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(54) **Title:** IMPROVED PROCESS FOR GAS-PHASE POLYMERIZATION HAVING HIGH POLYMER BED BULK DENSITY

(57) **Abstract:** The present invention relates to an improvement for gas-phase olefin polymerization process having relatively high polymer bed bulk density. The improvement involves the use of mixed external electron donors when polymerizing propylene in a gas-phase reactor having a polymer bed with a bulk density greater than 128 kg/m<sup>3</sup>, optionally with one or more comonomers, wherein the mixed external electron donor system comprises at least one first external electron donor and one second external electron donor, and wherein the first external electron donor is a carboxylate compound.



## IMPROVED PROCESS FOR GAS-PHASE POLYMERIZATION HAVING HIGH POLYMER BED BULK DENSITY

### Field of the Invention

The present invention relates to an improvement for gas-phase olefin polymerization processes having relatively high polymer bed bulk densities. The improvement involves the use of a mixed external electron donor system.

### Background and Summary of the Invention

The demand for high-performance polypropylene homopolymer and copolymer products has resulted in advanced manufacturing processes that have unique features. Gas-phase polymerization processes have been recognized as the most economical for the manufacture of polypropylene homopolymers, random copolymers, and impact copolymers. In such processes, the polymerization reactor contains a mixture of a solid bed of polymer particles and a gas phase that comprises propylene monomer, comonomer and hydrogen. Unlike slurry-phase polymerization processes, gas-phase processes do not require solid-liquid separation or product-catalyst separation. This feature makes the gas-phase processes easier to operate and more economical.

Operational issues may occur in gas-phase polymerization reactors if the process is not properly controlled. For example, polymer agglomerates or even polymer chunks may form and/or vessel surfaces may foul. These issues are typically caused by inadequate heat removal and/or strong electrostatic attraction. When the heat of reaction is not removed rapidly, the polymer particle heats up to a surface temperature higher than the polymer softening temperature or even higher than the melting temperature of the polymer. Such operational problems can force the shutdown of the reactor for clean up, resulting in severe financial penalties.

In reactors with relatively-high polymer bed bulk densities there usually are more active catalyst sites (sites where the polymerization reaction occurs) in the unit bed volume and more reaction heat generated in the unit bed volume. Moreover, the relatively-high polymer bed bulk density is often associated with, or caused by, a relatively-low gas velocity, and hence a relatively-low heat removal capability by the gas phase. This further increases the possibility of particle agglomeration. The term “bed bulk density” refers to the weight of solids in the unit

volume of the gas-solid bed in the reactor. This term is often equivalent to “fluidized bulk density (also known as “FBD”)” when the gas-phase reactor is a fluidized bed reactor. For the purposes of this invention, when extending this concept to the non-fluidized gas-phase reactors in this invention, such as mechanically agitated stirred polymer bed gas-phase reactors that have gas velocities smaller than the minimum fluidization velocity, both terminologies can still be used to mean the weight of solid per unit volume of the gas-solid system.

Previous attempts to solve the above-mentioned agglomeration problems include, for example, stirred polymer bed gas-phase reactors with mechanical agitators in either vertical orientation (*e.g.*, US 3,639,377) or horizontal orientation (*e.g.*, US 4,101,289). However, mechanically agitated stirred polymer beds do not always solve the agglomeration problem, and the mechanical agitator itself can provide an additional surface for fouling. “Chunk” formation in mechanically agitated stirred polymer bed gas-phase reactors is well reported, such as CN 101241023, and CISEC Journal, Vol. 60, No.3, pp. 585-592. In the latter document, it is stated that “*in horizontal stirred-bed polypropylene reactor, chunking is a severe threat to the long-term stable operation and product quality of the reactor.*” The authors further point to the stirred polymer bed gas-phase reactors of the Ineos’ Innovene and Chisso/JPP’s Horizone Polypropylene Processes. These are considered to be reactors with relatively high polymer bed bulk density, compared with gas-phase fluidized-bed reactors that are operated using relatively high velocities, such as the reactors of the UNIPOL™ Polypropylene Process.

Therefore, particle agglomeration in gas-phase polymerization reactors with high polymer bed bulk density could be a particular operational concern, and there is a need to develop a solution to the problem. The present invention provides an easy-to-apply, relatively low cost and low operational complexity solution to this problem without the need for significant changes in process equipment or operating conditions. The present invention is an improvement for gas-phase polymerization processes having a polymer bed bulk density greater than 128 kg/m<sup>3</sup>. The improvement involves the use of a mixed external electron donor system that comprises at least one activity limiting agent and at least one selectivity control agent.

### Detailed Description of the Invention

All references to the Periodic Table of the Elements herein shall refer to the “Periodic Table of the Elements,” published and copyrighted by CRC Press, Inc., 2003. Also, any references to a Group or Groups shall be to the Groups or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight. For purposes of United States patent practice, the contents of any patent, patent application, or publication referenced herein are hereby incorporated by reference in their entirety (or the equivalent US version thereof is so incorporated by reference), especially with respect to the disclosure of synthetic techniques, definitions (to the extent not inconsistent with any definitions provided herein) and general knowledge in the art.

The term “comprising,” and derivatives thereof, is not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein through use of the term “comprising” may include any additional additive, adjuvant, or compound whether polymeric or otherwise, unless stated to the contrary. In contrast, the term, “consisting essentially of” excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term “consisting of” excludes any component, step or procedure not specifically delineated or listed. The term “or”, unless stated otherwise, refers to the listed members individually as well as in any combination.

This invention involves the use of a catalyst composition comprising a pro-catalyst composition, a co-catalyst and a mixed external electron donor (M-EED) system which includes at least one activity limiting agent (ALA) and at least one selectivity control agent (SCA). The procatalyst composition of the present catalyst composition may be a Ziegler-Natta procatalyst composition. Any conventional Ziegler-Natta procatalyst may be used in the present catalyst composition as is commonly known in the art. In one embodiment, the Ziegler-Natta procatalyst composition contains titanium chloride, magnesium chloride, and optionally an internal electron donor.

The present invention relates to the use of a novel external electron donor system that can sufficiently modify the kinetic profile of the polymerization and thus prevent “hot” spots in the reactor that can be associated with polymer particle agglomeration or chunk formation.

With the modified kinetic profile of the catalyst system, catalyst activity decreases to a very low level or even zero before the temperature at the catalyst active site reaches the softening temperature or the melting temperature of the polymer. In this way, it is very unlikely the surface temperature of the particles reach the polymer softening temperature or the polymer melting temperature. Thus, particle agglomeration and fouling are prevented in the manufacturing process (polymerization reactor, product discharge system, reactor polymer transfer systems, gas-recycle piping, compressor, heat exchanger, etc.).

This invention benefits reactor systems that have either relatively high polymer bed bulk density or relatively high fluidized polymer bed bulk density (also known as “FBD”). Fluidized bulk density or FBD, as used herein, is the weight of solids in the unit volume of the gas-solid system. For purposes of this invention, when extending this concept to the non-fluidized gas-phase reactors of this invention, such as the mechanically agitated stirred polymer bed gas-phase reactors with gas velocities smaller than the minimum fluidization velocities, both terminologies can still be used to mean the weight of solid per unit volume of the gas-solid system. Polymer bed bulk density and FBD can be determined by different methods, such as pressure drop measurement, direct polymer bed weight and polymer bed height measurement (e.g., US 6,460,412). The present invention is particularly applicable for reactor systems having a polymer bed bulk density of  $128 \text{ kg/m}^3$  or higher, or  $160 \text{ kg/m}^3$  or higher, or even  $192 \text{ kg/m}^3$  or higher.

This invention especially benefits reactor systems that have polymer beds of relatively high solid holdup. A high solid holdup typically results in a higher possibility of particle agglomeration. The term “solid holdup” means the volumetric fraction of the solid in the gas-solid system. The solid holdup can be determined in different ways. One of the commonly used methods is to measure polymer bed weight and height via differential-pressure measurement (through pressure taps on the reactor wall). The volume and solid holdup in the reactor can then be estimated, with particle density information. In some embodiments, this invention is used with (but not limited to) reactor systems with the solid holdup larger than 0.17 (or 17%), preferably larger than 0.21 (or 21%) and most preferably larger than 0.25 (or 25%). As is known by those skilled in the art, the solid holdup will depend in part on the granular particle density, and so these typical values may be lower or higher for certain polymer bed bulk density if the granular particles are at the extremes of possible densities.

This invention can be applied to any gas-phase polymerization reactor system including those operated under conditions of packed bed (fixed bed), homogeneous fluidization, bubbling fluidization, turbulent fluidization, “high density circulating fluidized bed,” spouted bed, spout-fluid bed, dense-phase pneumatic conveying, and packed (or fixed) moving bed (including the mass flow and funnel flow). The invention is especially suitable for mechanically agitated stirred polymer bed and fluidized polymer bed gas-phase polymerization reactors. The gas and solid can contact in any way, including co-current, counter-current, solid batch, etc. The process of the present invention can optionally include pre-polymerization, but it is not mandatory.

Within a given reactor system, the values of polymer bed bulk density and solid holdup can be changed within certain ranges by manipulating the reactor operating conditions.

Similarly, this invention can particularly benefit those reactors with a relatively low gas velocity, since lower gas velocity typically results in a higher possibility of particle agglomeration. In some embodiments, this invention is used with (but not limited to) a reactor system in which the superficial gas velocity is less than 10 times of the minimum fluidization velocity, and preferably less than 8 times of the minimum fluidization velocity and most preferably less than 5 times of the minimum fluidization velocity. It is contemplated that the present invention also has particular applicability where the superficial velocity is near or even below the minimum fluidization velocity. The minimum fluidization velocity can be measured in the way described in any fluidization text book. However, in practice it is not convenient to measure minimum fluidization velocity under the reaction conditions and it is calculated using well-known equations such as Wen and Yu (AIChE J., Vol. 12, p. 610, 1966).

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

More specifically, this invention involves the use of a catalyst composition comprising: a procatalyst composition; a cocatalyst; and a mixed external electron donor (M-EED) system. The M-EED comprises at least one activity limiting agent (ALA) and at least one selectivity control agent (SCA). As used herein, a mixed “external electron donor” system is a composition added independent of procatalyst formation that modifies the catalyst performance. As used herein, an “activity limiting agent” is a composition that decreases catalyst activity as the catalyst temperature rises above a threshold temperature (*e.g.*, temperature greater than about 80°C, 85°C, or 90°C). A “selectivity control agent” is a component that improves polymer tacticity. It should be understood that the above definitions are not mutually exclusive and that a single compound may be classified, for example, as both an activity limiting agent and a selectivity control agent.

The mixed external electron donor system for use in the present invention preferably includes at least one carboxylate compound. The carboxylate compound can be either an ALA and/or an SCA component.

The selectivity control agent(s) (SCA) may be selected from one or more of the following: an alkoxysilane, an amine, an ether, a carboxylate, a ketone, an amide, a carbamate, a phosphine, a phosphate, a phosphite, a sulfonate, a sulfone, and/or a sulfoxide.

In one embodiment, the SCA includes an alkoxysilane. The alkoxysilane has the general formula:  $\text{SiR}_m(\text{OR}')_{4-m}$  (I) where R independently each occurrence is hydrogen or a hydrocarbyl or an amino group optionally substituted with one or more substituents containing one or more Group 14, 15, 16, or 17 heteroatoms, said R containing up to 20 atoms not counting hydrogen and halogen; R' is a C<sub>1-4</sub> alkyl group; and m is 0, 1, 2 or 3. In an embodiment, R is C<sub>6-12</sub> arylalkyl or aralkyl, C<sub>3-12</sub> cycloalkyl, C<sub>3-12</sub> branched alkyl, or C<sub>3-12</sub> cyclic or acyclic amino group, R' is C<sub>1-4</sub> alkyl, and m is 1 or 2. Nonlimiting examples of suitable silane compositions include dicyclopentylmethoxysilane, di-tert-butylmethoxysilane, methylcyclohexylmethoxysilane, methylcyclohexyldiethoxysilane, ethylcyclohexylmethoxysilane, diphenylmethoxysilane, diisopropylmethoxysilane, di-n-propylmethoxysilane, diisobutylmethoxysilane, diisobutyldiethoxysilane, isobutylisopropylmethoxysilane, di-n-butylmethoxysilane, cyclopentyltrimethoxysilane, isopropyltrimethoxysilane, n-propyltrimethoxysilane, n-propyltriethoxysilane, ethyltriethoxysilane, tetramethoxysilane, tetraethoxysilane, diethylaminotriethoxysilane,

cyclopentylpyrrolidinodimethoxysilane, bis(pyrrolidino)dimethoxysilane, bis(perhydroisoquinolino)dimethoxysilane, and dimethyldimethoxysilane. In an embodiment, the silane composition is dicyclopentyl dimethoxysilane (DCPDMS), methylcyclohexyldimethoxysilane (MChDMS), or n-propyltrimethoxysilane (NPTMS), and any combination of thereof.

In an embodiment, the selectivity control agent component can be a mixture of 2 or more alkoxysilanes. In a further embodiment, the mixture can be dicyclopentyl dimethoxysilane and methylcyclohexyldimethoxysilane, dicyclopentyl dimethoxysilane and tetraethoxysilane, or dicyclopentyl dimethoxysilane and n-propyltriethoxysilane.

In one embodiment, the mixed external electron donor system may include a benzoate, a succinate, and/or a diol ester. In one embodiment, the mixed external electron donor system includes 2,2,6,6-tetramethylpiperidine as an SCA. In another embodiment, the mixed external electron donor system includes a diether as both an SCA and an ALA.

The mixed external electron donor system also includes an activity limiting agent (ALA). An ALA inhibits or otherwise prevents polymerization reactor upset and ensures continuity of the polymerization process. Typically, the activity of the Ziegler-Natta catalyst increases as the reactor temperature rises. Ziegler-Natta catalysts also typically maintain high activity near the melting point temperature of the polymer produced. The heat generated by the exothermic polymerization reaction may cause polymer particles to form agglomerates and may ultimately lead to disruption of continuity for the polymer production process. The ALA reduces catalyst activity at elevated temperature, thereby preventing reactor upset, reducing (or preventing) particle agglomeration, and ensuring continuity of the polymerization process.

The activity limiting agent may be a carboxylic acid ester, a diether, a poly(alkene glycol), a diol ester, and combinations thereof. The carboxylic acid ester can be an aliphatic or aromatic, mono- or poly-carboxylic acid ester. Nonlimiting examples of suitable monocarboxylic acid esters include ethyl and methyl benzoate, ethyl p-methoxybenzoate, methyl p-ethoxybenzoate, ethyl p-ethoxybenzoate, ethyl p-isopropoxybenzoate, ethyl acrylate, methyl methacrylate, ethyl acetate, ethyl p-chlorobenzoate, hexyl p-aminobenzoate, isopropyl naphthenate, n-amyl toluate, ethyl cyclohexanoate and propyl pivalate.

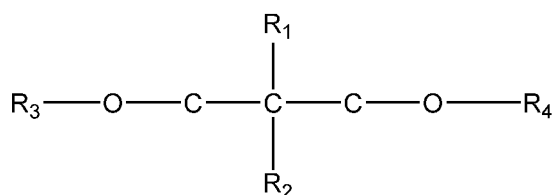


Nonlimiting examples of suitable polycarboxylic acid esters include dimethyl phthalate, diethyl phthalate, di-n-propyl phthalate, diisopropyl phthalate, di-n-butyl phthalate, diisobutyl phthalate, di-tert-butyl phthalate, diisoamyl phthalate, di-tert-amyl phthalate, dineopentyl phthalate, di-2-ethylhexyl phthalate, di-2-ethyldecyl phthalate, diethyl terephthalate, dioctyl terephthalate, and bis[4-(vinylloxy)butyl]terephthalate.

The aliphatic carboxylic acid ester may be a C<sub>4</sub>-C<sub>30</sub> aliphatic acid ester, may be a mono- or a poly- (two or more) ester, may be straight chain or branched, may be saturated or unsaturated, and any combination thereof. The C<sub>4</sub>-C<sub>30</sub> aliphatic acid ester may also be substituted with one or more Group 14, 15 or 16 heteroatom containing substituents. Nonlimiting examples of suitable C<sub>4</sub>-C<sub>30</sub> aliphatic acid esters include C<sub>1-20</sub> alkyl esters of aliphatic C<sub>4-30</sub> monocarboxylic acids, C<sub>1-20</sub> alkyl esters of aliphatic C<sub>8-20</sub> monocarboxylic acids, C<sub>1-4</sub> allyl mono- and diesters of aliphatic C<sub>4-20</sub> monocarboxylic acids and dicarboxylic acids, C<sub>1-4</sub> alkyl esters of aliphatic C<sub>8-20</sub> monocarboxylic acids and dicarboxylic acids, and C<sub>4-20</sub> mono- or polycarboxylate derivatives of C<sub>2-100</sub> (poly)glycols or C<sub>2-100</sub> (poly)glycol ethers. In a further embodiment, the C<sub>4</sub>-C<sub>30</sub> aliphatic acid ester may be a laurate, a myristate, a palmitate, a stearate, an oleate, a sebacate, (poly)(alkylene glycol) mono- or diacetates, (poly)(alkylene glycol) mono- or di-myristates, (poly)(alkylene glycol) mono- or di-laurates, (poly)(alkylene glycol) mono- or di-oleates, glyceryl tri(acetate), glyceryl tri-ester of C<sub>2-40</sub> aliphatic carboxylic acids, and mixtures thereof. In a further embodiment, the C<sub>4</sub>-C<sub>30</sub> aliphatic ester is isopropyl myristate or di-n-butyl sebacate.

In an embodiment, the activity limiting agent includes a diether. The diether can be a 1,3-diether compound represented by the following structure (VI):

(VI)

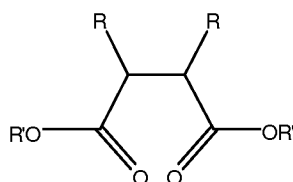


wherein R<sub>1</sub> to R<sub>4</sub> are independently of one another, an alkyl, aryl or aralkyl group having up to 20 carbon atoms, which may optionally contain a group 14, 15, 16, or 17 heteroatom, and R<sub>1</sub> and R<sub>2</sub> may be a hydrogen atom. The dialkylether may linear or branched, and may include one or

more of the following groups: alkyl, cycloaliphatic, aryl, alkylaryl or arylalkyl radicals with 1-18 carbon atoms, and hydrogen.  $R_1$  and  $R_2$  may be linked to form a cyclic structure, such as cyclopentadiene or fluorene.

In an embodiment, the activity limiting agent includes a succinate composition having the following structure (VII):

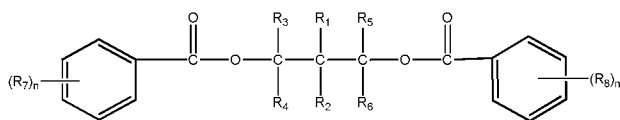
(VII)



wherein R and R' may be the same or different, R and/or R' including one or more of the following groups: hydrogen, linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms. One or more ring structures can be formed *via* one or both 2- and 3-position carbon atom.

In an embodiment, the activity limiting agent includes a diol ester as represented by the following structure (VIII):

(VIII)



wherein n is an integer from 1 to 5.  $R_1$  and  $R_2$ , may be the same or different, and each may be selected from hydrogen, methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, t-butyl, allyl, phenyl, or halophenyl group.  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ , and  $R_8$  may be the same or different, and each may be selected from hydrogen, halogen, substituted, or unsubstituted hydrocarbyl having 1 to 20 carbon atoms.  $R_1$ - $R_6$  groups may optionally contain one or more heteroatoms replacing carbon, hydrogen or both, the hetero-atom selected from nitrogen, oxygen, sulfur, silicon, phosphorus

and a halogen.  $R_7$  and  $R_8$ , may be the same or different, and may be bonded to any carbon atom of the 2-, 3-, 4-, 5-, and 6-position of either phenyl ring.

The individual components of the mixed external electron donor system can be added into the reactor separately or two or more can be mixed together in advance and then added into the reactor as a mixture. In the mixed external electron donor system, more than one selectivity control agent or more than one activity limiting agent can be used. Examples of mixed external electron donor systems are dicyclopentylmethoxysilane and isopropyl myristate, diisopropylmethoxysilane and isopropyl myristate, dicyclopentylmethoxysilane and poly(ethylene glycol) laurate, dicyclopentylmethoxysilane and isopropyl myristate and poly(ethylene glycol) dioleate, methylcyclohexylmethoxysilane and isopropyl myristate, n-propyltrimethoxysilane and isopropyl myristate, dimethyldimethoxysilane and methylcyclohexylmethoxysilane and isopropyl myristate, dicyclopentylmethoxysilane and n-propyltriethoxysilane and isopropyl myristate, diisopropylmethoxysilane and n-propyltriethoxysilane and isopropyl myristate, and dicyclopentylmethoxysilane and tetraethoxysilane and isopropyl myristate, dicyclopentylmethoxysilane and diisopropylmethoxysilane and n-propyltriethoxysilane and isopropyl myristate, and combinations thereof.

The M-EED system, whether added separately or pre-mixed, may be added at any point in the reactor, although the ALA should be present in the areas considered to be at greatest risk for agglomeration, such as the areas with highest solid holdup, highest FBD and/or lowest gas velocity.

The present catalyst composition includes a cocatalyst. The cocatalyst for use with the foregoing Ziegler-Natta procatalyst composition may be an aluminum containing composition. Nonlimiting examples of suitable aluminum containing compositions include organoaluminum compounds, such as trialkylaluminum-, dialkylaluminum hydride-, alkylaluminum dihydride-, dialkylaluminum halide-, alkylaluminum dihalide-, dialkylaluminum alkoxide-, and alkylaluminum dialkoxide- compounds containing from 1-10, or 1-6 carbon atoms in each alkyl- or alkoxide- group. In an embodiment, the cocatalyst is a C1-4 trialkylaluminum compound, such as triethylaluminum (TEA). The catalyst composition includes a mole ratio of Al to (SCA(s) + ALA(s)) of 0.5-25:1, or 1.0-20:1, or 1.5-15:1, or less than about 6.0, or less than about 5, or less than 4.5. In an embodiment, the Al: (SCA(s) + ALA(s)) mole ratio is 0.5-4.0:1.

The total-SCA to ALA mole ratio is 0.01-20:1, 0.10-5.00:1, 0.43-2.33:1, or 0.54-1.85:1, or 0.67-1.5:1.

### EXAMPLES

In order to demonstrate the effectiveness of the present invention, the following polymerization reactions can be carried out:

Example	Comparative 1	Comparative 2	3	4
Catalyst	Z-N (see Example 1 of US 6,825,146)			
External Electron Donor	DCPDMS (Dicyclopentyldimethoxysilane) (also called "D-Donor")		95% DBS (di-n-butyl sebacate) + 5% "C Donor" (methylcyclohexyldimethoxysilane)	
Product	Homo Polypropylene	Propylene- Ethylene Random Copolymer	Homo Polypropylene	Propylene- Ethylene Random Copolymer
Ethylene wt% in product	0	3%	0	3%
Reactor	Vertical Gas- Phase Reactor with mechanical agitation (similar to that of Example 2 in US 3,639,377)	Horizontal Fluidized-Bed Reactor with mechanical agitation (similar to that of Example 2 in US 6,350,054)	Vertical Gas- Phase Reactor with mechanical agitation (similar to that of Example 2 in US 3,639,377)	Horizontal Fluidized-Bed Reactor with mechanical agitation (similar to that of Example 2 in US 6,350,054)
Agitator Rotation Speed (RPM)	26	12	26	12
Reactor Flow Pattern	Non-fluidized	Dense-phase fluidization	Non-fluidized	Dense-phase fluidization
Vol% of bulk polymer bed in reactor	80%	50%	80%	50%
Average Particle Size (mm)	1.7	1.0	1.7	1.0
Particle Settled Bulk Density (kg/m <sup>3</sup> )	415	432	415	430
Average Reactor Total Pressure (Pa-gauge)	3.20x10 <sup>6</sup>	2.0x10 <sup>6</sup>	3.20x10 <sup>6</sup>	2.0x10 <sup>6</sup>
Controlled Reactor Temperature (°C)	72	65	72	65
Bed Bulk Density (FBD) (kg/m <sup>3</sup> )	382	256	381	258

**Comparative Examples 1 & 2**

After a steady operation is reached, there is a mechanical problem with the agitator, and the agitator stops moving. Although the kill gas is introduced into the reactor quickly to terminate the polymerization reaction, polymer agglomeration still forms. After the agitator problem is fixed, the reactor cannot return to the normal operation because the agitator is blocked by large pieces of polymer agglomerates (so-called “chunks”). Product discharge lines are also blocked by the “chunks.” The reactor has to be shut down for cleaning, before going back to the normal operation.

**Examples 3 & 4**

Everything is the same as the comparative examples, except the external electron donor is replaced by the mixed external electron donor system of this invention (see the above table for detailed donor composition). The same agitator problems as in Comparative Examples 1 & 2 are encountered. Catalyst and co-catalyst supply are shut off promptly, the kill gas is introduced into the reactor, and then the reactor is “idled.” After the agitator problem is fixed, the reactor is placed back into operation. Reaction is resumed without any operational issues and movement of agitator is not blocked by polymer agglomerates.

We claim:

1. A polymerization process for making polypropylene or propylene copolymer (C<sub>2</sub> to C<sub>8</sub>) comprising:  
polymerizing propylene, optionally with one or more comonomers, in a gas-phase reactor having a polymer bed with a bulk density greater than 128 kg/m<sup>3</sup>, in the presence of a mixed external electron donor system, wherein the mixed external electron donor system comprises at least one first external electron donor and one second external electron donor, and wherein the first external electron donor is a carboxylate compound.
2. The process of claim 1 wherein the gas-phase reactor is a mechanically stirred vertical gas-phase reactor.
3. The process of claim 2 wherein the gas-phase reactor discharges the product through a dip tube or eductor tube.
4. The process of claim 1 wherein the gas-phase reactor has a bed volume greater than or equal to 35% of the reactor volume.
5. The process of claim 1 wherein the gas-phase reactor is a horizontal gas-phase reactor that is mechanically stirred.
6. The process of claim 1 wherein the gas-phase reactor has separate gas and liquid feeds.
7. The process of claim 1 wherein the polymer bed is fluidized.
8. The process of claim 1 wherein the polymer bed is not fluidized.
9. The process of claim 1 further comprising one or more additional reactors.
10. The process of claim 9 wherein the reactors are arranged in parallel.
11. The process of claim 9 wherein the reactors are arranged in series.
12. The process of claim 9 wherein the reactors are arranged in a combination of parallel and series reactors.
13. The process of claim 1 wherein the mixed external electron donor system includes at least one selectivity control agent and at least one activity limiting agent.
14. The process of claim 1 wherein the activity limiting agent may be a carboxylic acid ester, a diether, a poly(alkene glycol), a diol ester, and combinations thereof.
15. The process of claims 1 wherein the activity limiting agent is selected from a benzoate and a C<sub>4</sub>-C<sub>30</sub> aliphatic acid ester.

16. The process of claim 1 wherein the activity limiting agent is selected from a laurate, a myristate, a palmitate, a stearate, and an oleate.
17. The process of claim 1 wherein the second external electron donor selectivity control agent is selected from the group consisting of an alkoxysilane, an amine, an ether, a carboxylate, a ketone, an amide, a carbamate, a phosphine, a phosphate, a phosphite, a sulfonate, a sulfone, and a sulfoxide.
18. The process of claims 1 wherein the selectivity control agent is selected from  $\text{SiR}_m(\text{OR}')_{4-m}$ , R is  $\text{C}_3\text{-C}_{12}$  cycloalkyl,  $\text{C}_3\text{-C}_{12}$  branched alkyl, or  $\text{C}_3\text{-C}_{12}$  cyclic or acyclic amino group, R' is C1-4 alkyl, and m is 0, 1, or 2.
19. The process of claim 1 wherein the gas-phase reactor has a solid holdup larger than 0.17.
20. The process of claim 1 wherein the gas-phase reactor has a superficial gas velocity which is less than 10 times of the minimum fluidization velocity.

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/042459

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. C08F10/06  
 ADD.

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 C08F

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

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

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/029487 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; CHEN LINFENG [US]; CAMPBELL RICHARD) 5 March 2009 (2009-03-05) paragraphs [0006] - [0010], [0028], [0079] - [0080], [0126], [0129], [0130], [0133] -----	1-18
X	US 2011/152424 A1 (CAI PING [US] ET AL) 23 June 2011 (2011-06-23) paragraphs [0002], [0013], [0014], [0015], [0017], [0020] - [0033] -----	1-8, 10, 12-20
X	WO 2005/030815 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; CHEN LINFENG [US]; CAMPBELL RICHARD) 7 April 2005 (2005-04-07) the whole document -----	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

10 September 2012

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19/09/2012

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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