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(54) Title: PROCESS FOR PRODUCING POLYOLEFINS		
(57) Abstract <p>A novel process for producing homopolymers and interpolymers of olefins which involves contacting an olefin and/or an olefin and at least one or more other olefin(s) under polymerization conditions with a metallocene catalyst and at least one ether comprising at least one carbon-oxygen-carbon linkage (C-O-C) of the formula $R^1-O(-R^2-O)_m-R^3$ in amounts sufficient to reduce the electrostatic charge in the polymerization medium. Also disclosed is a process for reducing electrostatic charge in an olefin polymerization medium.</p>		

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TITLE OF THE INVENTION

Process For Producing Polyolefins

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FIELD OF INVENTION

The present invention relates to a polymerization process for the production of polyolefins utilizing a metallocene catalyst and a compound containing an ether linkage in amounts sufficient to reduce the electrostatic charge in the polymerization reactor. The use of a compound containing an ether linkage as a catalytic agent further provides polyolefins that are suitable for molding and film applications.

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BACKGROUND OF INVENTION

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Polyolefins such as polyethylene are well known and are useful in many applications. In particular, linear polyethylene polymers possess properties which distinguish them from other polyethylene polymers, such as branched ethylene homopolymers commonly referred to as LDPE (low density polyethylene). Certain of these properties are described by Anderson et al, U.S. Patent No. 4,076,698.

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A particularly useful polymerization medium for producing polyethylene and polypropylene polymers is a gas phase process. Examples of such are given in U.S. Patent Nos. 3,709,853; 4,003,712; 4,011,382; 4,302,566; 4,543,399; 4,882,400; 5,352,749 and 5,541,270 and Canadian Patent No. 991,798 and Belgian Patent No. 839,380.

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There are known various catalysts for polymerizing olefins. Exemplary of such catalysts are as follow:

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1. chromium oxide catalysts which polymerize ethylene to high molecular weight high density polyethylene (HDPE),
2. organochromium catalysts used to polymerize ethylene,

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3. Ziegler-Natta type catalysts which typically consist of a transition metal component and a co-catalyst that is typically an organoaluminum compound,
4. metallocene catalysts which typically consist of a transition metal having a cyclopentadienyl ligand and a co-catalyst,
5. Group 13 catalysts described in U.S. Patent No. 5,777,120, such as cationic aluminum alkyl amidinate complexes,
6. catalysts of the type described in U.S. Patent No. 5,866,663, such as cationic nickel alkyl diimine complexes,
- 10 7. catalysts of the type described in Organometallics, 1998, Volume 17, pages 3149-3151, such as neutral nickel alkyl salicylaldiminato complexes,
8. catalysts of the type described in the Journal of the American Chemical Society, 1998, Volume 120, pages 7143-7144, such as cationic iron alkyl pyridinebisimine complexes, and
- 15 9. catalysts of the type described in the Journal of the American Chemical Society, 1996, Volume 118, pages 10008-10009, such as cationic titanium alkyl diamide complexes.

The above catalysts are, or can be, supported on inert porous particulate carriers.

20 A generally encountered problem in polymerization processes, in particular gas phase polymerization processes, is the formation of agglomerates. Agglomerates can form in various places such as the polymerization reactor and the lines for recycling the gaseous stream. As a consequence of agglomerate formation it may be necessary to shut down the reactor.

25 When agglomerates form within the polymerization reactor there can be many adverse effects. For example, the agglomerates can disrupt the removal of polymer from the polymerization reactor by plugging the polymer discharge system. Further, if the agglomerates fall and cover part of the fluidization grid a loss of fluidization efficiency may occur. This can result in the formation of larger

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agglomerates which can lead to the loss of the entire fluidized bed. In either case there may be the necessity for the shutdown of the reactor.

It has been found that agglomerates may be formed as a result of the presence of very fine polymer particles in the polymerization medium. These fine
5 polymer particles may be present as a result of introducing fine catalyst particles or breakage of the catalyst within the polymerization medium.

These fine particles are believed to deposit onto and electrostatically adhere to the inner walls of the polymerization reactor and the associated equipment for recycling the gaseous stream such as, for example, the heat exchanger. If the fine
10 particles remain active, and the polymerization reaction continues, then the particles will grow in size resulting in the formation of agglomerates. These agglomerates when formed within the polymerization reactor tend to be in the form of sheets.

Several solutions have been proposed to resolve the problem of formation
15 of agglomerates in gas phase polymerization processes. These solutions include the deactivation of the fine polymer particles, control of the catalyst activity and the reduction of the electrostatic charge. Exemplary of the solutions are as follows.

European Patent Application 0 359 444 A1 describes the introduction into the polymerization reactor of small amounts of an activity retarder in order to keep
20 substantially constant either the polymerization rate or the content of transition metal in the polymer produced. The process is said to produce a polymer without forming agglomerates.

U.S. Patent No. 4,739,015 describes the use of gaseous oxygen containing compounds or liquid or solid active-hydrogen containing compounds to prevent the
25 adhesion of the polymer to itself or to the inner wall of the polymerization apparatus.

In U.S. Patent No. 4,803,251 there is described a process for reducing sheeting utilizing a group of chemical additives which generate both positive and negative charges in the reactor, and which are fed to the reactor in an amount of a

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few parts per million (ppm) per part of the monomer in order to prevent the formation of undesired positive or negative charges.

Other processes and other additives that may be used to neutralize the electrostatic charge in the fluidized-bed reactor are found in U.S. Patents Nos.
5 4,792,592; 4,803,251; 4,855,370; 4,876,320; 5,162,463; 5,194,526 and 5,200,477.

Additional processes for reducing or eliminating electrostatic charge include (1) installation of grounding devices in a fluidized bed, (2) ionization of gas or particles by electrical discharge to generate ions which neutralize the electrostatic charge on the particles and (3) the use of radioactive sources to
10 produce radiation capable of generating ions which neutralize the electrostatic charge on the particles.

It would be desirable therefore to provide a process for producing polyolefins, particularly polyethylene, wherein the problems associated with electrostatic charge are reduced.
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SUMMARY OF THE INVENTION

The polymerization process of the present invention comprises the introduction into a polymerization medium comprising an olefin, particularly
20 ethylene, and optionally at least one or more other olefin(s), a metallocene catalyst and at least one compound comprising at least one carbon-oxygen-carbon linkage (C-O-C) of the formula $R^1-O(-R^2-O)_m-R^3$ where m ranges from 0 to 30, and R^1 , R^2 and R^3 independently contain from 1 to 30 carbon atoms and from 0 to 30
heteroatoms of an element, or mixtures thereof, selected from Groups 13, 14, 15,
25 16 and 17 of the Periodic Table of Elements, and further wherein R^1 , R^2 and/or R^3 can be linked and form part of a cyclic or polycyclic structure, herein referred to as the ether, wherein the ether is present in an amount sufficient to reduce the electrostatic charge in the polymerization medium to a level lower than would occur in the same polymerization process in the absence of the ether.

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The present invention also relates to a process for reducing the electrostatic charge in the polymerization of an olefin, particularly ethylene, and optionally at least one or more other olefin(s) in a polymerization medium, particularly gas phase, in the presence of a metallocene catalyst, and at least one ether comprising at least one carbon-oxygen-carbon linkage (C-O-C) of the formula $R^1-O(-R^2-O)_m-R^3$ where m ranges from 0 to 30, and R^1 , R^2 and R^3 independently contain from 1 to 30 carbon atoms and from 0 to 30 heteroatoms of an element, or mixtures thereof, selected from Groups 13, 14, 15, 16 and 17 of the Periodic Table of Elements, and further wherein R^1 , R^2 and/or R^3 can be linked and form part of a cyclic or polycyclic structure, comprising introducing the ether into the polymerization medium in an amount sufficient to reduce the electrostatic charge in the polymerization medium to a level lower than would occur in the same polymerization process in the absence of the ether.

Optionally a halogenated hydrocarbon may be added to the polymerization medium.

The ether as defined herein and the optional halogenated hydrocarbon may be added to the polymerization medium in any manner. The ether as defined herein and the halogenated hydrocarbon may be added to the metallocene catalyst just prior to addition to the polymerization medium, or added separately from the catalyst to the polymerization medium in any manner known in the art. For example, the ether as defined herein may optionally be premixed with the halogenated hydrocarbon prior to addition to the polymerization medium.

If a gas phase fluidized bed process is utilized for polymerization of the olefin, it may be advantageous to add the ether as defined herein prior to the heat removal means, e.g., the heat exchanger, to slow the rate of fouling of said heat removal means in addition to reducing the electrostatic charge in the polymerization reactor.

All mention herein to elements of Groups of the Periodic Table are made in reference to the Periodic Table of the Elements, as published in "Chemical and Engineering News", 63(5), 27, 1985. In this format, the Groups are numbered 1 to 18.

DETAILED DESCRIPTION OF THE INVENTION

The polymerization process of the present invention comprises the
5 introduction into a polymerization medium comprising an olefin, particularly
ethylene, and optionally at least one or more other olefin(s), a metallocene catalyst
and at least one compound comprising at least one carbon-oxygen-carbon linkage
(C-O-C) of the formula $R^1-O(-R^2-O)_m-R^3$ where m ranges from 0 to 30, and R^1 , R^2
and R^3 independently contain from 1 to 30 carbon atoms and from 0 to 30
10 heteroatoms of an element, or mixtures thereof, selected from Groups 13, 14, 15,
16 and 17 of the Periodic Table of Elements, and further wherein R^1 , R^2 and/or R^3
can be linked and form part of a cyclic or polycyclic structure, herein referred to as
the ether, wherein the ether is present in an amount sufficient to reduce the
electrostatic charge in the polymerization medium to a level lower than would
15 occur in the same polymerization process in the absence of the ether.

The present invention also relates to a process for reducing electrostatic
charge in the polymerization of an olefin, particularly ethylene, and optionally at
least one or more other olefin(s) in a polymerization medium, particularly gas
phase, in the presence of a metallocene catalyst, and at least one ether comprising at
20 least one carbon-oxygen-carbon linkage (C-O-C) of the formula $R^1-O(-R^2-O)_m-R^3$
where m ranges from 0 to 30, and R^1 , R^2 and R^3 independently contain from 1 to 30
carbon atoms and from 0 to 30 heteroatoms of an element, or mixtures thereof,
selected from Groups 13, 14, 15, 16 and 17 of the Periodic Table of Elements, and
further wherein R^1 , R^2 and/or R^3 can be linked and form part of a cyclic or
25 polycyclic structure, comprising introducing the ether into the polymerization
medium in an amount sufficient to reduce the electrostatic charge in the
polymerization medium to a level lower than would occur in the same
polymerization process in the absence of the ether.

30 Optionally a halogenated hydrocarbon may be added to the polymerization
medium.

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The ether used herein to reduce the electrostatic charge in the polymerization medium is any compound comprising at least one carbon-oxygen-carbon linkage (C-O-C) of the formula $R^1-O(-R^2-O)_m-R^3$ where m ranges from 0 to 30, and R^1 , R^2 and R^3 independently contain from 1 to 30 carbon atoms and from 0 to 30 heteroatoms of an element, or mixtures thereof, selected from Groups 13, 14, 15, 16 and 17 of the Periodic Table of Elements, and further wherein R^1 , R^2 and/or R^3 can be linked and form part of a cyclic or polycyclic structure.

Exemplary of the R^1 , R^2 and R^3 groups suitable for use herein are C_{1-30} alkyl, C_{2-30} alkenyl, C_{4-30} dienyl, C_{3-30} cycloalkyl, C_{3-30} cycloalkenyl, C_{4-30} cyclodienyl, C_{6-18} aryl, C_{7-30} aralkyl and C_{7-30} alkaryl. Also exemplary are hydrocarbons containing from 1 to 30 carbon atoms and from 1 to 30 heteroatoms of an element, or mixtures thereof, from Groups 13, 14, 15, 16 and 17 of the Periodic Table of Elements such as, for example, B_{1-30} borohydrocarbons, Si_{1-30} silahydrocarbons, P_{1-30} phosphahydrocarbons, S_{1-30} thiahydrocarbons, Cl_{1-30} chlorohydrocarbons and halogenated hydrocarbons containing mixtures of halogens.

It is also suitable to utilize herein as the ether to reduce the electrostatic charge, mixtures of compounds having the above formula.

Exemplary of compounds used herein to reduce the electrostatic charge are compounds comprising one carbon-oxygen-carbon linkage (C-O-C), such as alkyl, alkenyl, dienyl and aryl substituted compounds of the formula R^1-O-R^3 . Specific examples are dimethyl ether; diethyl ether; dipropyl ether; diisopropyl ether; dibutyl ether; dipentyl ether; dihexyl ether; dioctyl ether; diisoamyl ether; di-*tert*-butyl ether; diphenyl ether; dibenzyl ether; divinyl ether; diallyl ether; dicyclopropyl ether; dicyclopentyl ether; dicyclohexyl ether; allyl methyl ether; allyl ethyl ether; allyl cyclohexyl ether; allyl phenyl ether; allyl benzyl ether; allyl 2-tolyl ether; allyl 3-tolyl ether; benzyl methyl ether; benzyl ethyl ether; benzyl isoamyl ether; benzyl chloromethyl ether; benzyl cyclohexyl ether; benzyl phenyl ether; benzyl 1-naphthyl ether; benzyl 2-naphthyl ether; butyl methyl ether; butyl ethyl ether; *sec*-butyl methyl ether; *tert*-butyl methyl ether; butyl cyclopentyl ether;

butyl 2-chloroethyl ether; cyclopentyl methyl ether; cyclohexyl ethyl ether;
cyclohexyl vinyl ether; *tert*-amyl methyl ether; *sec*-butyl ethyl ether; *tert*-butyl
ethyl ether; *tert*-amyl ethyl ether; cyclododecyl methyl ether; bis(3-cyclopenten-1-
yl) ether; 1-methoxy-1,3-cyclohexadiene; 1-methoxy-1,4-cyclohexadiene;
5 chloromethyl methyl ether; chloromethyl ethyl ether; bis(2-tolyl) ether;
trimethylsilylmethyl methyl ether; bis(trimethylsilylmethyl) ether; bis(2,2,2-
trifluoroethyl) ether; benzyl 3-bromopropyl ether; benzyl 3-bromo-2-chloropropyl
ether; dimethyl 2-methoxyethyl borate; dimethyl methoxymethyl borate;
dimethoxy-2-methoxyethylborane; diphenyl-2-methoxyethylphosphine;
10 diphenylmethoxymethylphosphine; 2-(2-thienyl)ethyl ethyl ether; 2-(2-
thienyl)ethyl methyl ether; 2-(3-thienyl)ethyl ethyl ether; 2-(3-thienyl)ethyl methyl
ether; 2-(2-methoxymethyl)-1,3,2-dioxaphospholane; 1-(2-methoxyethyl)pyrrole;
1-(2-methoxyethyl)pyrazole; 1-(2-methoxyethyl)imidazole; 2-(2-
methoxyethyl)pyridine; bis(3-tolyl) ether; bis(1-naphthyl) ether; bis(2-naphthyl)
15 ether; allyl 1-naphthyl ether; allyl 2-naphthyl ether; benzyl 2-tolyl ether; benzyl 3-
tolyl ether; ethyl phenyl ether; ethyl 2-tolyl ether; ethyl 3-tolyl ether; ethyl 1-
naphthyl ether; ethyl 2-naphthyl ether; methyl phenyl ether; methyl 2-tolyl ether;
methyl 3-tolyl ether; methyl 1-naphthyl ether; methyl 2-naphthyl ether; 2-ethoxy-1-
methylpyrrole; 3-methoxy-1-methylpyrrole; 2-ethoxythiophene; 3-
20 methoxythiophene; 3-methoxy-1-methylpyrazole; 4-methoxy-1-methylpyrazole; 5-
methoxy-1-methylpyrazole; 2-methoxy-1-methylimidazole; 4-methoxy-1-
methylimidazole; 5-methoxy-1-methylimidazole; 3-methoxy-1-phenylpyrazole; 4-
methoxy-1-phenylpyrazole; 5-methoxy-1-phenylpyrazole; 2-methoxy-1-
phenylimidazole; 4-methoxy-1-phenylimidazole; 5-methoxy-1-phenylimidazole; 4-
25 methoxy-1-methyl-1,2,3-triazole; 5-methoxy-1-methyl-1,2,3-triazole; 4-methoxy-
1-phenyl-1,2,3-triazole; 5-methoxy-1-phenyl-1,2,3-triazole; 3-methoxy-1-methyl-
1,2,4-triazole; 5-methoxy-1-methyl-1,2,4-triazole; 3-methoxy-1-phenyl-1,2,4-
triazole; 5-methoxy-1-phenyl-1,2,4-triazole; 5-methoxy-1-methyltetrazole; 5-
methoxy-1-phenyltetrazole; 3-methoxyisoxazole; 4-methoxyisoxazole; 5-
30 methoxyisoxazole; 3-methoxy-1,2,4-oxadiazole; 5-methoxy-1,2,4-oxadiazole; 3-

methoxyisothiazole; 4-methoxyisothiazole; 5-methoxyisothiazole; 2-methoxythiazole; 4-methoxythiazole; 5-methoxythiazole; 2-methoxypyridine; 3-methoxypyridine; 4-methoxypyridine; 3-methoxypyridazine; 4-methoxypyridazine; 2-methoxypyrimidine; 4-methoxypyrimidine; 5-methoxypyrimidine; 2-methoxypyrazine; 3-methoxy-1,2,4-triazine; 5-methoxy-1,2,4-triazine; 6-methoxy-1,2,4-triazine; 2-methoxy-1,3,5-triazine and the like. Also exemplary are C₂₋₂₀ cyclic compounds where R¹ and R³ are linked and form part of a cyclic or polycyclic structure such as, for example, ethylene oxide; propylene oxide; 1,2-epoxybutane; cyclopentene oxide; epichlorohydrin; trimethylene oxide; 3,3-dimethyloxetane; furan; 2,3-dihydrofuran; 2,5-dihydrofuran; tetrahydrofuran; 2-methyltetrahydrofuran; 2,5-dimethyltetrahydrofuran; 4,5-dihydro-2-methylfuran; 2-methylfuran; 2,5-dimethylfuran; 3-bromofuran; 2,3-benzofuran; 2-methylbenzofuran; dibenzofuran; phthalan; xanthene; 1,2-pyran; 1,4-pyran; tetrahydropyran; 3-methyltetrahydropyran; 4-chlorotetrahydropyran; chroman; isochroman; oxocane; 2,3-epoxybutane; 1,2-epoxybut-3-ene; styrene oxide; 2-ethylfuran; 2-*tert*-butylfuran; 2,3-dimethylfuran; 2,3-dihydrobenzofuran; dimethyl 3-furylmethyl borate; 2-trimethylsilylfuran; 3-trimethylsilylfuran; oxazole; 1,3,4-oxadiazole; 3,4-dichloro-1,2-epoxybutane; 3,4-dibromo-1,2-epoxybutane and the like.

Exemplary compounds comprising more than one C-O-C linkage include alkyl, alkenyl, dienyl and aryl substituted compounds of the formula R¹-O(-R²-O)_m-R³ where m ranges from 1 to 30. Specific examples are, dimethoxymethane; 1,1-dimethoxyethane; 1,1,1-trimethoxyethane; 1,1,2-trimethoxyethane; 1,1-dimethoxypropane; 1,2-dimethoxypropane; 2,2-dimethoxypropane; 1,3-dimethoxypropane; 1,1,3-trimethoxypropane; 1,4-dimethoxybutane; 1,2-dimethoxybenzene; 1,3-dimethoxybenzene; 1,4-dimethoxybenzene; ethylene glycol dimethyl ether; ethylene glycol diethyl ether; ethylene glycol divinyl ether; ethylene glycol diphenyl ether; ethylene glycol *tert*-butyl methyl ether; ethylene glycol *tert*-butyl ethyl ether; di(ethylene glycol) dimethyl ether; di(ethylene glycol) diethyl ether; di(ethylene glycol) dibutyl ether; di(ethylene glycol) *tert*-butyl

methyl ether; tri(ethylene glycol) dimethyl ether; tri(ethylene glycol) diethyl ether; tetra(ethylene glycol) dimethyl ether; tetra(ethylene glycol) diethyl ether; ethylene glycol bis(trimethylsilylmethyl) ether; di(ethylene glycol) methyl trimethylsilyl ether; tris(2-methoxyethyl) borate; ethylene glycol chloromethyl bromomethyl ether; 2-(2-ethylhexyl)-1,3-dimethoxypropane; 2-isopropyl-1,3-dimethoxypropane; 2-butyl-1,3-dimethoxypropane; 2-*sec*-butyl-1,3-dimethoxypropane; 2-*tert*-butyl-1,3-dimethoxypropane; 2-cyclohexyl-1,3-dimethoxypropane; 2-phenyl-1,3-dimethoxypropane; 2-cumyl-1,3-dimethoxypropane; 2-(2-phenylethyl)-1,3-dimethoxypropane; 2-(2-cyclohexylethyl)-1,3-dimethoxypropane; 2-(*p*-chlorophenyl)-1,3-dimethoxypropane; 2-(*p*-fluorophenyl)-1,3-dimethoxypropane; 2-(diphenylmethyl)-1,3-dimethoxypropane; 2,2-dicyclohexyl-1,3-dimethoxypropane; 2,2-diethyl-1,3-dimethoxypropane; 2,2-dipropyl-1,3-dimethoxypropane; 2,2-diisopropyl-1,3-dimethoxypropane; 2,2-dibutyl-1,3-dimethoxypropane; 2,2-diisobutyl-1,3-dimethoxypropane; 2-methyl-2-ethyl-1,3-dimethoxypropane; 2-methyl-2-propyl-1,3-dimethoxypropane; 2-methyl-2-butyl-1,3-dimethoxypropane; 2-methyl-2-benzyl-1,3-dimethoxypropane; 2-methyl-2-methylcyclohexyl-1,3-dimethoxypropane; 2-isopropyl-2-isopentyl-1,3-dimethoxypropane; 2,2-bis(2-cyclohexylmethyl)-1,3-dimethoxypropane and the like. Also exemplary are C₃₋₂₀ cyclic compounds where R¹, R² and/or R³ are linked and form part of a cyclic or polycyclic structure. Specific examples are 2,5-dimethoxyfuran; 2-methoxyfuran; 3-methoxyfuran; 2-methoxytetrahydropyran; 3-methoxytetrahydropyran; 1,3-dioxolane; 2-methyl-1,3-dioxolane; 2,2-dimethyl-1,3-dioxolane; 2-ethyl-2-methyl-1,3-dioxolane; 2,2-tetramethylene-1,3-dioxolane; 2,2-pentamethylene-1,3-dioxolane; 2-vinyl-1,3-dioxolane; 2-chloromethyl-1,3-dioxolane; 2-methoxy-1,3-dioxolane; 1,4-dioxaspiro[4.4]non-6-ene; 1,4,9,12-tetraoxadispiro(4.2.4.2)tetradecane; 1,3-dioxane; 1,4-dioxane; 4-methyl-1,3-dioxane; 1,3,5-trioxane; 2,4,8,10-tetraoxaspiro(5.5)undecane; 12-crown-4; 15-crown-5; *cis*-4,7-dihydro-1,3-dioxepin; 1,7-dioxaspiro(5.5)undecane; 3,4-epoxytetrahydrofuran; 2,2-dimethyl-4-vinyl-1,3-dioxolane; tri-2-furylphosphine; 2-trimethylsilyl-1,3-dioxolane; 2-(3-thienyl)-1,3-dioxolane; 2-bromochloromethyl-

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1,3-dioxolane; 2-methoxyoxazole; 4-methoxyoxazole; 5-methoxyoxazole; 2-methoxy-1,3,4-oxadiazole and the like.

Preferred for use herein as compounds to reduce the electrostatic charge are dimethyl ether; diethyl ether; dipropyl ether; diisopropyl ether; dibutyl ether; 5 diisoamyl ether; di-*tert*-butyl ether; diphenyl ether; dibenzyl ether; divinyl ether; butyl methyl ether; butyl ethyl ether; *sec*-butyl methyl ether; *tert*-butyl methyl ether; cyclopentyl methyl ether; cyclohexyl ethyl ether; *tert*-amyl methyl ether; *sec*-butyl ethyl ether; chloromethyl methyl ether; trimethylsilylmethyl methyl ether; bis(trimethylsilylmethyl) ether; bis(2,2,2-trifluoroethyl) ether; methyl phenyl ether; 10 ethylene oxide; propylene oxide; 1,2-epoxybutane; cyclopentene oxide; epichlorohydrin; furan; 2,3-dihydrofuran; 2,5-dihydrofuran; tetrahydrofuran; 2-methyltetrahydrofuran; 2,5-dimethyltetrahydrofuran; 2-methylfuran; 2,5-dimethylfuran; tetrahydropyran; 1,2-epoxybut-3-ene; styrene oxide; 2-ethylfuran; oxazole; 1,3,4-oxadiazole; 3,4-dichloro-1,2-epoxybutane; 3,4-dibromo-1,2- 15 epoxybutane ; dimethoxymethane; 1,1-dimethoxyethane; 1,1,1-trimethoxymethane; 1,1,1-trimethoxyethane; 1,1,2-trimethoxyethane; 1,1-dimethoxypropane; 1,2-dimethoxypropane; 2,2-dimethoxypropane; 1,3-dimethoxypropane; 1,1,3-trimethoxypropane; 1,4-dimethoxybutane; 1,2-dimethoxybenzene; 1,3-dimethoxybenzene; 1,4-dimethoxybenzene; ethylene glycol dimethyl ether; 20 di(ethylene glycol) dimethyl ether; di(ethylene glycol) diethyl ether; di(ethylene glycol) dibutyl ether; di(ethylene glycol) *tert*-butyl methyl ether; tri(ethylene glycol) dimethyl ether; tri(ethylene glycol) diethyl ether; tetra(ethylene glycol) dimethyl ether; 2,2-diethyl-1,3-dimethoxypropane; 2-methyl-2-ethyl-1,3-dimethoxypropane; 2-methoxyfuran; 3-methoxyfuran; 1,3-dioxolane; 2-methyl-1,3-dioxolane; 2,2-dimethyl-1,3-dioxolane; 2-ethyl-2-methyl-1,3-dioxolane; 2,2-tetramethylene-1,3-dioxolane; 2,2-pentamethylene-1,3-dioxolane; 1,3-dioxane; 1,4-dioxane; 4-methyl-1,3-dioxane; 1,3,5-trioxane and 3,4-epoxytetrahydrofuran. 25

Most preferred for use herein as compounds to reduce the electrostatic charge are tetrahydrofuran, diethyl ether, dipropyl ether, diisopropyl ether, dibutyl

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ether, dioctyl ether, tert-butyl methyl ether, trimethylene oxide and tetrahydropyran.

Any halogenated hydrocarbon may be used in the process of the present invention. If desired more than one halogenated hydrocarbon can be used. Typical
5 of such halogenated hydrocarbons are monohalogen and polyhalogen substituted saturated or unsaturated aliphatic, alicyclic, or aromatic hydrocarbons having 1 to 12 carbon atoms. Preferred for use in the process of the present invention are dichloromethane, chloroform, carbon tetrachloride, chlorofluoromethane, chlorodifluoromethane, dichlorodifluoromethane, fluorodichloromethane,
10 chlorotrifluoromethane, fluorotrichloromethane and 1,2-dichloroethane. Most preferred for use in the process of the present invention is chloroform.

Metallocene catalysts are well known in the industry and are comprised of at least one transition metal component and at least one co-catalyst component. The transition metal component of the metallocene catalyst comprises a compound
15 having at least one moiety selected from substituted or unsubstituted cyclopentadienyl, substituted or unsubstituted pentadienyl, substituted or unsubstituted pyrrole, substituted or unsubstituted phosphole, substituted or unsubstituted arsole, substituted or unsubstituted boratabenzene, and substituted or unsubstituted carborane, and at least one transition metal. Preferably the moiety is a substituted or unsubstituted cyclopentadienyl. The transition metal is selected
20 from Groups 3, 4, 5, 6, 7, 8, 9 and 10 of the Periodic Table of the Elements. Exemplary of such transition metals are scandium, titanium, zirconium, hafnium, vanadium, chromium, manganese, iron, cobalt, nickel, and the like, and mixtures thereof. In a preferred embodiment the transition metal is selected from Groups 4,
25 5 or 6 such as, for example, titanium, zirconium, hafnium, vanadium and chromium, and in a still further preferred embodiment, the transition metal is titanium or zirconium or mixtures thereof.

The co-catalyst component of the metallocene catalyst can be any
30 compound, or mixtures thereof, that can activate the transition metal component of

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the metallocene catalyst in olefin polymerization. Typically the co-catalyst is an alkylaluminumoxane such as, for example, methylaluminumoxane (MAO) and aryl substituted boron compounds such as, for example, tris(perfluorophenyl)borane and the salts of tetrakis(perfluorophenyl)borate.

5 There are many references describing metallocene catalysts in great detail. For example, metallocene catalyst are described in U.S. Patent Nos. 4,564,647; 4,752,597; 5,106,804; 5,132,380; 5,227,440; 5,296,565; 5,324,800; 5,331,071; 5,332,706; 5,350,723; 5,399,635; 5,466,766; 5,468,702; 5,474,962; 5,578,537 and 5,863,853.

10 The above metallocene catalysts can be introduced in the process of the present invention in any manner. For example, the catalyst components can be introduced directly into the polymerization medium in the form of a solution, a slurry or a dry free flowing powder. The catalyst and the co-catalyst can be premixed to form an activated catalyst prior to addition to the polymerization
15 medium, or the components can be added separately to the polymerization medium, or the components can be premixed and then contacted with one or more olefins to form a prepolymer and then added to the polymerization medium in prepolymer form. When the catalyst components are premixed prior to
20 introduction into the reactor, any electron donor compound may be added to the catalyst to control the level of activity of the catalyst. Furthermore during the polymerization reaction being carried out in the presence of the metallocene catalyst, as above described, there may be added additional organometallic compounds. The additional organometallic compounds may be the same or
25 different from the co-catalyst.

25 Any or all of the components of the metallocene catalyst can be supported on a carrier. The carrier can be any particulate organic or inorganic material. Preferably the carrier particle size should not be larger than about 200 microns in diameter. The most preferred particle size of the carrier material can be easily established by experiment. Preferably, the carrier should have an average particle

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size of 5 to 200 microns in diameter, more preferably 10 to 150 microns and most preferably 20 to 100 microns.

5 Examples of suitable inorganic carriers include metal oxides, metal hydroxides, metal halogenides or other metal salts, such as sulphates, carbonates, phosphates, nitrates and silicates. Exemplary of inorganic carriers suitable for use herein are compounds of metals from Groups 1 and 2 of the Periodic Table of the Elements, such as salts of sodium or potassium and oxides or salts of magnesium or calcium, for instance the chlorides, sulphates, carbonates, phosphates or silicates of sodium, potassium, magnesium or calcium and the oxides or hydroxides of, for instance, magnesium or calcium. Also suitable for use are inorganic oxides such as silica, titania, alumina, zirconia, chromia, boron oxide, silanized silica, silica hydrogels, silica xerogels, silica aerogels, and mixed oxides such as talcs, silica/chromia, silica/chromia/titania, silica/alumina, silica/titania, silica/magnesia, silica/magnesia/titania, aluminum phosphate gels, silica co-gels and the like. The inorganic oxides may contain small amounts of carbonates, nitrates, sulfates and oxides such as Na_2CO_3 , K_2CO_3 , CaCO_3 , MgCO_3 , Na_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, BaSO_4 , KNO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, Na_2O , K_2O and Li_2O . Carriers containing at least one component selected from the group consisting of SiO_2 , Al_2O_3 or mixtures thereof as a main component are preferred.

20 Examples of suitable organic carriers include polymers such as, for example, polyethylene, polypropylene, interpolymers of ethylene and alpha-olefins, polystyrene, and functionalized polystyrene.

The metallocene catalyst may be prepared by any method known in the art. The catalyst can be in the form of a solution, a slurry or a dry free flowing powder. 25 The amount of metallocene catalyst used is that which is sufficient to allow production of the desired amount of the polyolefin.

In carrying out the polymerization process of the present invention the co-catalyst(s) is added to the transition metal component of the metallocene catalyst in any amount sufficient to effect production of the desired polyolefin. It is preferred 30 to utilize the co-catalyst(s) in a molar ratio of co-catalyst(s) to the transition metal

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component ranging from about 0.5:1 to about 10000:1. In a more preferred embodiment, the molar ratio of co-catalyst(s) to transition metal component ranges from about 0.5:1 to about 1000:1.

5 The polymerization process of the present invention may be carried out using any suitable process, for example, solution, slurry and gas phase. A particularly desirable method for producing polyolefin polymers according to the present invention is a gas phase polymerization process preferably utilizing a fluidized bed reactor. This type reactor and means for operating the reactor are well known and completely described in U.S Patents Nos. 3,709,853; 4,003,712; 10 4,011,382; 4,012,573; 4,302,566; 4,543,399; 4,882,400; 5,352,749; 5,541,270; Canadian Patent No. 991,798 and Belgian Patent No. 839,380. These patents disclose gas phase polymerization processes wherein the polymerization medium is either mechanically agitated or fluidized by the continuous flow of the gaseous monomer and diluent. The entire contents of these patents are incorporated herein 15 by reference.

In general, the polymerization process of the present invention may be effected as a continuous gas phase process such as a fluid bed process. A fluid bed reactor for use in the process of the present invention typically comprises a reaction zone and a so-called velocity reduction zone. The reaction zone comprises a bed of 20 growing polymer particles, formed polymer particles and a minor amount of catalyst particles fluidized by the continuous flow of the gaseous monomer and diluent to remove heat of polymerization through the reaction zone. Optionally, some of the recirculated gases may be cooled and compressed to form liquids that increase the heat removal capacity of the circulating gas stream when readmitted to the reaction zone. A suitable rate of gas flow may be readily determined by simple 25 experiment. Make up of gaseous monomer to the circulating gas stream is at a rate equal to the rate at which particulate polymer product and monomer associated therewith is withdrawn from the reactor and the composition of the gas passing through the reactor is adjusted to maintain an essentially steady state gaseous 30 composition within the reaction zone. The gas leaving the reaction zone is passed

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to the velocity reduction zone where entrained particles are removed. Finer entrained particles and dust may be removed in a cyclone and/or fine filter. The gas is passed through a heat exchanger wherein the heat of polymerization is removed, compressed in a compressor and then returned to the reaction zone.

5 In more detail, the reactor temperature of the fluid bed process herein ranges from about 30°C to about 150°C. In general, the reactor temperature is operated at the highest temperature that is feasible taking into account the sintering temperature of the polymer product within the reactor.

10 The process of the present invention is suitable for the production of homopolymers of olefins, particularly ethylene, and/or copolymers, terpolymers, and the like, of olefins, particularly ethylene, and at least one or more other olefin(s). Preferably the olefins are alpha-olefins. The olefins, for example, may contain from 2 to 16 carbon atoms. Particularly preferred for preparation herein by the process of the present invention are polyethylenes. Such polyethylenes are
15 preferably homopolymers of ethylene and interpolymers of ethylene and at least one alpha-olefin wherein the ethylene content is at least about 50% by weight of the total monomers involved. Exemplary olefins that may be utilized herein are ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 4-methylpent-1-ene, 1-decene, 1-dodecene, 1-hexadecene and the like. Also
20 utilizable herein are polyenes such as 1,3-hexadiene, 1,4-hexadiene, cyclopentadiene, dicyclopentadiene, 4-vinylcyclohex-1-ene, 1,5-cyclooctadiene, 5-vinylidene-2-norbornene and 5-vinyl-2-norbornene, and olefins formed in situ in the polymerization medium. When olefins are formed in situ in the polymerization medium, the formation of polyolefins containing long chain branching may occur.

25 In carrying out the polymerization process of the present invention the ether used to reduce the electrostatic charge in the polymerization medium is added in any manner. For example, the ether may be added to the preformed catalyst, to the prepolymer during the prepolymerization step, to the preformed prepolymer and/or to the polymerization medium. The ether may optionally be premixed with the co-
30 catalyst when utilized. The ether is added in any amount sufficient to reduce the

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electrostatic charge in the polymerization medium to a level lower than would occur in the same polymerization process in the absence of the ether. It is preferred to incorporate the ether in a molar ratio of compound to transition metal component of the metallocene catalyst ranging from about 0.001:1 to about 100:1. In a more preferred embodiment, the molar ratio of the ether to transition metal component ranges from about 0.01:1 to about 50:1.

In carrying out the polymerization process of the present invention, the halogenated hydrocarbon may be added to the polymerization medium in any amount sufficient to effect production of the desired polyolefin. It is preferred to incorporate the halogenated hydrocarbon in a molar ratio of halogenated hydrocarbon to transition metal component of the metallocene catalyst ranging from about 0.001:1 to about 100:1. In a more preferred embodiment, the molar ratio of halogenated hydrocarbon to transition metal component ranges from about 0.001:1 to about 10:1.

The molecular weight of the polyolefin produced by the present invention can be controlled in any known manner, for example, by using hydrogen. The molecular weight control of polyethylene, for example, may be evidenced by an increase in the melt index (I_2) of the polymer when the molar ratio of hydrogen to ethylene in the polymerization medium is increased.

Any conventional additive may be added to the polyolefins obtained by the present invention. Examples of the additives include nucleating agents, heat stabilizers, antioxidants of phenol type, sulfur type and phosphorus type, lubricants, antistatic agents, dispersants, copper harm inhibitors, neutralizing agents, foaming agents, plasticizers, anti-foaming agents, flame retardants, crosslinking agents, flowability improvers such as peroxides, ultraviolet light absorbers, light stabilizers, weathering stabilizers, weld strength improvers, slip agents, anti-blocking agents, antifogging agents, dyes, pigments, natural oils, synthetic oils, waxes, fillers and rubber ingredients.

The polyolefins, particularly polyethylenes, of the present invention may be fabricated into films by any technique known in the art. For example, films may be

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produced by the well known cast film, blown film and extrusion coating techniques.

Further, the polyolefins, particularly polyethylenes, may be fabricated into other articles of manufacture, such as molded articles, by any of the well known techniques.

The invention will be more readily understood by reference to the following examples. There are, of course, many other forms of this invention which will become obvious to one skilled in the art, once the invention has been fully disclosed, and it will accordingly be recognized that these examples are given for the purpose of illustration only, and are not to be construed as limiting the scope of this invention in any way. All U.S. Patents referred to herein are incorporated by reference in their entirety.

Examples

Polymerization Process

The polymerization process utilized in Examples 1-15 herein is carried out in a fluidized-bed reactor for gas-phase polymerization, consisting of a vertical cylinder of diameter 0.74 meters and height 7 meters and surmounted by a velocity reduction chamber. The reactor is provided in its lower part with a fluidization grid and with an external line for recycling gas, which connects the top of the velocity reduction chamber to the lower part of the reactor, at a point below the fluidization grid. The recycling line is equipped with a compressor for circulating gas and a heat transfer means such as a heat exchanger. In particular the lines for supplying ethylene, an olefin such as 1-butene, 1-pentene and 1-hexene, hydrogen and nitrogen, which represent the main constituents of the gaseous reaction mixture passing through the fluidized bed, feed into the recycling line. Above the fluidization grid, the reactor contains a fluidized bed consisting of a polyethylene powder made up of particles with a weight-average diameter of about 0.5 mm to about 1.4 mm. The gaseous reaction mixture, which contains ethylene, olefin

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comonomer, hydrogen, nitrogen and minor amounts of other components, passes through the fluidized bed under a pressure ranging from about 280 psig to about 300 psig with an ascending fluidization speed, referred to herein as fluidization velocity, ranging from about 1.6 feet per second to about 2.0 feet per second.

5 The electrostatic charge of the fluidized bed was measured by a Correflow Model 3400 Electrostatic Monitor (ESM) supplied by Auburn International, Inc. of Danvers, Massachusetts. The electrostatic probe was installed in the vertical cylindrical section of the reactor at a height such as to be within the fluidized bed of polymer particles. The electrostatic probe measures the current flow between the
10 polymerization medium and the ground. A reduction in electrostatic charge is defined as a reduction in the absolute magnitude of the measured current and/or a reduction in the variability of the measured current.

15

EXAMPLE 1

Preparation of an Ethylene/1-Hexene Interpolymer with a Metallocene Catalyst and the Addition of a Compound to Reduce the Electrostatic Charge

The polymerization process is carried out as described above. The olefins used herein are ethylene and 1-hexene. Hydrogen is used to control molecular
20 weight. The metallocene catalyst contains bis(1-butyl-3-methylcyclopentadienyl)zirconium dichloride and methylaluminoxane supported on silica. The ether introduced to reduce the electrostatic charge is tetrahydrofuran.

The level of the electrostatic charge in the polymerization medium is expected to be reduced as a result of incorporating the tetrahydrofuran in the
25 polymerization medium.

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EXAMPLES 2 - 6Preparation of an Ethylene/1-Hexene Interpolymer with a Metallocene Catalyst and the Addition of a Compound to Reduce the Electrostatic Charge

5 The process of Example 1 is followed with the exception that the ether utilized to reduce the electrostatic charge is as follows:

Example 2	diethyl ether,
Example 3	dibutyl ether,
Example 4	diisopropyl ether,
Example 5	tert-butyl methyl ether,
10 Example 6	dimethoxyethane.

In each of the above Examples 2-6 the level of electrostatic charge in the polymerization medium is expected to be reduced as a result of incorporating the particular compound in the polymerization medium.

EXAMPLES 7Preparation of HDPE with a Metallocene Catalyst and with the Addition of a Compound to Reduce the Electrostatic Charge

15 The process of Example 1 is followed with the exception that a homopolymer of ethylene is produced. The level of electrostatic charge in the
20 polymerization medium is expected to be reduced as a result of incorporating the tetrahydrofuran in the polymerization medium.

EXAMPLES 8-12Preparation of Ethylene/Olefin Interpolymers with a Metallocene Catalyst and with the Addition of a Compound to Reduce the Electrostatic Charge

25 The process of Example 1 is followed with the exception that in place of the 1-hexene is there is utilized the following comonomers:

Example 8	propylene,
Example 9	1-butene,
30 Example 10	1-pentene,

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Example 11 4-methylpent-1-ene,

Example 12 1-octene.

5 In each of the above Examples 8-12 the level of electrostatic charge in the polymerization medium is expected to be reduced as a result of incorporating THF in the polymerization medium.

EXAMPLES 13-17

Preparation of LLDPE with a Metallocene Catalyst with the Addition of a Compound to Reduce the Electrostatic Charge

10 The process of Example 1 is followed with the exception that the supported metallocene catalyst is replaced with the following silica supported metallocene catalysts:

- | | | |
|----|------------|---|
| 15 | Example 13 | bis(1-butyl-3-methylcyclopentadienyl)dimethylzirconium and tris(perfluorophenyl)borane, |
| | Example 14 | bis(1-butyl-3-methylcyclopentadienyl)dimethylzirconium and triphenylmethylm tetraakis(perfluorophenyl)borate, |
| 20 | Example 15 | (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitaniumdimethyl and triphenylmethylm tetraakis(perfluorophenyl)borate, |
| | Example 16 | (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitaniumdimethyl and tris(perfluorophenyl)borane, |
| 25 | Example 17 | (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitaniumdimethyl and methylaluminumoxane. |

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In each of the above Examples 13-17 the level of electrostatic charge in the polymerization medium is expected to be reduced as a result of incorporating THF as the ether to reduce the electrostatic charge.

Films are prepared from the polyolefins of the present invention.

5 Articles such as molded items are also prepared from the polyolefins of the present invention.

10 It should be clearly understood that the forms of the invention herein described are illustrative only and are not intended to limit the scope of the invention. The present invention includes all modifications falling within the scope of the following claims.

CLAIMS

We claim:

- 5 1. A process for polymerizing an olefin and/or an olefin and at least one or more other olefin(s) comprising contacting, under polymerization conditions, the olefin and/or the olefin and at least one or more other olefin(s) with a metallocene catalyst comprising a transition metal component and a co-catalyst component, and at least one ether comprising at least one carbon-oxygen-
10 carbon linkage (C-O-C) having the formula,
$$R^1-O(-R^2-O)_m-R^3$$
wherein
m ranges from 0 to 30,
 R^1 , R^2 and R^3 independently contain from 1 to 30 carbon atoms and from 0 to
15 30 heteroatoms of an element, or mixtures thereof, selected from Groups 13, 14, 15, 16 and 17 of the Periodic Table of Elements as defined herein, and further wherein R^1 , R^2 and/or R^3 can be linked and form part of a cyclic or polycyclic structure, wherein the ether is present in an amount sufficient to reduce the electrostatic charge in the polymerization medium.
- 20 2. The process according to Claim 1 wherein the metal of the transition metal component comprises at least one metal selected from Groups 4, 5, 6, 7, 8, 9 and 10 of the Periodic Table of the Elements, as defined herein.
3. The process according to Claim 2 wherein the metal is selected from the group consisting of titanium, zirconium, hafnium, vanadium and chromium.
- 25 4. The process according to Claim 3 wherein the metal is selected from the group consisting of titanium, zirconium and mixtures thereof.
5. The process according to Claim 1 wherein the metallocene catalyst is supported on a carrier.
- 30 6. The process according to Claim 5 wherein the carrier is selected from the group consisting of silica, alumina, magnesium chloride and mixtures thereof.

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7. The process according to Claim 1 further comprising adding a halogenated hydrocarbon to the polymerization medium.
8. The process according to Claim 7 wherein the halogenated hydrocarbon is selected from the group consisting of dichloromethane, chloroform, carbon
5 tetrachloride, chlorofluoromethane, chlorodifluoromethane, dichlorodifluoromethane, fluorodichloromethane, chlorotrifluoromethane, fluorotrichloromethane and 1,2-dichloroethane.
9. The process according to Claim 8 wherein the halogenated hydrocarbon is chloroform.
10. The process according to Claim 1 wherein the at least one ether is selected from
10 the group consisting of tetrahydrofuran, diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, dioctyl ether, tert-butyl methyl ether, trimethylene oxide and tetrahydropyran.
11. The process according to Claim 10 wherein the ether is selected from the group
15 consisting of tetrahydrofuran, diethyl ether, dipropyl ether, diisopropyl ether, tert-butyl methyl ether and tetrahydropyran.
12. The process according to Claim 1 wherein the ether is added in a molar ratio of ether to transition metal component of the metallocene catalyst ranging from about 0.01:1 to about 100:1.
- 20 13. The process according to Claim 12 wherein the molar ratio of the ether to transition metal component of the metallocene catalyst ranges from about 0.1:1 to about 50:1.
14. The process according to Claim 1 wherein the polymerization medium is gas phase.
- 25 15. The process according to Claim 1 wherein the polymerization medium is slurry phase.
16. The process according to Claim 1 wherein the olefin is ethylene and the at least one or more other olefin(s) is selected from the group consisting of olefins having 3 to 16 carbon atoms.

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17. The process according to Claim 16 wherein the at least one or more other olefin(s) is selected from the group consisting of 1-octene, 1-hexene, 4-methylpent-1-ene, 1-pentene, 1-butene and propylene.
18. The process according to Claim 16 wherein the interpolymer resulting from the polymerization of ethylene and at least one or more olefin(s) comprises ethylene in an amount of at least about 50% by weight of the interpolymer.
19. A process for reducing the electrostatic charge generated in the polymerization of an olefin and/or an olefin and at least one or more other olefin(s) in a polymerization medium in the presence of a metallocene catalyst comprising a transition metal component and a co-catalyst component, comprising introducing into the polymerization medium at least one ether comprising at least one carbon-oxygen-carbon linkage (C-O-C) having the formula,
- $$R^1-O(-R^2-O)_m-R^3$$
- wherein
- m ranges from 0 to 30,
- R^1 , R^2 and R^3 independently contain from 1 to 30 carbon atoms and from 0 to 30 heteroatoms of an element, or mixtures thereof, selected from Groups 13, 14, 15, 16 and 17 of the Periodic Table of Elements as defined herein, and further wherein R^1 , R^2 and/or R^3 can be linked and form part of a cyclic or polycyclic structure, in an amount sufficient to reduce the electrostatic charge in the polymerization medium.
20. The process according to Claim 19 wherein the metal of the transition metal component comprises at least one metal selected from Groups 4, 5, 6, 7, 8, 9 and 10 of the Periodic Table of the Elements, as defined herein.
21. The process according to Claim 20 wherein the metal is selected from the group consisting of titanium, zirconium, hafnium, vanadium and chromium.
22. The process according to Claim 21 wherein the metal is selected from the group consisting of titanium, zirconium and mixtures thereof.
23. The process according to Claim 19 wherein the metallocene catalyst is supported on a carrier.

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24. The process according to Claim 23 wherein the carrier is selected from the group consisting of silica, alumina, magnesium chloride and mixtures thereof.
25. The process according to Claim 19 further comprising adding a halogenated hydrocarbon to the polymerization medium.
- 5 26. The process according to Claim 25 wherein the halogenated hydrocarbon is selected from the group consisting of dichloromethane, chloroform, carbon tetrachloride, chlorofluoromethane, chlorodifluoromethane, dichlorodifluoromethane, fluorodichloromethane, chlorotrifluoromethane, fluorotrichloromethane and 1,2-dichloroethane.
- 10 27. The process according to Claim 26 wherein the halogenated hydrocarbon is chloroform.
28. The process according to Claim 19 wherein the at least one ether is selected from the group consisting of tetrahydrofuran, diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, dioctyl ether, tert-butyl methyl ether,
- 15 trimethylene oxide and tetrahydropyran.
29. The process according to Claim 28 wherein the ether is selected from the group consisting of tetrahydrofuran, diethyl ether, dipropyl ether, diisopropyl ether, tert-butyl methyl ether and tetrahydropyran.
- 20 30. The process according to Claim 19 wherein the ether is added in a molar ratio of ether to transition metal component of the metallocene catalyst ranging from about 0.01:1 to about 100:1.
31. The process according to Claim 30 wherein the molar ratio of the ether to transition metal component of the metallocene catalyst ranges from about 0.1:1 to about 50:1.
- 25 32. The process according to Claim 19 wherein the polymerization medium is gas phase.
33. The process according to Claim 19 wherein the polymerization medium is slurry phase.

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34. The process according to Claim 19 wherein the olefin is ethylene and the at least one or more other olefin(s) is selected from the group consisting of olefins having 3 to 16 carbon atoms.
- 5 35. The process according to Claim 34 wherein the at least one or more other olefin(s) is selected from the group consisting of 1-octene, 1-hexene, 4-methylpent-1-ene, 1-pentene, 1-butene and propylene.
36. The process according to Claim 34 wherein the interpolymer resulting from the polymerization of ethylene and at least one or more olefin(s) comprises ethylene in an amount of at least about 50% by weight of the interpolymer.
- 10 37. A film fabricated from the polyolefin produced in accordance with Claim 1.
38. An article fabricated from the polyolefin produced in accordance with Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/23897

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F10/00 C08F2/00 C08F4/602

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)

IPC 7 C08F

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 4 876 320 A (AIKMAN COLLIN D ET AL) 24 October 1989 (1989-10-24) cited in the application page 4, line 22 - line 33 page 3, line 36; claims; examples --- -/--	1-3,5,6, 10-14, 16-21, 23,24, 28-32, 34-38

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- | | |
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| <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> | <p>"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</p> <p>"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</p> <p>"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.</p> <p>"&" document member of the same patent family</p> |
|--|--|

Date of the actual completion of the international search <p style="text-align: center;">1 February 2000</p>	Date of mailing of the international search report <p style="text-align: center;">10/02/2000</p>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer <p style="text-align: center;">Kaumann, E</p>

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/23897

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International Application No

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