.

2. The method as recited in claim 1, wherein the first material is toluene.
3. The method as recited in claim 1, wherein the first material is methyl alumoxane (MAO).

4. The method as recited in claim 1, wherein the first material is at least one metallocene.
5. The method as recited in claim 1, wherein the first material is a mixture of at least two materials selected from a group consisting of toluene, methyl alumoxane, and at least one metallocene.
6. The method as recited in claim 1, wherein the catalyst is at least one metallocene catalyst.
7. The method as recited in claim 1, wherein the catalyst least one Ziegler-Natta catalyst.
8. The method as recited in claim 1, wherein the catalyst is at least one Cr-based catalyst.
9. The method of any one of preceding claims, wherein performing the further action comprises adding an additional amount of the first material to the second container.
10. The method of any one of claims 1-8, wherein performing the further action comprises analyzing a composition of any materials in the second container.
11. The method of any one of claims 1-8, wherein performing the further action comprises adding an amount of a second material to the second container to obtain a predetermined ratio of the first material to the second material.
12. The method of any one of preceding claims, wherein the second container is a reaction vessel.
13. The method of any one of claims 1-11, wherein the second container is a premix vessel for preparation of a batch charge.
14. The method of any one of preceding claims, further comprising determining a starting weight of a third container or of a second material stored

therein using a second weight scale, the second material being a component used for the catalyst fabrication; transferring the second material to the second container; determining a weight of the second material transferred to the second container using a second mass flow meter; determining an ending weight of the third container or of the second material stored therein using the second weight scale; determining a change of weight of the third container or of the second material stored therein; comparing the weight determined by the second mass flow meter, or derivative thereof, to the change of weight, or derivative thereof, of the third container or of the second material stored therein; and performing a further action if the weight determined by the second mass flow meter, or derivative thereof, is different than the change of weight, or derivative thereof, of the third container or of the second material stored therein.

15. A method for monitoring the manufacture of a catalyst, comprising:

determining a starting weight of a second container using a weight scale;

after at least some of a first material is transferred from a first container to the second container, determining a weight of the first material transferred to the second container using a mass flow meter, the first material being a component used for catalyst manufacture;

determining an ending weight of the second container using the weight scale;

determining a change of weight of the second container;

comparing the weight determined by the mass flow meter, or derivative thereof, to the change of weight, or derivative thereof, of the second container; and

performing a further action if the weight determined by the mass flow meter, or derivative thereof, is different than the change of weight of the second container, or derivative thereof.

16. The method as recited in claim 15, wherein the first material is toluene.

17. The method as recited in claim 15, wherein the first material is methyl alumoxane (MAO).
18. The method as recited in claim 15, wherein the first material is at least one metallocene.
19. The method as recited in claim 15, wherein the first material is a mixture of at least two materials selected from a group consisting of toluene, methyl alumoxane, and at least one metallocene.
20. The method as recited in claim 15, wherein the catalyst is at least one metallocene catalyst.
21. The method as recited in claim 15, wherein the catalyst is at least one Ziegler-Natta catalyst.
22. The method as recited in claim 15, wherein the catalyst is at least one Cr-based catalyst.
23. The method of any one of claims 15-22, wherein performing the further action comprises adding an additional amount of the first material to the second container.
24. The method of any one of claims 15-22, wherein performing the further action comprises analyzing a composition of any materials in the second container.
25. The method of any one of claims 15-22, wherein performing the further action comprises adding an amount of a second material to the second container to obtain a predetermined ratio of the first material to the second material.
26. The method of any one of claims 15-25, wherein the second container is a reaction vessel.
27. The method of any one of claims 15-25, wherein the second container is a premix vessel for preparation of a batch charge.

28. The method of any one of claims 15-27, further comprising determining a starting weight of a third container or of a second material stored therein using a second weight scale, the second material being a component used for the catalyst fabrication; transferring the second material to the second container; determining a weight of the second material transferred to the second container using a second mass flow meter; determining an ending weight of the third container or of the second material stored therein using the second weight scale; determining a change of weight of the third container or of the second material stored therein; comparing the weight determined by the second mass flow meter, or derivative thereof, to the change of weight, or derivative thereof, of the third container or of the second material stored therein; and performing a further action if the weight determined by the second mass flow meter, or derivative thereof, is different than the change of weight, or derivative thereof, of the third container or of the second material stored therein.

29. A method for monitoring the manufacture of a catalyst, comprising:

determining a change in weight, or derivative thereof, of a first container or of a first material stored therein using a weight scale, the first material being a component used for catalyst manufacture;

determining a volume of the first material in the first container;

calculating a weight, or derivative thereof, of the first material in the first container based on the volume;

comparing the change in weight, or derivative thereof, to the calculated weight, or derivative thereof; and

performing a further action if the change in weight, or derivative thereof, is different than the calculated weight, or derivative thereof.

30. A method for monitoring the manufacture of a catalyst, comprising:

determining a weight, or derivative thereof, of the first material transferred to the second container using a mass flow meter, the first material being a component used for catalyst manufacture;

determining a volume of the first material in one of the containers;

calculating a weight, or derivative thereof, of the first material the one of the containers based on the volume;

comparing the weight determined using the mass flow meter, or derivative thereof, to the calculated weight, or derivative thereof; and

performing a further action if the weight determined using the mass flow meter, or derivative thereof, is different than the calculated weight, or derivative thereof.

31. A method for manufacturing at least one metallocene catalyst, comprising:

adding a solid material to a reaction vessel, the solid material being a component used for metallocene catalyst manufacture;

adding a first liquid to the reaction vessel, the first liquid being another component used for the metallocene catalyst manufacture; and

determining an amount of the first liquid added to the reaction vessel using at least one of a mass flow meter and a weight scale.

32. The method as recited in claim 31, wherein an amount of the first liquid added to the reaction vessel is determined using both a mass flow meter and a weight scale, wherein a further action is performed if the amount determined by the flow meter is different than the amount determined by the weight scale.

33. The method of claim 31 or 32, wherein the first liquid comprises toluene.

34. The method of claim 31 or 32, wherein the first liquid comprises methyl alumoxane (MAO).

35. The method of claim 31 or 32, wherein the first liquid comprises metallocene.

36. The method of claim 31 or 32, wherein the first liquid is a mixture of at least two materials selected from a group consisting of toluene, methyl alumoxane, and at least one metallocene.

37. The method of any one of claims 31-36, further comprising determining an amount of the first liquid added to the reaction vessel as a function of time using both the mass flow meter and the weight scale.

38. The method of any one of claims 31-36, further comprising adjusting a flow rate of the first liquid for altering a reaction condition in the reaction vessel based on the amount of first liquid added as a function of time.

39. The method of any one of claims 31-36, further comprising adjusting a flow rate of a second material into the reaction vessel for altering a reaction condition in the reaction vessel based on the amount of first material added as a function of time.

40. A system for manufacturing a catalyst, comprising:

a first container containing a first material, the first material being a component used for catalyst manufacture;

a reaction vessel for receiving the first material;

a mass flow meter for determining a weight of the first material transferred to the reaction vessel; and

at least one weight scale for selectively determining a weight of at least one of: the first container, the first material stored in the first container, the reaction vessel, and materials stored in the reaction vessel.

41. The system as recited in claim 40, wherein the first material is toluene.

42. The system as recited in claim 40, wherein the first material is methyl alumoxane (MAO).

43. The system as recited in claim 40, wherein the first material is at least one metallocene.

44. The system as recited in claim 40, wherein the first material is a mixture of at least two materials selected from a group consisting of toluene, methyl alumoxane, and at least one metallocene.

45. The system as recited in claim 40, wherein the catalyst is at least one metallocene catalyst.

46. The system as recited in claim 40, wherein the catalyst is at least one Ziegler-Natta catalyst.

47. The system as recited in claim 40, wherein the catalyst is at least one Cr-based catalyst.

48. The system of any one of claims 40-47, further comprising a processing unit for comparing a reading of the mass flow meter to a reading of the at least one weight scale.

49. The system of any one of claims 40-47, further comprising a processing unit for determining an amount of the first material added to the reaction vessel as a function of time using both the mass flow meter and the at least one weight scale.

50. The system of any one of claims 40-47, further comprising a processing unit for adjusting a flow rate of the first material into the reaction vessel for altering a reaction condition in the reaction vessel based on the amount of first material added as a function of time.

51. The system of any one of claims 40-47, further comprising a processing unit for adjusting a flow rate of a second material into the reaction vessel for altering a reaction condition in the reaction vessel based on the amount of first material added as a function of time.

52. A method for manufacturing at least one metallocene catalyst, comprising:

determining a starting weight of a first container or of a first material stored therein using a weight scale, the first material being a material used in metallocene catalyst manufacture;

transferring at least some of the first material to a second container;

determining an ending weight of the first container or of the first material stored therein using the weight scale;

determining a change of weight of the first container or of the first material stored therein;

comparing the weight determined by the weight scale, or derivative thereof, to a predefined weight, or derivative thereof; and

performing a further action if the change in weight determined by the weight scale, or derivative thereof, is different than the predefined weight, or derivative thereof.

53. A method for manufacturing at least one metallocene catalyst, comprising:

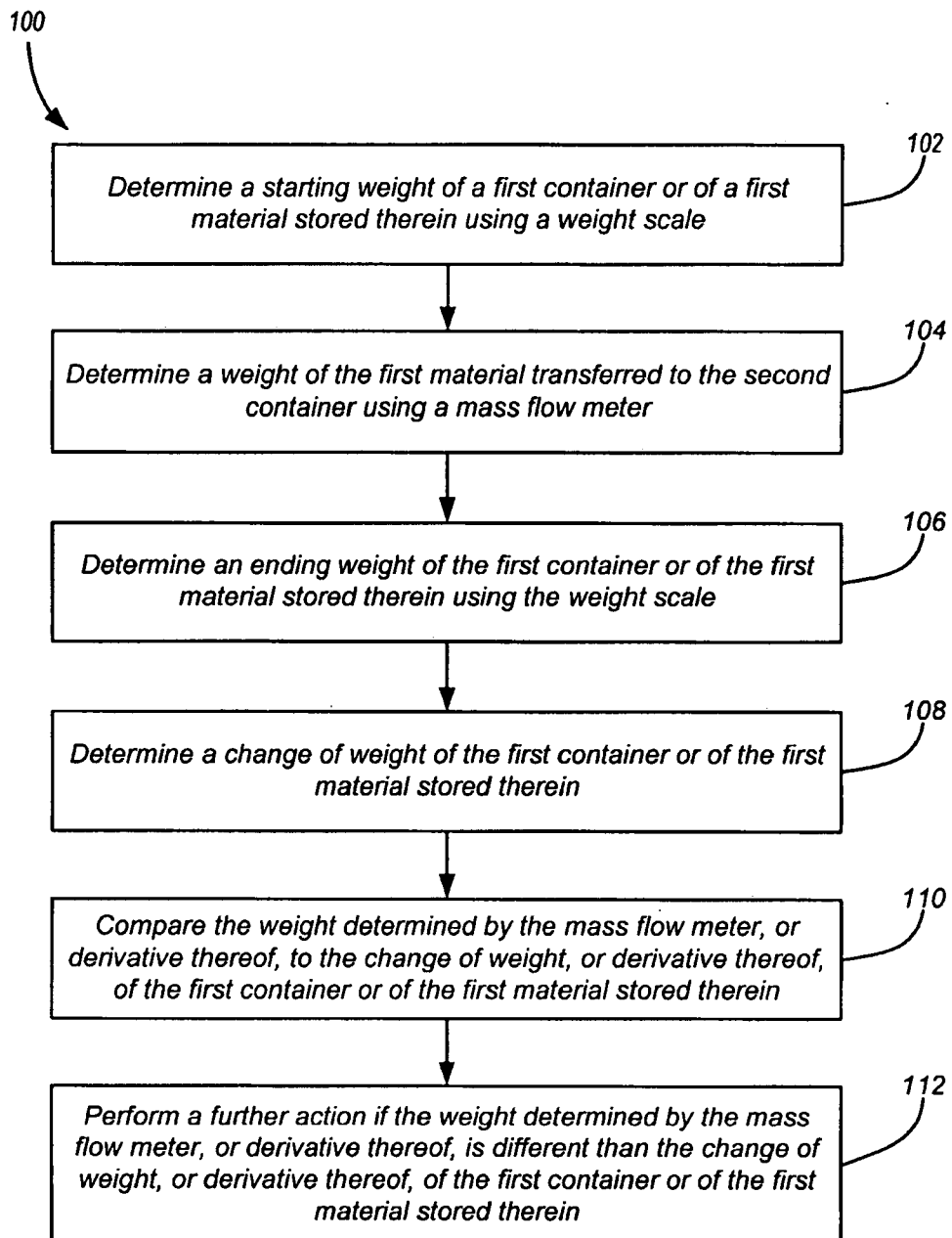
transferring a first material to a container, the first material being a material used in metallocene catalyst manufacture;

determining a weight of the first material transferred to the container using a mass flow meter;

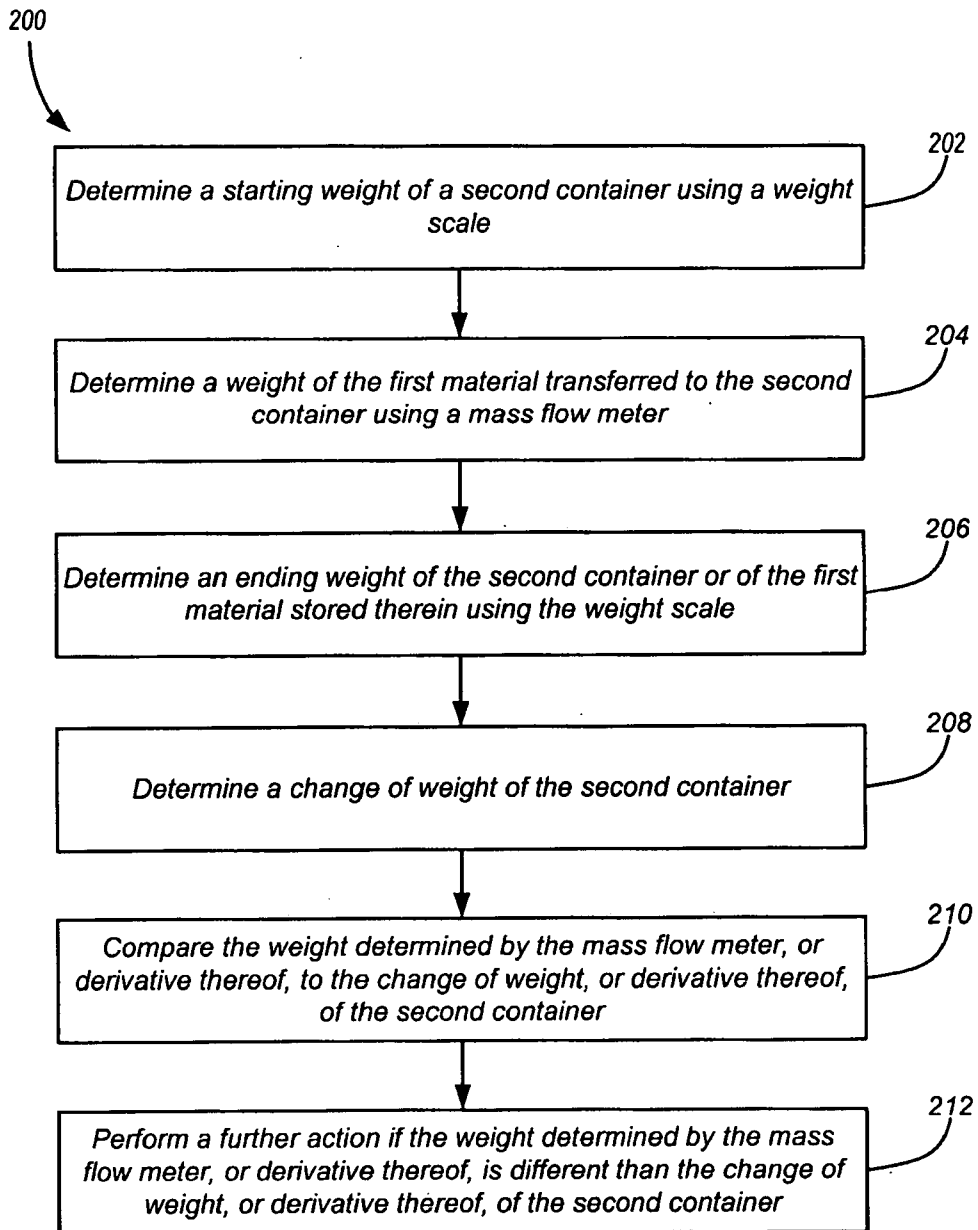
comparing the weight determined by the mass flow meter, or derivative thereof, to a predefined weight, or derivative thereof; and

performing a further action if the weight determined by the mass flow meter, or derivative thereof, is different than the predefined weight, or derivative thereof.

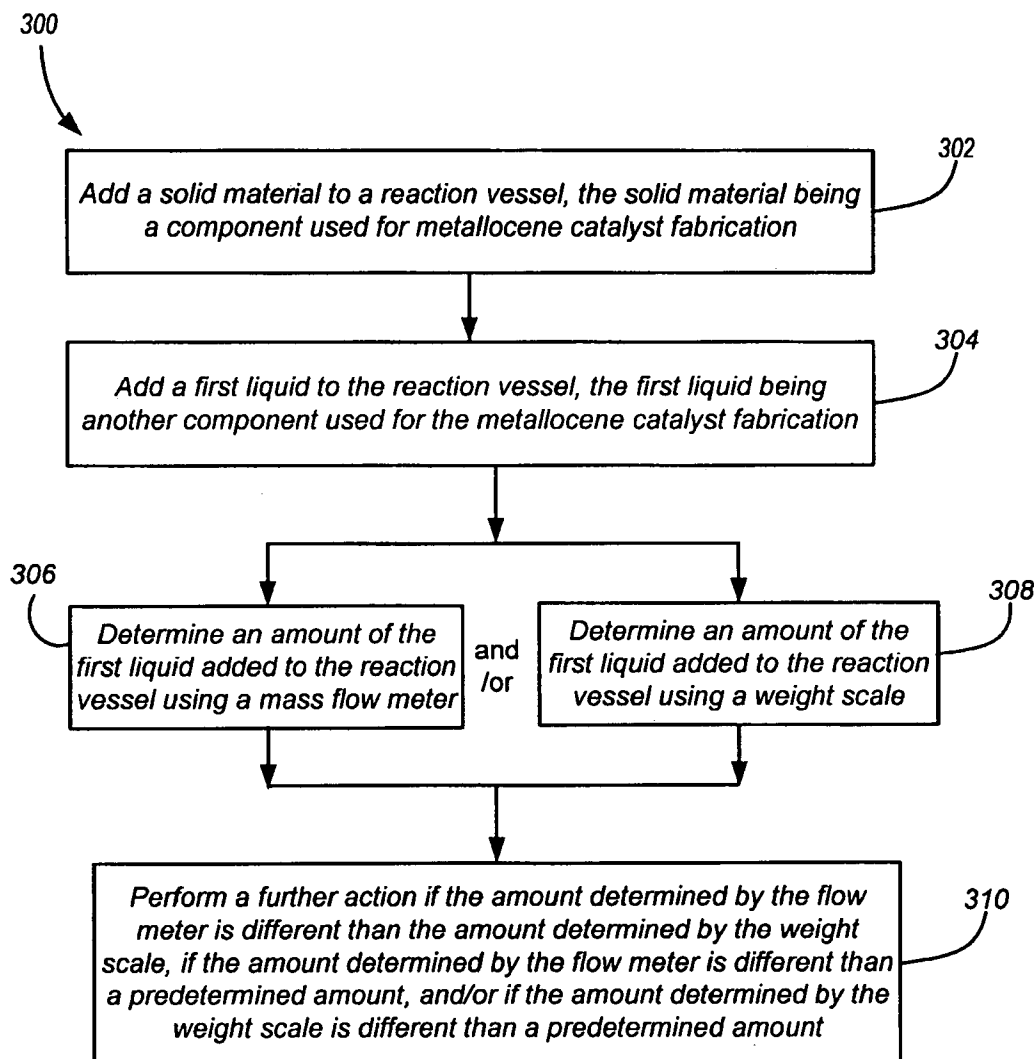
1 / 5

**Figure 1**

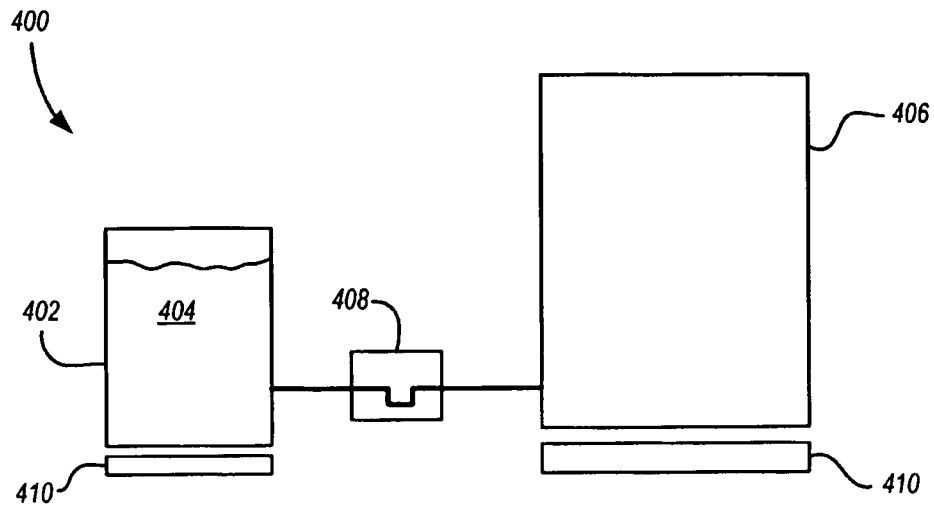
2 / 5

**Figure 2**

3 / 5

**Figure 3**

4 / 5

**Figure 4**

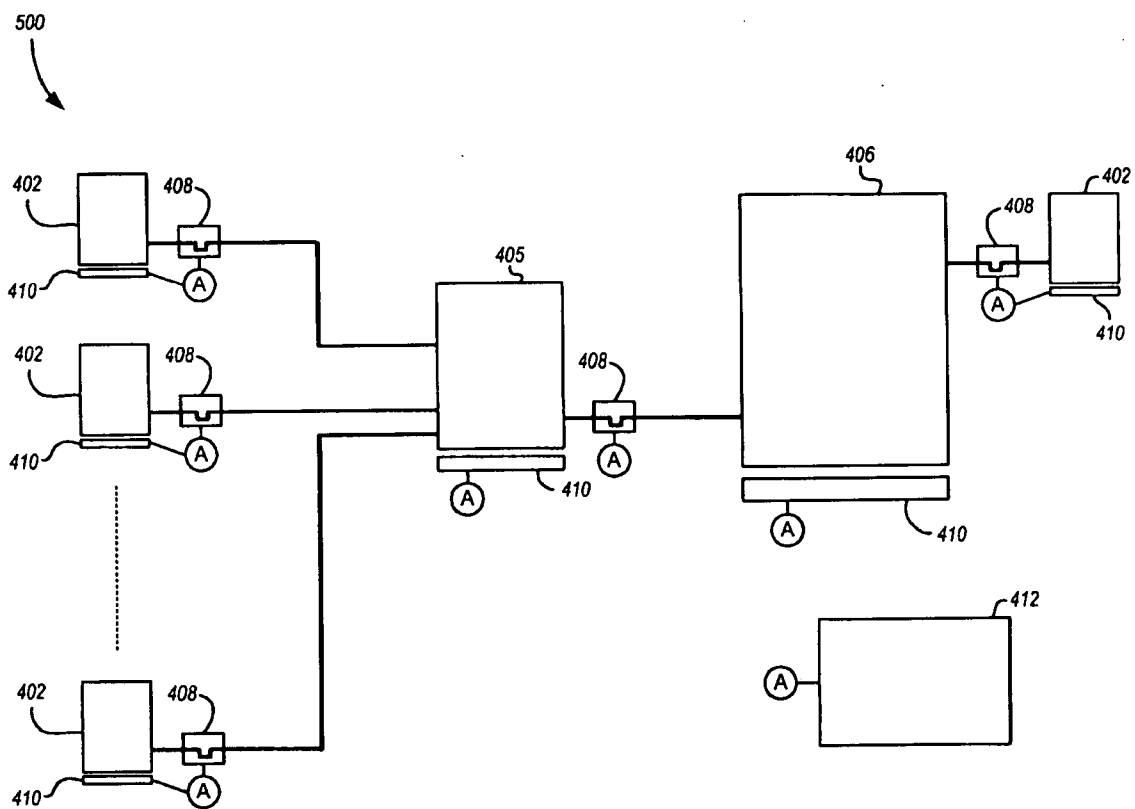


Figure 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 07/04733

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 21/00 (2007.01)

USPC - 502/439, 514, 523

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)

USPC: 502/439, 514, 523

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 practicable, search terms used)

Electronic Databases Searched: USPTO WEST (PGPUB, EPAB, JPAB, USPT), Google, Thomson dialog

Search Terms Used: container, metallocene, aluminosilane, catalyst, toluene, Cr, mass flow, preparation or synthesis, manufacturing, monitor\$

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,982,238 B2 (Jens et al.) 03 January 2006 (03.01.2006) entire document especially examples 4-5; col 8, ln 58 to col 9, ln 67; col 6, ln 16; col 7, ln 32-35; col 4, ln 35-40	1-11, 15-25, 29-36 and 40-53
Y	US 5,869,591 A (McKay et al.) 09 February 1999 (09.02.1999) col 37, ln 64 to col 39, ln 13	1-11, 15-25, 29-36 and 40-53

☐ Further documents are listed in the continuation of Box C.

* 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 application or patent 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

11 August 2007 (11.08.2007)

Date of mailing of the international search report

28 SEP 2007

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 07/04733

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 12-14, 26-28 and 37-39
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.