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(54) Title: DE-FOAMING SPRAY DRIED CATALYST SLURRIES

(57) Abstract: A method for preparing a spray dried catalyst and a low viscosity, low foam spray dried catalyst system for olefin polymerization are provided. In one aspect, the method includes preparing a catalyst system comprising one or more components selected from the group consisting of metallocenes, non-metallocenes, and activators, adding mineral oil to the catalyst system to form a slurry, and adding one or more liquid alkanes having three or more carbon atoms to the slurry in an amount sufficient to reduce foaming and viscosity of the slurry. In one aspect, the catalyst system includes one or more catalysts selected from the group consisting of metallocenes, non-metallocenes, and a combination thereof, wherein the catalyst system is spray dried. The system further includes mineral oil to form a slurry comprising the catalyst system, and one or more liquid alkanes having three or more carbon atoms in an amount sufficient to reduce foaming and viscosity of the slurry.

# DE-FOAMING SPRAY DRIED CATALYST SLURRIES

## BACKGROUND OF THE INVENTION

### Field of the Invention

[0001] Embodiments of the present invention generally relate to a spray dried catalyst slurry. More particularly, embodiments of the present invention relate to a spray died catalyst slurry for gas phase olefin polymerization.

### Description of the Related Art

[0002] A number of methodologies used for delivering catalysts to reactors require the catalyst to be supported on an inert carrier such as silica. Impregnating a catalyst on a support has often been found to cause a significant decrease in catalyst activity. In addition, large particles (>25 micrometers) of the support material have frequently been found in the finished polymer product. These particles may adversely affect polymer properties. This has been observed in film applications where unexploded silica particles appear as defects or gels.

[0003] Spray-drying techniques have been employed as an alternative to supported particles. Once a catalyst has been spray dried, the spray dried catalyst is added to a diluent to form a catalyst slurry and pumped to a polymerization reactor. A high solids concentration within the catalyst slurry is desirable to reduce the amount of slurry. A reduction in the amount of slurry reduces transportation expenses. A reduction in the amount of slurry also reduces the amount of diluent that must be ultimately isolated and either discarded or recycled. This separation process is timely and can greatly increase capital cost.

[0004] However, a high solids concentration typically increases the slurry viscosity. A high solids concentration also increases the amount of foaming which is typically generated by cooling gas during formation of the spray dried catalysts. A high slurry viscosity and foaming often cause handling problems, storage problems as well as reactor injection problems.

[0005] There is a need, therefore, for a spray dried catalyst slurry that has an increased solids content, a low viscosity, and a limited amount of foam.

## SUMMARY OF THE INVENTION

[0001] A method for preparing a spray dried catalyst and a low viscosity, low foam spray dried catalyst system for olefin polymerization are provided. In one aspect, the method includes preparing a catalyst system comprising one or more components selected from the group consisting of metallocenes, non-metallocenes, and activators, adding mineral oil to the catalyst system to form a slurry, and adding one or more liquid alkanes having three or more carbon atoms to the slurry in an amount sufficient to reduce foaming and viscosity of the slurry. In one aspect, the catalyst system includes one or more catalysts selected from the group consisting of metallocenes, non-metallocenes, and a combination thereof, wherein the catalyst system is spray dried. The catalyst system further includes mineral oil to form a slurry comprising the catalyst system, and one or more liquid alkanes having three or more carbon atoms in an amount sufficient to reduce foaming and viscosity of the slurry.

[0002] Further, a method for olefin polymerization is provided. In one aspect, the method comprises preparing a catalyst system useful for olefin polymerization, adding mineral oil to the catalyst system to form a slurry, adding one or more liquid alkanes having three or more carbon atoms to the slurry in an amount sufficient to reduce foaming and viscosity of the slurry, and transferring the slurry to a gas phase reactor.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0003] A spray dried catalyst slurry and a method for delivering the slurry to a polymerization reactor are provided. In one aspect, the spray dried catalyst slurry includes mineral oil, at least one catalyst system, and one or more liquid alkanes having from three to twelve carbon atoms.

It has been surprisingly found that the one or more liquid alkanes reduces the viscosity of the slurry by at least 30 percent, and also reduces foaming. Foaming is typically a result of evolved gas formed by a reaction of volatile components and impurities within the catalyst slurry, whereby this evolved gas forms a foam due to the surface tension of the oil slurry.

[0011] The concentration of the components in the slurry is controlled to reduce the viscosity of the slurry and to reduce foaming. In one aspect, the spray dried catalyst slurry contains up to 20 percent by weight of the one or more liquid alkanes. In another aspect, the slurry contains up to 15 percent by weight of the one or more liquid alkanes. In yet another aspect, the slurry contains up to 10 percent by weight of the one or more liquid alkanes. Preferably, the slurry contains between about 2 percent by weight and 15 percent by weight of the one or more liquid alkanes. More preferably, the slurry contains between about 2 percent by weight and 10 percent by weight of the one or more liquid alkanes.

[0012] The concentration of the components in the slurry is also controlled to maximize the amount of the catalyst system within the slurry. Due to the presence of the liquid alkane, the slurry may contain up to 50 percent by weight of the catalyst system. In one aspect, the slurry contains at least 10 percent by weight of the catalyst system. In another aspect, the slurry contains at least 15 percent by weight of the catalyst system. In yet another aspect, the slurry contains at least 20 percent by weight of the catalyst system. Preferably, the slurry contains from 5 percent by weight to about 35 percent by weight of the catalyst system. More preferably, the slurry contains from 10 percent by weight to about 30 percent by weight of the catalyst system or from 15 percent by weight to about 25 percent by weight of the catalyst system.

[0013] The one or more liquid alkanes are preferably liquid under polymerization conditions and relatively inert. Exemplary liquid alkanes include, but are not limited to, isopentane, hexane and heptane. Preferably, the liquid alkane is hexane.

[0014] The spray dried catalyst slurry preferably has a viscosity of from 300 to 1,500 centipoise (cP), such as from 300 to 400 centipoise (cP) at 25°C. In one aspect, the spray dried catalyst slurry has a viscosity of from 300 to 1,000 cP at 25°C. In another aspect, the spray dried catalyst slurry has a viscosity of from 300 to 500 cP at 25°C. In yet another aspect, the spray dried catalyst slurry has a viscosity of from 300 to 400 cP at 25°C.

[0015] The spray dried catalyst slurry may be utilized in conjunction with any suitable polymerization catalyst. Exemplary polymerization catalysts include, but are not limited to, metallocenes, Group 15 containing compounds, phenoxide transition metal compositions, Group 5 or 6 metal imido complexes, bridged bis(arylamido) Group 4 compounds, derivatives thereof, and combinations thereof.

[0016] The term "catalyst system" may include any number of catalysts in any combination as described herein, as well as any activator in any combination as described herein. The term "catalyst" is used interchangeably with the term "catalyst component", and includes any compound or component, or combination of compounds or components, that is capable of increasing the rate of a chemical reaction, such as the polymerization or oligomerization of one or more olefins. As used herein, in reference to Periodic Table "Groups" of Elements, the "new" numbering scheme for the Periodic Table Groups are used as in the CRC Handbook of Chemistry and Physics (David R. Lide ed., CRC Press 81st ed. 2000).

[0017] In one aspect, the catalyst system is a mixed catalyst system of at least one metallocene catalyst component and at least one non-metallocene component. The mixed catalyst system may be described as a bimetallic catalyst composition or a multi-catalyst composition. As used herein, the terms "bimetallic catalyst composition" and "bimetallic catalyst" include any composition, mixture, or system that includes two or more different catalyst components, each having a different metal group. The terms "multi-catalyst composition" and "multi-catalyst" include any composition, mixture, or system that includes two or more different catalyst components regardless of the metals. Therefore, terms "bimetallic catalyst composition," "bimetallic catalyst," "multi-catalyst composition," and "multi-catalyst" will be collectively referred to herein as a "mixed catalyst system" unless specifically noted otherwise.

**Non-metallocene Component**

[0018] Exemplary non-metallocene component include, but are not limited to, a Group 15-containing catalyst. "Group 15-containing catalysts", as referred to herein, include Group 3 to Group 12 metal complexes, wherein the metal is 2 to 4 coordinate and the coordinating moiety or moieties include at least two Group 15 atoms, and up to four Group 15 atoms. In one embodiment, the Group 15-containing catalyst is a complex of a Group 4 metal and from one

to four ligands such that the Group 4 metal is at least 2 coordinate and the coordinating moiety or moieties include at least two nitrogens.

[0019] In one embodiment, the Group 15-containing catalyst may include, but is not limited to, Group 4 imino-phenol complexes, Group 4 bis(amide) complexes, and Group 4 pyridyl-amide complexes that are active towards olefin polymerization to any extent. In another embodiment, the Group 15-containing catalyst may be described by the following formula (I):

$$\alpha_a\beta_b\gamma_gMX_n \qquad (I)$$

[0020] Each X is independently selected from halogen ions, hydrides, $C_1$ to $C_{12}$ alkyls, $C_2$ to $C_{12}$ alkenyls, $C_6$ to $C_{12}$ aryls, $C_7$ to $C_{20}$ alkylaryls, $C_1$ to $C_{12}$ alkoxys, $C_6$ to $C_{16}$ aryloxys, $C_7$ to $C_{18}$ alkylaryloxys, $C_1$ to $C_{12}$ fluoroalkyls, $C_6$ to $C_{12}$ fluoroaryls, $C_1$ to $C_{12}$ heteroatom-containing hydrocarbons, halogenated $C_6$ to $C_{16}$ aryloxys, and substituted derivatives thereof.

[0021] M is selected from Group 3 to Group 12 atoms in one embodiment; and selected from Group 3 to Group 10 atoms in a more particular embodiment; and selected from Group 3 to Group 6 atoms in yet a more particular embodiment; and selected from Ni, Cr, Ti, Zr and Hf in yet a more particular embodiment; and selected from Zr and Hf in yet a more particular embodiment.

[0022] Each β and γ are groups that each comprise at least one Group 14 to Group 16 atom; and β (when present) and γ are groups bonded to M through between 2 and 6 Group 14 to Group 16 atoms, at least two atoms being Group 15-containing atoms.

[0023] More particularly, β and γ are groups selected from Group 14 and Group 15-containing: alkyls, aryls, alkylaryls, and heterocyclic hydrocarbons, and chemically bonded combinations thereof in one embodiment; and selected from Group 14 and Group 15-containing: $C_1$ to $C_{10}$ alkyls, $C_6$ to $C_{12}$ aryls, $C_6$ to $C_{18}$ alkylaryls, and $C_4$ to $C_{12}$ heterocyclic hydrocarbons, and chemically bonded combinations thereof in a more particular embodiment; and selected from $C_1$ to $C_{10}$ alkylamines, $C_1$ to $C_{10}$ alkoxys, $C_6$ to $C_{20}$ alkylarylamines, $C_6$ to $C_{18}$ alkylaryloxys, and $C_4$ to $C_{12}$ nitrogen containing heterocyclic hydrocarbons, and $C_4$ to $C_{12}$ alkyl substituted nitrogen containing heterocyclic hydrocarbons and chemically bonded combinations thereof in yet a more particular embodiment; and selected from anilinyls, pyridyls, quinolyls, pyrrolyls,

pyrimidyls, purinyls, imidazyls, indolyls, $C_1$ to $C_6$ alkyl substituted groups selected from anilinyls, pyridyls, quinolyls, pyrrolyls, pyrimidyls, purinyls, imidazyls, indolyls; $C_1$ to $C_6$ alkylamine substituted groups selected from anilinyls, pyridyls, quinolyls, pyrrolyls, pyrimidyls, purinyls, imidazyls, indolyls, amine substituted anilinyls, pyridyls, quinolyls, pyrrolyls, pyrimidyls, purinyls, imidazyls, and indolyls; hydroxy substituted groups selected from anilinyls, pyridyls, quinolyls, pyrrolyls, pyrimidyls, purinyls, imidazyls, and indolyls; methyl-substituted phenylamines, and chemically bonded combinations thereof in yet a more particular embodiment;

**[0024]** Each α is a linking (or "bridging") moiety that, when present, forms a chemical bond to each of β and γ, or two γ's, thus forming a "γαγ" or "γαβ" ligand bound to M; α may also comprise a Group 14 to Group 16 atom which may be bonded to M through the Group 14 to Group 16 atom in one embodiment; and more particularly, α is a divalent bridging group selected from alkylenes, arylenes, alkenylenes, heterocyclic arylenes, alkylarylenes, heteroatom containing alkylenes, heteroatom containing alkenylenes and heterocyclic hydrocarbonylenes in one embodiment; and selected from $C_1$ to $C_{10}$ alkylenes, $C_2$ to $C_{10}$ alkenylenes, $C_6$ to $C_{12}$ arylenes, $C_1$ to $C_{10}$ divalent ethers, $C_6$ to $C_{12}$ O- or N-containing arylenes, $C_2$ to $C_{10}$ alkyleneamines, $C_6$ to $C_{12}$ aryleneamines, and substituted derivatives thereof in yet a more particular embodiment;

**[0025]** a is an integer from 0 to 2; a is either 0 or 1 in a more particular embodiment; and a is 1 in yet a more particular embodiment; b is an integer from 0 to 2; g is an integer from 1 to 2; wherein in one embodiment, a is 1, b is 0 and g is 2; and

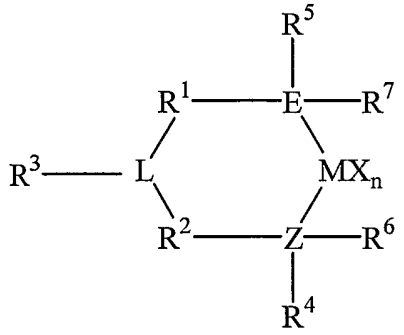
**[0026]** n is an integer from 0 to 4 in one embodiment; and an integer from 1 to 3 in a more particular embodiment; and an integer from 2 to 3 in yet a more particular embodiment.

**[0027]** As used herein, "chemically bonded combinations thereof" means that adjacent groups, (β and γ groups) may form a chemical bond between them. In one embodiment, the β and γ groups are chemically bonded through one or more α groups there between.

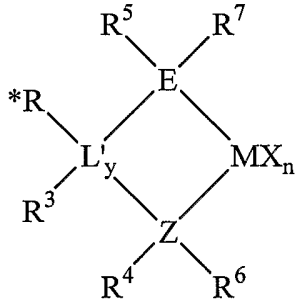
**[0028]** As used herein, the terms "alkyleneamines" and "aryleneamines" describe alkylamines and arylamines (respectively) that are deficient by two hydrogens, thus forming chemical bonds with two adjacent γ groups, or adjacent β and γ groups. Thus, an example of an alkyleneamine is $-CH_2CH_2N(CH_3)CH_2CH_2-$, and an example of a heterocyclic hydrocarbylene

or aryleneamine is $-C_5H_3N-$ (divalent pyridine). An "alkylene-arylamine" is a group such as, for example, $-CH_2CH_2(C_5H_3N)CH_2CH_2-$.

[0029] In yet another embodiment, the Group 15-containing catalyst may be represented by the structures (II) and (III):



[0030] (II)



[0031] (III)

[0032] wherein E and Z are Group 15 elements independently selected from nitrogen and phosphorus in one embodiment; and nitrogen in a more particular embodiment;

[0033] L is selected from Group 15 atoms, Group 16 atoms, Group 15-containing hydrocarbylenes and a Group 16 containing hydrocarbylenes in one embodiment; wherein $R^3$ is absent when L is a Group 16 atom; in yet a more particular embodiment, when $R^3$ is absent, L is selected from heterocyclic hydrocarbylenes; and in yet a more particular embodiment, L is selected from nitrogen, phosphorous, anilinyls, pyridyls, quinolyls, pyrrolyls, pyrimidyls, purinyls, imidazyls, indolyls; $C_1$ to $C_6$ alkyl substituted groups selected from anilinyls, pyridyls, quinolyls, pyrrolyls, pyrimidyls, purinyls, imidazyls, and indolyls; $C_1$ to $C_6$

alkylamine substituted groups selected from anilinyls, pyridyls, quinolyls, pyrrolyls, pyrimidyls, purinyls, imidazyls, indolyls; amine substituted anilinyls, pyridyls, quinolyls, pyrrolyls, pyrimidyls, purinyls, imidazyls, and indolyls; hydroxy substituted groups selected from anilinyls, pyridyls, quinolyls, pyrrolyls, pyrimidyls, purinyls, imidazyls, and indolyls; methyl-substituted phenylamines, substituted derivatives thereof, and chemically bonded combinations thereof;

[0034] L' is selected from Group 15 atoms, Group 16 atoms, and Group 14 atoms in one embodiment; and selected from Group 15 and Group 16 atoms in a more particular embodiment; and is selected from groups as defined by L above in yet a more particular embodiment, wherein "EZL" and "EZL'" may be referred to as a "ligand", the EZL and EZL' ligands comprising the R* and $R^1$-$R^7$ groups;

[0035] L and L' may or may not form a bond with M;

[0036] y is an integer ranging from 0 to 2 (when y is 0, group L', *R and $R^3$ are absent);

[0037] M is selected from Group 3 to Group 5 atoms, Group 4 atoms in a more particular embodiment, and selected from Zr and Hf in yet a more particular embodiment;

[0038] n is an integer ranging from 1 to 4 in one embodiment; n is an integer ranging from 2 to 3 in a more particular embodiment;

[0039] $R^1$ and $R^2$ are independently: divalent bridging groups selected from alkylenes, arylenes, heteroatom containing alkylenes, heteroatom containing arylenes, substituted alkylenes, substituted arylenes and substituted heteroatom containing alkylenes, wherein the heteroatom is selected from silicon, oxygen, nitrogen, germanium, phosphorous, boron and sulfur in one embodiment; selected from $C_1$ to $C_{20}$ alkylenes, $C_6$ to $C_{12}$ arylenes, heteroatom-containing $C_1$ to $C_{20}$ alkylenes and heteroatom-containing $C_6$ to $C_{12}$ arylenes in a more particular embodiment; and in yet a more particular embodiment selected from $-CH_2-$, $-C(CH_3)_2-$, $-C(C_6H_5)_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-Si(CH_3)_2-$, $-Si(C_6H_5)_2-$, $-C_6H_{10}-$, $-C_6H_4-$, and substituted derivatives thereof, the substitutions including $C_1$ to $C_4$ alkyls, phenyl, and halogen radicals;

[0040] $R^3$ is absent in one embodiment; a group selected from hydrocarbyl groups, hydrogen radical, halogen radicals, and heteroatom-containing groups in a more particular embodiment;

and selected from linear alkyls, cyclic alkyls, and branched alkyls having 1 to 20 carbon atoms in yet a more particular embodiment;

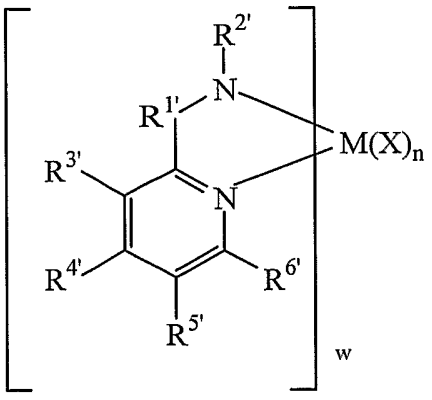
[0041] *R is absent in one embodiment; a group selected from hydrogen radical, Group 14 atom containing groups, halogen radicals, and a heteroatom-containing groups in yet a more particular embodiment;

[0042] $R^4$ and $R^5$ are independently: groups selected from alkyls, aryls, substituted aryls, cyclic alkyls, substituted cyclic alkyls, cyclic arylalkyls, substituted cyclic arylalkyls and multiple ring systems in one embodiment, each group having up to 20 carbon atoms, and between 3 and 10 carbon atoms in a more particular embodiment; selected from $C_1$ to $C_{20}$ alkyls, $C_1$ to $C_{20}$ aryls, $C_1$ to $C_{20}$ arylalkyls, and heteroatom-containing groups (for example $PR_3$, where R is an alkyl group) in yet a more particular embodiment; and

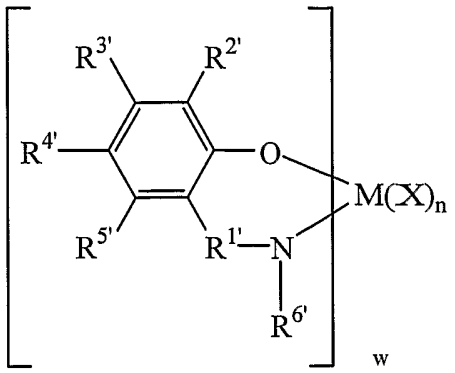
[0043] $R^6$ and $R^7$ are independently: absent in one embodiment; groups selected from hydrogen radicals, halogen radicals, heteroatom-containing groups and hydrocarbyls in a more particular embodiment; selected from linear, cyclic and branched alkyls having from 1 to 20 carbon atoms in yet a more particular embodiment;

[0044] $R^1$ and $R^2$ may be associated with one another, and/or $R^4$ and $R^5$ may be associated with one another as through a chemical bond.

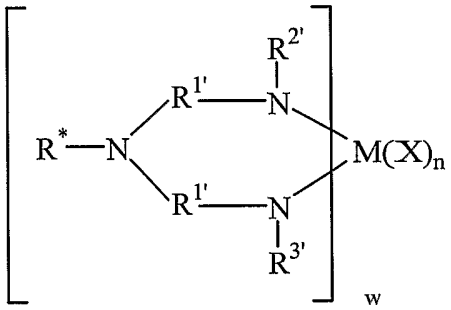
[0045] Described yet more particularly, the Group 15-containing catalyst can be described as the embodiments shown in structures (IV), (V) and (VI) (where "N" is nitrogen):




[0046] (IV)



[0047] (V)



[0048] (VI)

[0049] The structure (IV) represents pyridyl-amide structures, structure (V) represents imino-phenol structures, and structure (VI) represents bis(amide) structures;

[0050] w is an integer from 1 to 3, and 1 or 2 in a more particular embodiment, and 1 in yet a more particular embodiment;

[0051] M is a Group 3 to Group 13 element, a Group 3 to Group 6 element in a more particular embodiment, and a Group 4 element in yet a more particular embodiment; and

[0052] n is an integer ranging from 0 to 4, and from 1 to 3 in a more particular embodiment, and from 2 to 3 in yet a more particular embodiment, and 2 in yet a more particular embodiment.

[0053] Each X is independently selected from halogen ions, hydrides, $C_1$ to $C_{12}$ alkyls, $C_2$ to $C_{12}$ alkenyls, $C_6$ to $C_{12}$ aryls, $C_7$ to $C_{20}$ alkylaryls, $C_1$ to $C_{12}$ alkoxys, $C_6$ to $C_{16}$ aryloxys, $C_7$ to $C_{18}$ alkylaryloxys, $C_1$ to $C_{12}$ fluoroalkyls, $C_6$ to $C_{12}$ fluoroaryls, $C_1$ to $C_{12}$ heteroatom-containing hydrocarbons, halogenated $C_6$ to $C_{16}$ aryloxys, and substituted derivatives thereof.

[0054] In structures (IV), (V), and (VI), $R^{1'}$ is selected from hydrocarbylenes and heteroatom-containing hydrocarbylenes in one embodiment, and selected from $-SiR_2-$, alkylenes, arylenes, alkenylenes and substituted alkylenes, substituted alkenylenes and substituted arylenes in another embodiment; and selected from $-SiR_2-$, $C_1$ to $C_6$ alkylenes, $C_6$ to $C_{12}$ arylenes, $C_1$ to $C_6$ substituted alkylenes and $C_6$ to $C_{12}$ substituted arylenes in another embodiment.

[0055] R is selected from $C_1$ to $C_6$ alkyls and $C_6$ to $C_{12}$ aryls; and $R^{2'}$, $R^{3'}$, $R^{4'}$, $R^{5'}$, $R^{6'}$ and $R^*$ are independently selected from hydride, $C_1$ to $C_{10}$ alkyls, $C_6$ to $C_{12}$ aryls, $C_6$ to $C_{18}$ alkylaryls, $C_4$ to $C_{12}$ heterocyclic hydrocarbyls, substituted $C_1$ to $C_{10}$ alkyls, substituted $C_6$ to $C_{12}$ aryls, substituted $C_6$ to $C_{18}$ alkylaryls, and substituted $C_4$ to $C_{12}$ heterocyclic hydrocarbyls and chemically bonded combinations thereof in one embodiment.

[0056] R* is absent in a particular embodiment; and in another embodiment, R*–N represents a nitrogen containing group or ring such as a pyridyl group or a substituted pyridyl group that is bridged by the $R^{1'}$ groups. In yet another embodiment, R*–N is absent, and the $R^{1'}$ groups form a chemical bond to one another.

[0057] In one embodiment of structures (IV), (V), and (VI), $R^{1'}$ is selected from methylene, ethylene, 1-propylene, 2-propylene, $=Si(CH_3)_2$, $=Si(phenyl)_2$, $-CH=$, $-C(CH_3)=$, $-C(phenyl)_2-$, $-C(phenyl)=$ (wherein "=" represents two chemical bonds), and the like.

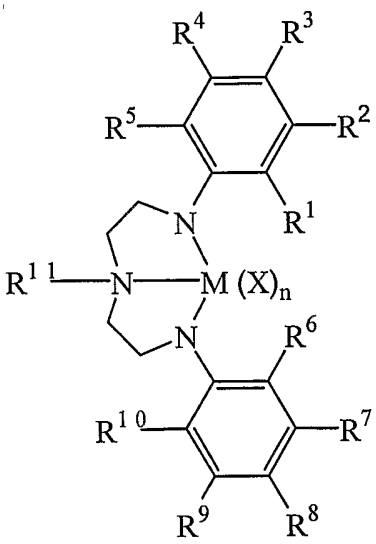
[0058] In a particular embodiment of structure (V), $R^{2'}$ and $R^{4'}$ are selected from 2-methylphenyl, 2-n-propylphenyl, 2-iso-propylphenyl, 2-iso-butylphenyl, 2-tert-butylphenyl, 2-fluorophenyl, 2-chlorophenyl, 2-bromophenyl, 2-methyl-4-chlorophenyl, 2-n-propyl-4-chlorophenyl, 2-iso-propyl-4-chlorophenyl, 2-iso-butyl-4-chlorophenyl, 2-tert-butyl-4-chlorophenyl, 2-methyl-4-fluorophenyl, 2-n-propyl-4-fluorophenyl, 2-iso-propyl-4-fluorophenyl, 2-iso-butyl-4-fluorophenyl, 2-tert-butyl-4-fluorophenyl, 2-methyl-4-bromophenyl, 2-n-propyl-4-bromophenyl, 2-iso-propyl-4-bromophenyl, 2-iso-butyl-4-bromophenyl, 2-tert-butyl-4-bromophenyl, and the like.

[0059] In yet another particular embodiment of structures (IV) and (VI), $R^{2'}$ and $R^{3'}$ are selected from 2-methylphenyl, 2-n-propylphenyl, 2-iso-propylphenyl, 2-iso-butylphenyl, 2-tert-butylphenyl, 2-fluorophenyl, 2-chlorophenyl, 2-bromophenyl, 4-methylphenyl, 4-n-propylphenyl, 4-iso-propylphenyl, 4-iso-butylphenyl, 4-tert-butylphenyl, 4-fluorophenyl, 4-chlorophenyl, 4-bromophenyl, 6-methylphenyl, 6-n–propylphenyl, 6-iso-propylphenyl, 6-iso-butylphenyl, 6-tert-butylphenyl, 6-fluorophenyl, 6-chlorophenyl, 6-bromophenyl, 2,6-dimethylphenyl, 2,6-di-n-propylphenyl, 2,6-di-iso-propylphenyl, 2,6-di-isobutylphenyl, 2,6-di-tert-butylphenyl, 2,6-difluorophenyl, 2,6-dichlorophenyl, 2,6-dibromophenyl, 2,4,6-trimethylphenyl, 2,4,6-tri-n-propylphenyl, 2,4,6-tri-iso-propylphenyl, 2,4,6-tri-iso-butylphenyl, 2,4,6-tri-tert-butylphenyl, 2,4,6-trifluorophenyl, 2,4,6-trichlorophenyl, 2,4,6-tribromophenyl, 2,3,4,5,6-pentafluorophenyl, 2,3,4,5,6-pentachlorophenyl, 2,3,4,5,6-pentabromophenyl, and the like.

[0060] In another embodiment of structures (IV), (V), and (VI), X is independently selected from fluoride, chloride, bromide, methyl, ethyl, phenyl, benzyl, phenyloxy, benzloxy, 2-phenyl-2-propoxy, 1-phenyl-2-propoxy, 1-phenyl-2-butoxy, 2-phenyl-2-butoxy and the like.

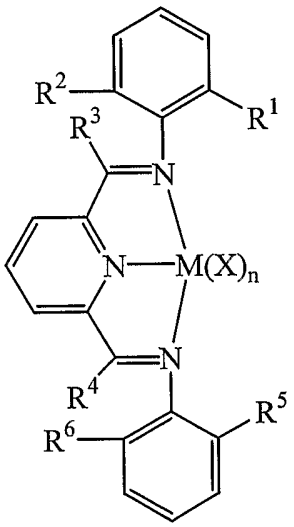
[0061] As used herein, "chemically bonded combinations" means that adjacent groups may form a chemical bond between them, thus forming a ring system, either saturated, partially unsaturated, or aromatic.

[0062] Non-limiting examples of the Group 15-containing catalyst are represented by the structures (VIIa) - (VIIf) (where "N" is nitrogen):

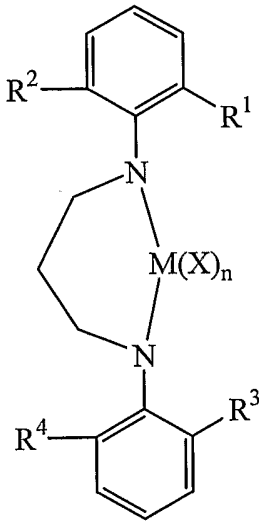


(VIIa)

[0063]

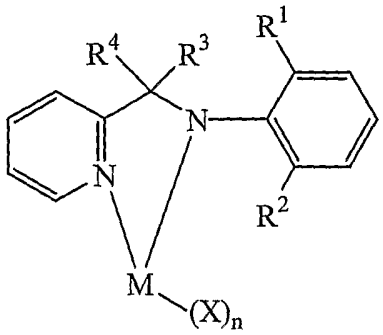


(VIIb)

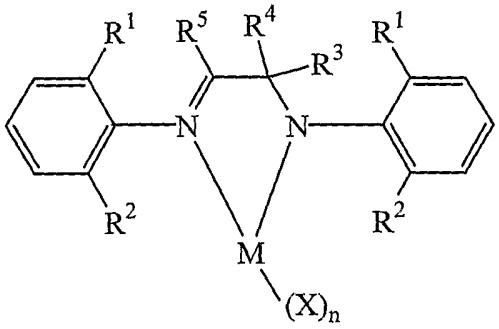


(VIIc)

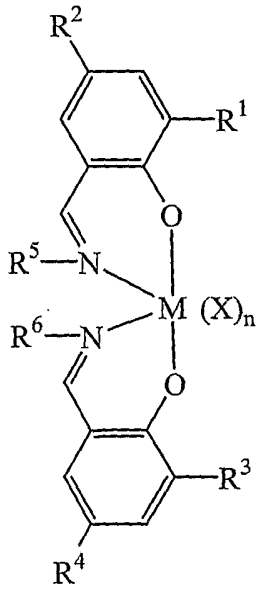
[0064]



[0065] (VIId)



[0066] (VIIe)



[0067] (VIIf)

)068] In structures (VIIa) through (VIIf) M is selected from Group 4 atoms in one mbodiment; and M is selected from Zr and Hf in a more particular embodiment;

)069] n is an integer ranging from 0 to 4, and from 2 to 3 in a more particular embodiment; nd

0070] $R^1$ through $R^{11}$ in structures (VIIa) through (VIIf) are selected from hydride, fluorine adical, chlorine radical, bromine radical, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, ert-butyl and phenyl.

0071] Each X is independently selected from halogen ions, hydrides, $C_1$ to $C_{12}$ alkyls, $C_2$ to $C_{12}$ alkenyls, $C_6$ to $C_{12}$ aryls, $C_7$ to $C_{20}$ alkylaryls, $C_1$ to $C_{12}$ alkoxys, $C_6$ to $C_{16}$ aryloxys, $C_7$ to $C_{18}$ alkylaryloxys, $C_1$ to $C_{12}$ fluoroalkyls, $C_6$ to $C_{12}$ fluoroaryls, $C_1$ to $C_{12}$ heteroatom-containing hydrocarbons, halogenated $C_6$ to $C_{16}$ aryloxys, and substituted derivatives thereof. Preferably, at least one X is a halogentated aryloxy group or a derivative thereof. More preferably, at least one X is a pentafluorophenoxy group.

**Metallocene Catalyst Component**

[0072] Exemplary metallocene catalyst components include, but are not limited to, "half sandwich" and "full sandwich" compounds having one or more Cp ligands (cyclopentadienyl and ligands isolobal to cyclopentadienyl) bound to at least one Group 3 to Group 12 metal atom, and one or more leaving group(s) bound to the at least one metal atom. Hereinafter, these compounds will be referred to as "metallocenes" or "metallocene catalyst components".

[0073] The Cp ligands are one or more rings or ring system(s), at least a portion of which includes π-bonded systems, such as cycloalkadienyl ligands and heterocyclic analogues. The ring(s) or ring system(s) typically comprise atoms selected from the group consisting of Groups 13 to 16 atoms, and more particularly, the atoms that make up the Cp ligands are selected from the group consisting of carbon, nitrogen, oxygen, silicon, sulfur, phosphorous, germanium, boron and aluminum and combinations thereof, wherein carbon makes up at least 50% of the ring members. Even more particularly, the Cp ligand(s) are selected from the group consisting of substituted and unsubstituted cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl, non-limiting examples of which include cyclopentadienyl, indenyl, fluorenyl and other structures. Further non-limiting examples of such ligands include cyclopentadienyl, cyclopentaphenanthreneyl, indenyl, benzindenyl, fluorenyl, octahydrofluorenyl,

cyclooctatetraenyl, cyclopentacyclododecene, phenanthrindenyl, 3,4-benzofluorenyl, 9-phenylfluorenyl, 8-H-cyclopent[a]acenaphthylenyl, 7H-dibenzofluorenyl, indeno[1,2-9]anthrene, thiophenoindenyl, thiophenofluorenyl, hydrogenated versions thereof (*e.g.*, 4,5,6,7-tetrahydroindenyl, or "$H_4$Ind"), substituted versions thereof (as described in more detail below), and heterocyclic versions thereof.

[0074] The metal atom "M" of the metallocene catalyst compound, as described throughout the specification and claims, may be selected from the group consisting of Groups 3 through 12 atoms and lanthanide Group atoms in one embodiment; and selected from the group consisting of Groups 3 through 10 atoms in a more particular embodiment, and selected from the group consisting of Sc, Ti, Zr, Hf, V, Nb, Ta, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, and Ni in yet a more particular embodiment; and selected from the group consisting of Groups 4, 5 and 6 atoms in yet a more particular embodiment, and a Ti, Zr, Hf atoms in yet a more particular embodiment, and Zr in yet a more particular embodiment. The oxidation state of the metal atom "M" may range from 0 to +7 in one embodiment; and in a more particular embodiment, is +1, +2, +3, +4 or +5; and in yet a more particular embodiment is +2, +3 or +4. The groups bound the metal atom "M" are such that the compounds described below in the formulas and structures are neutral, unless otherwise indicated. The Cp ligand(s) form at least one chemical bond with the metal atom M to form the "metallocene catalyst compound". The Cp ligands are distinct from the leaving groups bound to the catalyst compound in that they are not highly susceptible to substitution/abstraction reactions.

[0075] In one aspect, the one or more metallocene catalyst components are represented by the formula (II):

[0076] $Cp^ACp^BMX_n$ (VIII)

[0077] wherein M is as described above; each X is chemically bonded to M; each Cp group is chemically bonded to M; and n is 0 or an integer from 1 to 4, and either 1 or 2 in a particular embodiment.

[0078] The ligands represented by $Cp^A$ and $Cp^B$ in formula (VIII) may be the same or different cyclopentadienyl ligands or ligands isolobal to cyclopentadienyl, either or both of which may contain heteroatoms and either or both of which may be substituted by a group R. In one

embodiment, $Cp^A$ and $Cp^B$ are independently selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, and substituted derivatives of each.

[0079] Independently, each $Cp^A$ and $Cp^B$ of formula (VIII) may be unsubstituted or substituted with any one or combination of substituent groups R. Non-limiting examples of substituent groups R as used in structure (II) include hydrogen radicals, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, and combinations thereof.

[0080] More particular non-limiting examples of alkyl substituents R associated with formula (II) includes methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl, phenyl, methylphenyl, and tert-butylphenyl groups and the like, including all their isomers, for example tertiary-butyl, isopropyl, and the like. Other possible radicals include substituted alkyls and aryls such as, for example, fluoromethyl, fluroethyl, difluroethyl, iodopropyl, bromohexyl, chlorobenzyl and hydrocarbyl substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, methyldiethylsilyl and the like; and halocarbyl-substituted organometalloid radicals including tris(trifluoromethyl)silyl, methylbis(difluoromethyl)silyl, bromomethyldimethylgermyl and the like; and disubstituted boron radicals including dimethylboron for example; and disubstituted Group 15 radicals including dimethylamine, dimethylphosphine, diphenylamine, methylphenylphosphine, Group 16 radicals including methoxy, ethoxy, propoxy, phenoxy, methylsulfide and ethylsulfide. Other substituents R include olefins such as but not limited to olefinically unsaturated substituents including vinyl-terminated ligands, for example 3-butenyl, 2-propenyl, 5-hexenyl and the like. In one embodiment, at least two R groups, two adjacent R groups in one embodiment, are joined to form a ring structure having from 3 to 30 atoms selected from the group consisting of carbon, nitrogen, oxygen, phosphorous, silicon, germanium, aluminum, boron and combinations thereof. Also, a substituent group R group such as 1-butanyl may form a bonding association to the element M.

[0081] Each X in formula (VIII) is independently selected from the following: halogen ions, hydrides, $C_1$ to $C_{12}$ alkyls, $C_2$ to $C_{12}$ alkenyls, $C_6$ to $C_{12}$ aryls, $C_7$ to $C_{20}$ alkylaryls, $C_1$ to $C_{12}$ alkoxys, $C_6$ to $C_{16}$ aryloxys, $C_7$ to $C_{18}$ alkylaryloxys, $C_1$ to $C_{12}$ fluoroalkyls, $C_6$ to $C_{12}$ fluoroaryls, and $C_1$ to $C_{12}$ heteroatom-containing hydrocarbons and substituted derivatives

thereof in a more particular embodiment; hydride, halogen ions, $C_1$ to $C_6$ alkyls, $C_2$ to $C_6$ alkenyls, $C_7$ to $C_{18}$ alkylaryls, $C_1$ to $C_6$ alkoxys, $C_6$ to $C_{14}$ aryloxys, $C_7$ to $C_{16}$ alkylaryloxys, $C_1$ to $C_6$ alkylcarboxylates, $C_1$ to $C_6$ fluorinated alkylcarboxylates, $C_6$ to $C_{12}$ arylcarboxylates, $C_7$ to $C_{18}$ alkylarylcarboxylates, $C_1$ to $C_6$ fluoroalkyls, $C_2$ to $C_6$ fluoroalkenyls, and $C_7$ to $C_{18}$ fluoroalkylaryls in yet a more particular embodiment; hydride, chloride, fluoride, methyl, phenyl, phenoxy, benzoxy, tosyl, fluoromethyls and fluorophenyls in yet a more particular embodiment; $C_1$ to $C_{12}$ alkyls, $C_2$ to $C_{12}$ alkenyls, $C_6$ to $C_{12}$ aryls, $C_7$ to $C_{20}$ alkylaryls, substituted $C_1$ to $C_{12}$ alkyls, substituted $C_6$ to $C_{12}$ aryls, substituted $C_7$ to $C_{20}$ alkylaryls and $C_1$ to $C_{12}$ heteroatom-containing alkyls, $C_1$ to $C_{12}$ heteroatom-containing aryls and $C_1$ to $C_{12}$ heteroatom-containing alkylaryls in yet a more particular embodiment; chloride, fluoride, $C_1$ to $C_6$ alkyls, $C_2$ to $C_6$ alkenyls, $C_7$ to $C_{18}$ alkylaryls, halogenated $C_1$ to $C_6$ alkyls, halogenated $C_2$ to $C_6$ alkenyls, and halogenated $C_7$ to $C_{18}$ alkylaryls in yet a more particular embodiment; fluoride, methyl, ethyl, propyl, phenyl, methylphenyl, dimethylphenyl, trimethylphenyl, fluoromethyls (mono-, di- and trifluoromethyls) and fluorophenyls (mono-, di-, tri-, tetra- and pentafluorophenyls) in yet a more particular embodiment.

**[0082]** Other non-limiting examples of X groups in formula (VIII) include amines, phosphines, ethers, carboxylates, dienes, hydrocarbon radicals having from 1 to 20 carbon atoms, fluorinated hydrocarbon radicals (*e.g.*, $-C_6F_5$ (pentafluorophenyl)), fluorinated alkylcarboxylates (*e.g.*, $CF_3C(O)O^-$), hydrides and halogen ions and combinations thereof. Other examples of X ligands include alkyl groups such as cyclobutyl, cyclohexyl, methyl, heptyl, tolyl, trifluoromethyl, tetramethylene, pentamethylene, methylidene, methyoxy, ethyoxy, propoxy, phenoxy, bis(N-methylanilide), dimethylamide, dimethylphosphide radicals and the like. In one embodiment, two or more X's form a part of a fused ring or ring system.

**[0083]** In another aspect, the metallocene catalyst component includes those of formula (VIII) where $Cp^A$ and $Cp^B$ are bridged to each other by at least one bridging group, (A), such that the structure is represented by formula (IX):

**[0084]** $Cp^A(A)Cp^BMX_n$ (IX)

**[0085]** These bridged compounds represented by formula (IX) are known as "bridged metallocenes". $Cp^A$, $Cp^B$, M, X and n are as defined above for formula (VIII); and wherein each Cp ligand is chemically bonded to M, and (A) is chemically bonded to each Cp. Non-limiting examples of bridging group (A) include divalent hydrocarbon groups containing at

least one Group 13 to 16 atom, such as but not limited to at least one of a carbon, oxygen, nitrogen, silicon, aluminum, boron, germanium and tin atom and combinations thereof; wherein the heteroatom may also be $C_1$ to $C_{12}$ alkyl or aryl substituted to satisfy neutral valency. The bridging group (A) may also contain substituent groups R as defined above for formula (VIII) including halogen radicals and iron. More particular non-limiting examples of bridging group (A) are represented by $C_1$ to $C_6$ alkylenes, substituted $C_1$ to $C_6$ alkylenes, oxygen, sulfur, $R'_2C=$, $R'_2Si=$, $-Si(R')_2Si(R'_2)-$, $R'_2Ge=$, $R'P=$ (wherein "=" represents two chemical bonds), where R' is independently selected from the group consisting of hydride, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted Group 15 atoms, substituted Group 16 atoms, and halogen radical; and wherein two or more R' may be joined to form a ring or ring system. In one embodiment, the bridged metallocene catalyst component of formula (IX) has two or more bridging groups (A).

[0086] Other non-limiting examples of bridging group (A) include methylene, ethylene, ethylidene, propylidene, isopropylidene, diphenylmethylene, 1,2-dimethylethylene, 1,2-diphenylethylene, 1,1,2,2-tetramethylethylene, dimethylsilyl, diethylsilyl, methyl-ethylsilyl, trifluoromethylbutylsilyl, bis(trifluoromethyl)silyl, di(n-butyl)silyl, di(n-propyl)silyl, di(i-propyl)silyl, di(n-hexyl)silyl, dicyclohexylsilyl, diphenylsilyl, cyclohexylphenylsilyl, t-butylcyclohexylsilyl, di(t-butylphenyl)silyl, di(p-tolyl)silyl and the corresponding moieties wherein the Si atom is replaced by a Ge or a C atom; dimethylsilyl, diethylsilyl, dimethylgermyl and diethylgermyl.

[0087] In another embodiment, bridging group (A) may also be cyclic, comprising, for example 4 to 10, 5 to 7 ring members in a more particular embodiment. The ring members may be selected from the elements mentioned above, from one or more of B, C, Si, Ge, N and O in a particular embodiment. Non-limiting examples of ring structures which may be present as or part of the bridging moiety are cyclobutylidene, cyclopentylidene, cyclohexylidene, cycloheptylidene, cyclooctylidene and the corresponding rings where one or two carbon atoms are replaced by at least one of Si, Ge, N and O, in particular, Si and Ge. The bonding arrangement between the ring and the Cp groups may be either cis-, trans-, or a combination.

[0088] The cyclic bridging groups (A) may be saturated or unsaturated and/or carry one or more substituents and/or be fused to one or more other ring structures. If present, the one or

more substituents are selected from the group consisting of hydrocarbyl (*e.g.*, alkyl such as methyl) and halogen (*e.g.*, F, Cl) in one embodiment. The one or more Cp groups which the above cyclic bridging moieties may optionally be fused to may be saturated or unsaturated and are selected from the group consisting of those having 4 to 10, more particularly 5, 6 or 7 ring members (selected from the group consisting of C, N, O and S in a particular embodiment) such as, for example, cyclopentyl, cyclohexyl and phenyl. Moreover, these ring structures may themselves be fused such as, for example, in the case of a naphthyl group. Moreover, these (optionally fused) ring structures may carry one or more substituents. Illustrative, non-limiting examples of these substituents are hydrocarbyl (particularly alkyl) groups and halogen atoms.

**[0089]** The ligands $Cp^A$ and $Cp^B$ of formula (VIII) and (IX) are different from each other in one embodiment, and the same in another embodiment.

**[0090]** In yet another aspect, the metallocene catalyst components include mono-ligand metallocene compounds (*e.g.*, mono cyclopentadienyl catalyst components) such as described in WO 93/08221 for example. In this embodiment, the at least one metallocene catalyst component is a bridged "half-sandwich" metallocene represented by the formula (X):

**[0091]** $Cp^A(A)QMX_n$ (X)

**[0092]** wherein $Cp^A$ is defined above and is bound to M; (A) is a bridging group bonded to Q and $Cp^A$; and wherein an atom from the Q group is bonded to M; and n is 0 or an integer from 1 to 3; 1 or 2 in a particular embodiment. In formula (X), $Cp^A$, (A) and Q may form a fused ring system. The X groups and n of formula (X) are as defined above in formula (VIII) and (IX). In one embodiment, $Cp^A$ is selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, substituted versions thereof, and combinations thereof.

**[0093]** In formula (X), Q is a heteroatom-containing ligand in which the bonding atom (the atom that is bonded with the metal M) is selected from the group consisting of Group 15 atoms and Group 16 atoms in one embodiment, and selected from the group consisting of nitrogen, phosphorus, oxygen or sulfur atom in a more particular embodiment, and nitrogen and oxygen in yet a more particular embodiment. Non-limiting examples of Q groups include alkylamines, arylamines, mercapto compounds, ethoxy compounds, carboxylates (*e.g.*, pivalate), carbamates, azenyl, azulene, pentalene, phosphoyl, phosphinimine, pyrrolyl, pyrozolyl,

carbazolyl, borabenzene other compounds comprising Group 15 and Group 16 atoms capable of bonding with M.

**[0094]** In yet another aspect, the at least one metallocene catalyst component is an unbridged "half sandwich" metallocene represented by the formula (XI):

**[0095]** $Cp^AMQ_qX_n$ (XI)

**[0096]** wherein $Cp^A$ is defined as for the Cp groups in (VIII) and is a ligand that is bonded to M; each Q is independently bonded to M; Q is also bound to $Cp^A$ in one embodiment; X is a leaving group as described above in (VIII); n ranges from 0 to 3, and is 1 or 2 in one embodiment; q ranges from 0 to 3, and is 1 or 2 in one embodiment. In one embodiment, $Cp^A$ is selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, substituted version thereof, and combinations thereof.

**[0097]** In formula (XI), Q is selected from the group consisting of $ROO^-$, RO–, R(O)–, –NR–, $–CR_2–$, –S–, $–NR_2$, $–CR_3$, –SR, $–SiR_3$, $–PR_2$, –H, and substituted and unsubstituted aryl groups, wherein R is selected from the group consisting of $C_1$ to $C_6$ alkyls, $C_6$ to $C_{12}$ aryls, $C_1$ to $C_6$ alkylamines, $C_6$ to $C_{12}$ alkylarylamines, $C_1$ to $C_6$ alkoxys, $C_6$ to $C_{12}$ aryloxys, and the like. Non-limiting examples of Q include $C_1$ to $C_{12}$ carbamates, $C_1$ to $C_{12}$ carboxylates (*e.g.*, pivalate), $C_2$ to $C_{20}$ allyls, and $C_2$ to $C_{20}$ heteroallyl moieties.

**[0098]** Described another way, the "half sandwich" metallocenes above can be described for example, US 6,069,213:

**[0099]** $Cp^AM(Q_2GZ)X_n$ or $T(Cp^AM(Q_2GZ)X_n)_m$ (XII)

**[00100]** wherein M, $Cp^A$, X and n are as defined above;

**[00101]** $Q_2GZ$ forms a polydentate ligand unit (*e.g.*, pivalate), wherein at least one of the Q groups form a bond with M, and is defined such that each Q is independently selected from the group consisting of –O–, –NR–, $–CR_2—$ and –S–; G is either carbon or silicon; and Z is selected from the group consisting of R, –OR, $–NR_2$, $–CR_3$, –SR, $–SiR_3$, $–PR_2$, and hydride, providing that when Q is –NR–, then Z is selected from the group consisting of –OR, $–NR_2$, –SR, $–SiR_3$, $–PR_2$; and provided that neutral valency for Q is satisfied by Z; and wherein each R is independently selected from the group consisting of $C_1$ to $C_{10}$ heteroatom containing groups, $C_1$ to $C_{10}$ alkyls, $C_6$ to $C_{12}$ aryls, $C_6$ to $C_{12}$ alkylaryls, $C_1$ to $C_{10}$ alkoxys, and $C_6$ to $C_{12}$ aryloxys;

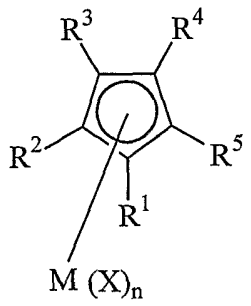
[00102] n is 1 or 2 in a particular embodiment; and

[00103] T is a bridging group selected from the group consisting of $C_1$ to $C_{10}$ alkylenes, $C_6$ to $C_{12}$ arylenes and $C_1$ to $C_{10}$ heteroatom containing groups, and $C_6$ to $C_{12}$ heterocyclic groups; wherein each T group bridges adjacent "$Cp^AM(Q_2GZ)X_n$" groups, and is chemically bonded to the $Cp^A$ groups.

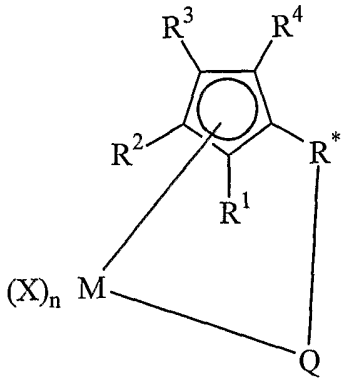
[00104] m is an integer from 1 to 7; m is an integer from 2 to 6 in a more particular embodiment.

[00105] In another aspect, the at least one metallocene catalyst component can be described more particularly in structures (XIIIa), (XIIIb), (XIIIc), (XIIId), (XIIIe), and (XIIIf):

[00106]



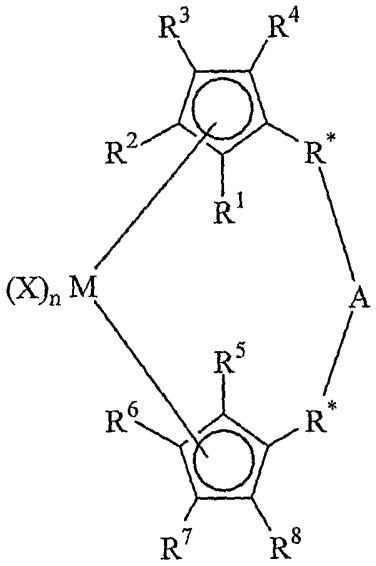

(XIIIa-i)




(XIIIa-ii)

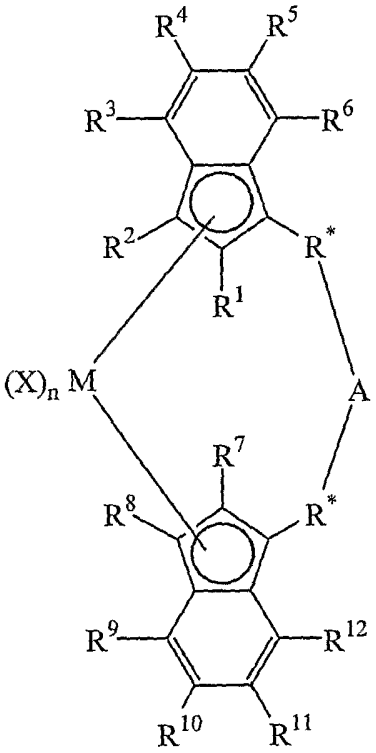
[00107]

[00108]



[00109] (XIIIb)

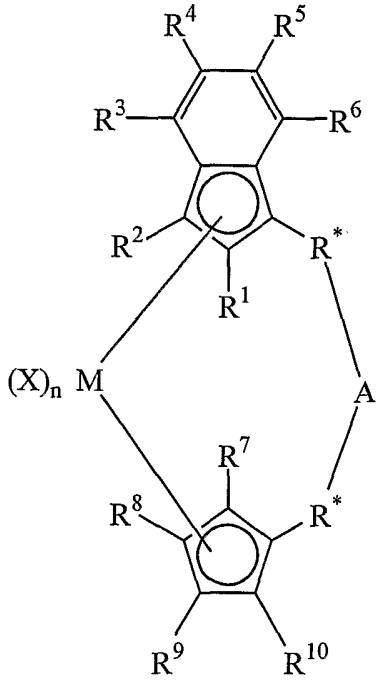
[00110]



[00111]

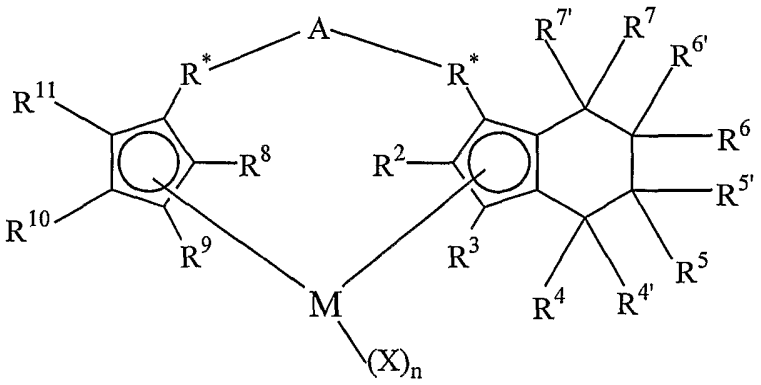
[00112] (XIIIc)

[00113]



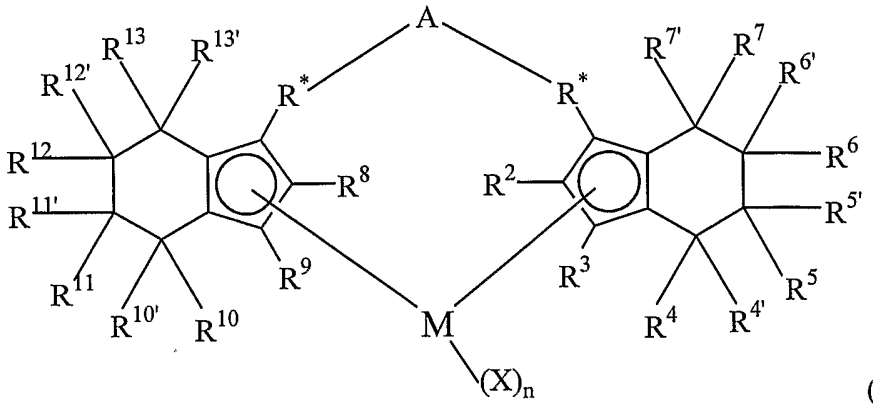
[00114] (XIIId)

[00115]



[00116] (XIIIe)

[00117]



[00118] (XIIIf)

[00119] wherein in structures (XIIIa) to (XIIIf), M is selected from the group consisting of Group 3 to Group 12 atoms, and selected from the group consisting of Group 3 to Group 10 atoms in a more particular embodiment, and selected from the group consisting of Group 3 to Group 6 atoms in yet a more particular embodiment, and selected from the group consisting of Group 4 atoms in yet a more particular embodiment, and selected from the group consisting of Zr and Hf in yet a more particular embodiment; and is Zr in yet a more particular embodiment;

[00120] wherein Q in (XIIIa) to (XIIIf) is selected from the group consisting of alkylenes, aryls, arylenes, alkoxys, aryloxys, amines, arylamines (*e.g.*, pyridyl) alkylamines, phosphines, alkylphosphines, substituted alkyls, substituted aryls, substituted alkoxys, substituted aryloxys, substituted amines, substituted alkylamines, substituted phosphines, substituted alkylphosphines, carbamates, heteroallyls, carboxylates (non-limiting examples of suitable carbamates and carboxylates include trimethylacetate, trimethylacetate, methylacetate, p-toluate, benzoate, diethylcarbamate, and dimethylcarbamate), fluorinated alkyls, fluorinated aryls, and fluorinated alkylcarboxylates; wherein the saturated groups defining Q comprise from 1 to 20 carbon atoms in one embodiment; and wherein the aromatic groups comprise from 5 to 20 carbon atoms in one embodiment;

[00121] wherein each $R^*$ is independently: selected from the group consisting of hydrocarbylenes and heteroatom-containing hydrocarbylenes in one embodiment; and selected from the group consisting of alkylenes, substituted alkylenes and heteroatom-containing hydrocarbylenes in another embodiment; and selected from the group consisting of $C_1$ to $C_{12}$ alkylenes, $C_1$ to $C_{12}$ substituted alkylenes, and $C_1$ to $C_{12}$ heteroatom-containing hydrocarbylenes in a more particular embodiment; and selected from the group consisting of $C_1$

to $C_4$ alkylenes in yet a more particular embodiment; and wherein both R* groups are identical in another embodiment in structures (XIIIf);

**[00122]** A is as described above for (A) in structure (IX), and more particularly, selected from the group consisting of a chemical bond, –O–, –S–, $–SO_2–$, –NR–, $=SiR_2$, $=GeR_2$, $=SnR_2$, $—R_2SiSiR_2—$, RP=, $C_1$ to $C_{12}$ alkylenes, substituted $C_1$ to $C_{12}$ alkylenes, divalent $C_4$ to $C_{12}$ cyclic hydrocarbons and substituted and unsubstituted aryl groups in one embodiment; and selected from the group consisting of $C_5$ to $C_8$ cyclic hydrocarbons, $–CH_2CH_2–$, $=CR_2$ and $=SiR_2$ in a more particular embodiment; wherein and R is selected from the group consisting of alkyls, cycloalkyls, aryls, alkoxys, fluoroalkyls and heteroatom-containing hydrocarbons in one embodiment; and R is selected from the group consisting of $C_1$ to $C_6$ alkyls, substituted phenyls, phenyl, and $C_1$ to $C_6$ alkoxys in a more particular embodiment; and R is selected from the group consisting of methoxy, methyl, phenoxy, and phenyl in yet a more particular embodiment;

**[00123]** wherein A may be absent in yet another embodiment, in which case each R* is defined as for $R^1$-$R^{13}$;

**[00124]** each X is as described above in (VIII);

**[00125]** n is an integer from 0 to 4, and from 1 to 3 in another embodiment, and 1 or 2 in yet another embodiment; and

**[00126]** $R^1$ through $R^{13}$ are independently: selected from the group consisting of hydrogen radical, halogen radicals, $C_1$ to $C_{12}$ alkyls, $C_2$ to $C_{12}$ alkenyls, $C_6$ to $C_{12}$ aryls, $C_7$ to $C_{20}$ alkylaryls, $C_1$ to $C_{12}$ alkoxys, $C_1$ to $C_{12}$ fluoroalkyls, $C_6$ to $C_{12}$ fluoroaryls, and $C_1$ to $C_{12}$ heteroatom-containing hydrocarbons and substituted derivatives thereof in one embodiment; selected from the group consisting of hydrogen radical, fluorine radical, chlorine radical, bromine radical, $C_1$ to $C_6$ alkyls, $C_2$ to $C_6$ alkenyls, $C_7$ to $C_{18}$ alkylaryls, $C_1$ to $C_6$ fluoroalkyls, $C_2$ to $C_6$ fluoroalkenyls, $C_7$ to $C_{18}$ fluoroalkylaryls in a more particular embodiment; and hydrogen radical, fluorine radical, chlorine radical, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary butyl, hexyl, phenyl, 2,6-di-methylpheyl, and 4-tertiarybutylpheyl groups in yet a more particular embodiment; wherein adjacent R groups may form a ring, either saturated, partially saturated, or completely saturated.

[00127] The structure of the metallocene catalyst component represented by (XIIIa) may take on many forms such as disclosed in, for example, US 5,026,798, US 5,703,187, and US 5,747,406, including a dimmer or oligomeric structure, such as disclosed in, for example, US 5,026,798 and US 6,069,213.

[00128] In a particular embodiment of the metallocene represented in (XIIId), $R^1$ and $R^2$ form a conjugated 6-membered carbon ring system that may or may not be substituted.

[00129] Non-limiting examples of metallocene catalyst components consistent with the description herein include:

[00130] cyclopentadienylzirconium $X_n$,

[00131] indenylzirconium $X_n$,

[00132] (1-methylindenyl)zirconium $X_n$,

[00133] (2-methylindenyl)zirconium $X_n$,

[00134] (1-propylindenyl)zirconium $X_n$,

[00135] (2-propylindenyl)zirconium $X_n$,

[00136] (1-butylindenyl)zirconium $X_n$,

[00137] (2-butylindenyl)zirconium $X_n$,

[00138] (methylcyclopentadienyl)zirconium $X_n$,

[00139] tetrahydroindenylzirconium $X_n$,

[00140] (pentamethylcyclopentadienyl)zirconium $X_n$,

[00141] cyclopentadienylzirconium $X_n$,

[00142] pentamethylcyclopentadienyltitanium $X_n$,

[00143] tetramethylcyclopentyltitanium $X_n$,

[00144] 1,2,4-trimethylcyclopentadienylzirconium $X_n$,

[00145] dimethylsilyl(1,2,3,4-tetramethylcyclopentadienyl)(cyclopentadienyl)zirconium $X_n$,

[00146] dimethylsilyl(1,2,3,4-tetramethylcyclopentadienyl)(1,2,3-trimethyl-cyclopentadienyl)zirconium $X_n$,

[00147] dimethylsilyl(1,2,3,4-tetramethylcyclopentadienyl)(1,2-dimethyl-cyclopentadienyl)zirconium $X_n$,

[00148] dimethylsilyl(1,2,3,4-tetramethyl-cyclopentadienyl)(2-methylcyclopentadienyl)zirconium $X_n$,

[00149] dimethylsilyl(cyclopentadienyl)(indenyl)zirconium $X_n$,

[00150] dimethylsilyl(2-methylindenyl)(fluorenyl)zirconium $X_n$,

[00151] diphenylsilyl(1,2,3,4-tetramethyl-cyclopentadienyl)(3-propylcyclopentadienyl)zirconium $X_n$,

[00152] dimethylsilyl(1,2,3,4-tetramethylcyclopentadienyl)(3-t-butylcyclopentadienyl)zirconium $X_n$,

[00153] dimethylgermyl(1,2-dimethylcyclopentadienyl)(3-isopropylcyclopentadienyl)zirconium $X_n$,

[00154] dimethylsilyl(1,2,3,4-tetramethyl-cyclopentadienyl)(3-methylcyclopentadienyl) zirconium $X_n$,

[00155] diphenylmethylidene(cyclopentadienyl)(9-fluorenyl)zirconium $X_n$,

[00156] diphenylmethylidene(cyclopentadienyl)(indenyl)zirconium $X_n$,

[00157] iso-propylidenebis(cyclopentadienyl)zirconium $X_n$,

[00158] iso-propylidene(cyclopentadienyl)(9-fluorenyl)zirconium $X_n$,

[00159] iso-propylidene(3-methylcyclopentadienyl)(9-fluorenyl)zirconium $X_n$,

[00160] ethylenebis(9-fluorenyl)zirconium $X_n$,

[00161] meso-ethylenebis(1-indenyl)zirconium $X_n$,

[00162] ethylenebis(1-indenyl)zirconium $X_n$,

[00163] ethylenebis(2-methyl-1-indenyl)zirconium $X_n$,

[00164] ethylenebis(2-methyl-4,5,6,7-tetrahydro-1-indenyl)zirconium $X_n$,

[00165] ethylenebis(2-propyl-4,5,6,7-tetrahydro-1-indenyl)zirconium $X_n$,

[00166] ethylenebis(2-isopropyl-4,5,6,7-tetrahydro-1-indenyl)zirconium $X_n$,

[00167] ethylenebis(2-butyl-4,5,6,7-tetrahydro-1-indenyl)zirconium $X_n$,

[00168] ethylenebis(2-isobutyl-4,5,6,7-tetrahydro-1-indenyl)zirconium $X_n$,

[00169] dimethylsilyl(4,5,6,7-tetrahydro-1-indenyl)zirconium $X_n$,

[00170] diphenyl(4,5,6,7-tetrahydro-1-indenyl)zirconium $X_n$,

[00171] ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium $X_n$,

[00172] dimethylsilylbis(cyclopentadienyl)zirconium $X_n$,

[00173] dimethylsilylbis(9-fluorenyl)zirconium $X_n$,

[00174] dimethylsilylbis(1-indenyl)zirconium $X_n$,

[00175] dimethylsilylbis(2-methylindenyl)zirconium $X_n$,

[00176] dimethylsilylbis(2-propylindenyl)zirconium $X_n$,

[00177] dimethylsilylbis(2-butylindenyl)zirconium $X_n$,

[00178] diphenylsilylbis(2-methylindenyl)zirconium $X_n$,

[00179] diphenylsilylbis(2-propylindenyl)zirconium $X_n$,

[00180] diphenylsilylbis(2-butylindenyl)zirconium $X_n$,

[00181] dimethylgermylbis(2-methylindenyl)zirconium $X_n$

[00182] dimethylsilylbis(tetrahydroindenyl)zirconium $X_n$,

[00183] dimethylsilylbis(tetramethylcyclopentadienyl)zirconium $X_n$,

[00184] dimethylsilyl(cyclopentadienyl)(9-fluorenyl)zirconium $X_n$,

[00185] diphenylsilyl(cyclopentadienyl)(9-fluorenyl)zirconium $X_n$,

[00186] diphenylsilylbis(indenyl)zirconium $X_n$,

[00187] cyclotrimethylenesilyl(tetramethylcyclopentadienyl)(cyclopentadienyl)zirconium $X_n$,

[00188] cyclotetramethylenesilyl(tetramethylcyclopentadienyl)(cyclopentadienyl) zirconium $X_n$,

[00189] cyclotrimethylenesilyl(tetramethylcyclopentadienyl)(2-methylindenyl)zirconium $X_n$,

[00190] cyclotrimethylenesilyl(tetramethylcyclopentadienyl)(3-methylcyclopentadienyl)zirconium $X_n$,

[00191] cyclotrimethylenesilylbis(2-methylindenyl)zirconium $X_n$,

[00192] cyclotrimethylenesilyl(tetramethylcyclopentadienyl)(2,3,5-trimethylcyclopentadienyl)zirconium $X_n$,

[00193] cyclotrimethylenesilylbis(tetramethylcyclopentadienyl)zirconium $X_n$,

[00194] dimethylsilyl(tetramethylcyclopentadieneyl)(N-tert-butylamido)titanium $X_n$,

[00195] bis(cyclopentadienyl)chromium $X_n$,

[00196] bis(cyclopentadienyl)zirconium $X_n$,

[00197] bis(n-butylcyclopentadienyl)zirconium $X_n$,

[00198] bis(n-dodecyclcyclopentadienyl)zirconium $X_n$,

[00199] bis(ethylcyclopentadienyl)zirconium $X_n$,

[00200] bis(iso-butylcyclopentadienyl)zirconium $X_n$,

[00201] bis(iso-propylcyclopentadienyl)zirconium $X_n$,

[00202] bis(methylcyclopentadienyl)zirconium $X_n$,

[00203] bis(n-oxtylcyclopentadienyl)zirconium $X_n$,

[00204] bis(n-pentylcyclopentadienyl)zirconium $X_n$,

[00205] bis(n-propylcyclopentadienyl)zirconium $X_n$,

[00206] bis(trimethylsilylcyclopentadienyl)zirconium $X_n$,

[00207] bis(1,3-bis(trimethylsilyl)cyclopentadienyl)zirconium $X_n$,

[00208] bis(1-ethyl-2-methylcyclopentadienyl)zirconium $X_n$,

[00209] bis(1-ethyl-3-methylcyclopentadienyl)zirconium $X_n$,

[00210] bis(pentamethylcyclopentadienyl)zirconium $X_n$,

[00211] bis(pentamethylcyclopentadienyl)zirconium $X_n$,

[00212] bis(1-propyl-3-methylcyclopentadienyl)zirconium $X_n$,

[00213] bis(1-n-butyl-3-methylcyclopentadienyl)zirconium $X_n$,

[00214] bis(1-isobutyl-3-methylcyclopentadienyl)zirconium $X_n$,

[00215] bis(1-propyl-3-butylcyclopentadienyl)zirconium $X_n$,

[00216] bis(1,3-n-butylcyclopentadienyl)zirconium $X_n$,

[00217] bis(4,7-dimethylindenyl)zirconium $X_n$,

[00218] bis(indenyl)zirconium $X_n$,

[00219] bis(2-methylindenyl)zirconium $X_n$,

[00220] cyclopentadienylindenylzirconium $X_n$,

[00221] bis(n-propylcyclopentadienyl)hafnium $X_n$,

[00222] bis(n-butylcyclopentadienyl)hafnium $X_n$,

[00223] bis(n-pentylcyclopentadienyl)hafnium $X_n$,

[00224] (n-propyl cyclopentadienyl)(n-butyl cyclopentadienyl)hafnium $X_n$,

[00225] bis[(2-trimethylsilylethyl)cyclopentadienyl]hafnium $X_n$,

[00226] bis(trimethylsilyl cyclopentadienyl)hafnium $X_n$,

[00227] bis(2-n-propylindenyl)hafnium $X_n$,

[00228] bis(2-n-butylindenyl)hafnium $X_n$,

[00229] dimethylsilylbis(n-propylcyclopentadienyl)hafnium $X_n$,

[00230] dimethylsilylbis(n-butylcyclopentadienyl)hafnium $X_n$,

[00231] bis(9-n-propylfluorenyl)hafnium $X_n$,

[00232] bis(9-n-butylfluorenyl)hafnium $X_n$,

[00233] (9-n-propylfluorenyl)(2-n-propylindenyl)hafnium $X_n$,

[00234] bis(1-n-propyl-2-methylcyclopentadienyl)hafnium $X_n$,

[00235] (n-propylcyclopentadienyl)(1-n-propyl-3-n-butylcyclopentadienyl)hafnium $X_n$,

[00236] dimethylsilyl(tetramethylcyclopentadienyl)(cyclopropylamido)titanium $X_n$,

[00237] dimethylsilyl(tetramethyleyclopentadienyl)(cyclobutylamido)titanium $X_n$,

[00238] dimethylsilyl(tetramethyleyclopentadienyl)(cyclopentylamido)titanium $X_n$,

[00239] dimethylsilyl(tetramethylcyclopentadienyl)(cyclohexylamido)titanium $X_n$,

[00240] dimethylsilyl(tetramethylcyclopentadienyl)(cycloheptylamido)titanium $X_n$,

[00241] dimethylsilyl(tetramethylcyclopentadienyl)(cyclooctylamido)titanium $X_n$,

[00242] dimethylsilyl(tetramethylcyclopentadienyl)(cyclononylamido)titanium $X_n$,

[00243] dimethylsilyl(tetramethylcyclopentadienyl)(cyclodecylamido)titanium $X_n$,

[00244] dimethylsilyl(tetramethylcyclopentadienyl)(cycloundecylamido)titanium $X_n$,

[00245] dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium $X_n$,

[00246] dimethylsilyl(tetramethylcyclopentadienyl)(sec-butylamido)titanium $X_n$,

[00247] dimethylsilyl(tetramethylcyclopentadienyl)(n-octylamido)titanium $X_n$,

[00248] dimethylsilyl(tetramethylcyclopentadienyl)(n-decylamido)titanium $X_n$,

[00249] dimethylsilyl(tetramethylcyclopentadienyl)(n-octadecylamido)titanium $X_n$,

[00250] methylphenylsilyl(tetramethylcyclopentadienyl)(cyclopropylamido)titanium $X_n$,

[00251] methylphenylsilyl(tetramethylcyclopentadienyl)(cyclobutylamido)titanium $X_n$,

[00252] methylphenylsilyl(tetramethylcyclopentadienyl)(cyclopentylamido)titanium $X_n$,

[00253] methylphenylsilyl(tetramethylcyclopentadienyl)(cyclohexylamido)titanium $X_n$,

[00254] methylphenylsilyl(tetramethylcyclopentadienyl)(cycloheptylamido)titanium $X_n$,

[00255] methylphenylsilyl(tetramethylcyclopentadienyl)(cyclooctylamido)titanium $X_n$,

[00256] methylphenylsilyl(tetramethylcyclopentadienyl)(cyclononylamido)titanium $X_n$,

[00257] methylphenylsilyl(tetramethylcyclopentadienyl)(cyclodecylamido)titanium, $X_n$,

[00258] methylphenylsilyl(tetramethylcyclopentadienyl)(cycloundecylamido)titanium $X_n$,

[00259] methylphenylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium $X_n$,

[00260] methylphenylsilyl(tetramethylcyclopentadienyl)(sec-butylamido)titanium $X_n$,

[00261] methylphenylsilyl(tetramethylcyclopentadienyl)(n-octylamido)titanium $X_n$,

[00262] methylphenylsilyl(tetramethylcyclopentadienyl)(n-decylamido)titanium $X_n$,

[00263] methylphenylsilyl(tetramethylcyclopentadienyl)(n-octadecylamido)titanium $X_n$,

[00264] diphenylsilyl(tetramethylcyclopentadienyl)(cyclopropylamido)titanium $X_n$,

[00265] diphenylsilyl(tetramethylcyclopentadienyl)(cyclobutylamido)titanium $X_n$,

[00266] diphenylsilyl(tetramethylcyclopentadienyl)(cyclopentylamido)titanium $X_n$,

[00267] diphenylsilyl(tetramethylcyclopentadienyl)(cyclohexylamido)titanium $X_n$,

[00268] diphenylsilyl(tetramethylcyclopentadienyl)(cycloheptylamido)titanium $X_n$,

[00269] diphenylsilyl(tetramethylcyclopentadienyl)(cyclooctylamido)titanium $X_n$,

[00270] diphenylsilyl(tetramethylcyclopentadienyl)(cyclononylamido)titanium $X_n$,

[00271] diphenylsilyl(tetramethylcyclopentadienyl)(cyclodecylamido)titanium $X_n$,

[00272] diphenylsilyl(tetramethylcyclopentadienyl)(cycloundecylamido)titanium $X_n$,

[00273] diphenylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium $X_n$,

[00274] diphenylsilyl(tetramethylcyclopentadienyl)(sec-butylamido)titanium $X_n$,

[00275] diphenylsilyl(tetramethyleyclopentadienyl)(n-octylamido)titanium $X_n$,

[00276] diphenylsilyl(tetramethyleyclopentadienyl)(n-decylamido)titanium $X_n$,

[00277] diphenylsilyl(tetramethylcyclopentadienyl)(n-octadecylamido)titanium $X_n$,

[00278] and derivatives thereof.

[00279] By "derivatives thereof", it is meant any substitution or ring formation as described above; and in particular, replacement of the metal "M" (Cr, Zr, Ti or Hf) with an atom selected from the group consisting of Cr, Zr, Hf and Ti; and replacement of the "X" group with any of $C_1$ to $C_5$ alkyls, $C_6$ aryls, $C_6$ to $C_{10}$ alkylaryls, fluorine or chlorine; n is 1, 2 or 3.

[00280] It is contemplated that the metallocene catalysts components described above include their structural or optical or enantiomeric isomers (racemic mixture), and may be a pure enantiomer in one embodiment.

[00281] As used herein, a single, bridged, asymmetrically substituted metallocene catalyst component having a racemic and/or meso isomer does not, itself, constitute at least two different bridged, metallocene catalyst components.

[00282] The "metallocene catalyst component" may comprise any combination of any "embodiment" described herein.

**Activators**

[00283] The catalyst system may also include one or more activators. As used herein, the term "activator" is defined to be any compound or combination of compounds, supported or unsupported, which can activate a single-site catalyst compound (*e.g.*, metallocenes, non-metallocenes, etc.), such as by creating a cationic species from the catalyst component.

[00284] In certain embodiments, either or both of the catalyst components may be contacted with a catalyst activator, herein simply referred to as an "activator." Typically, this involves the abstraction of at least one leaving group (X group in the formulas/structures above) from the metal center of the catalyst component. The catalyst components of the present invention are thus activated towards olefin polymerization using such activators. Embodiments of such activators include Lewis acids such as cyclic or oligomeric poly(hydrocarbylaluminum oxides) and so called non-coordinating activators ("NCA") (alternately, "ionizing activators" or "stoichiometric activators"), or any other compound that can convert a neutral metallocene catalyst component to a metallocene cation that is active with respect to olefin polymerization.

[00285] More particularly, it is within the scope of this invention to use Lewis acids such as alumoxane (*e.g.*, "MAO"), modified alumoxane (e.g., "TIBAO"), and alkylaluminum compounds as activators, and/or ionizing activators (neutral or ionic) such as tri (n-butyl)ammonium tetrakis(pentafluorophenyl)boron and/or a trisperfluorophenyl boron metalloid precursors to activate desirable metallocenes described herein. MAO and other aluminum-based activators are well known in the art. Ionizing activators are well known in the art and are described by, for example, Eugene You-Xian Chen & Tobin J. Marks, *Cocatalysts for Metal-Catalyzed Olefin Polymerization: Activators, Activation Processes, and Structure-Activity Relationships* 100(4) CHEMICAL REVIEWS 1391-1434 (2000). The activators may be associated with or bound to a support, either in association with the catalyst component (*e.g.*, metallocene) or separate from the catalyst component, such as described by Gregory G. Hlatky, *Heterogeneous Single-Site Catalysts for Olefin Polymerization* 100(4) CHEMICAL REVIEWS 1347-1374 (2000).

[00286] The aluminum alkyl ("alkylaluminum") activator may be described by the formula $AlR^{\S}_3$, wherein $R^{\S}$ is selected from the group consisting of $C_1$ to $C_{20}$ alkyls, $C_1$ to $C_{20}$ alkoxys, halogen (chlorine, fluorine, bromine) $C_6$ to $C_{20}$ aryls, $C_7$ to $C_{25}$ alkylaryls, and $C_7$ to $C_{25}$ arylalkyls. Non-limiting examples of aluminum alkyl compounds which may be utilized as activators for the catalyst precursor compounds for use in the methods of the present invention include trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum and the like.

[00287] Examples of neutral ionizing activators include Group 13 tri-substituted compounds, in particular, tri-substituted boron, tellurium, aluminum, gallium and indium compounds, and mixtures thereof. The three substituent groups are each independently selected from alkyls, alkenyls, halogen, substituted alkyls, aryls, arylhalides, alkoxy and halides. In one embodiment, the three groups are independently selected from halogen, mono or multicyclic (including halosubstituted) aryls, alkyls, and alkenyl compounds and mixtures thereof. In another embodiment, the three groups are selected from alkenyl groups having 1 to 20 carbon atoms, alkyl groups having 1 to 20 carbon atoms, alkoxy groups having 1 to 20 carbon atoms and aryl groups having 3 to 20 carbon atoms (including substituted aryls), and combinations thereof. In yet another embodiment, the three groups are selected from alkyls having 1 to 4 carbon groups, phenyl, naphthyl and mixtures thereof. In yet another embodiment, the three groups are selected from highly halogenated alkyls having 1 to 4 carbon groups, highly halogenated phenyls, and highly halogenated naphthyls and mixtures thereof By "highly halogenated", it is meant that at least 50% of the hydrogens are replaced by a halogen group selected from fluorine, chlorine and bromine. In yet another embodiment, the neutral stoichiometric activator is a tri-substituted Group 13 compound comprising highly fluorided aryl groups, the groups being highly fluorided phenyl and highly fluorided naphthyl groups.

[00288] In another embodiment, the neutral tri-substituted Group 13 compounds are boron compounds such as a trisperfluorophenyl boron, trisperfluoronaphthyl boron, tris(3,5-di(trifluoromethyl)phenyl)boron, tris(di-t-butylmethylsilyl)perfluorophenylboron, and other highly fluorinated trisarylboron compounds and combinations thereof, and their aluminum equivalents. Other suitable neutral ionizing activators are described in US 6,399,532 B1, US 6,268,445 B1, and in 19 ORGANOMETALLICS 3332-3337 (2000), and in 17 ORGANOMETALLICS 3996-4003 (1998).

[00289] Illustrative, not limiting examples of ionic ionizing activators include trialkyl-substituted ammonium salts such as triethylammonium tetra(phenyl)boron, tripropylammonium tetra(phenyl)boron, tri(n-butyl)ammonium tetra(phenyl)boron, trimethylammonium tetra(p-tolyl)boron, trimethylammonium tetra(o-tolyl)boron, tributylammonium tetra(pentafluorophenyl)boron, tripropylammonium tetra(o,p-dimethylphenyl)boron, tributylammonium tetra(m,m-dimethylphenyl)boron, tributylammonium tetra(p-trifluoromethylphenyl)boron, tributylammonium tetra(pentafluorophenyl)boron, tri(n-butyl)ammonium tetra(o-tolyl)boron and the like; N,N-dialkyl anilinium salts such as N,N-dimethylanilinium tetra(phenyl)boron, N,N-diethylanilinium tetra(phenyl)boron, N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron and the like; dialkyl ammonium salts such as di-(isopropyl)ammonium tetra(pentafluorophenyl)boron, dicyclohexylammonium tetra(phenyl)boron and the like; triaryl carbonium salts (trityl salts) such as triphenylcarbonium tetra(phenyl)boron and triphenylcarbonium tetra(pentafluorophenyl)boron; and triaryl phosphonium salts such as triphenylphosphonium tetra(phenyl)boron, triphenylphosphonium tetra(pentafluorophenyl)boron, tri(methylphenyl)phosphonium tetra(phenyl)boron, tri(dimethylphenyl)phosphonium tetra(phenyl)boron and the like, and their aluminum equivalents.

[00290] In yet another embodiment of the activator of the invention, an alkylaluminum can be used in conjunction with a heterocyclic compound. The heterocyclic compound includes at least one nitrogen, oxygen, and/or sulfur atom, and includes at least one nitrogen atom in a particular embodiment. The heterocyclic compound includes 4 or more ring members in one embodiment, and 5 or more ring members in another embodiment.

[00291] The heterocyclic compound for use as an activator with an alkylaluminum may be unsubstituted or substituted with one or a combination of substituent groups. Examples of suitable substituents include halogen, alkyl, alkenyl or alkynyl radicals, cycloalkyl radicals, aryl radicals, aryl substituted alkyl radicals, acyl radicals, aroyl radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals, dialkylamino radicals, alkoxycarbonyl radicals, aryloxycarbonyl radicals, carbomoyl radicals, alkyl- or dialkyl- carbamoyl radicals, acyloxy radicals, acylamino radicals, aroylamino radicals, straight, branched or cyclic, alkylene radicals, or any combination thereof. The substituents groups may also be substituted with halogens, particularly fluorine or bromine, heteroatoms or the like.

[00292] Non-limiting examples of hydrocarbon substituents include methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl or phenyl groups and the like, including all their isomers, for example tertiary butyl, isopropyl, and the like. Other examples of substituents include fluoromethyl, fluoroethyl, difluoroethyl, iodopropyl, bromohexyl or chlorobenzyl.

[00293] In one embodiment, the heterocyclic compound is unsubstituted. In another embodiment one or more positions on the heterocyclic compound are substituted with a halogen atom or a halogen atom containing group, for example a halogenated aryl group. In one embodiment the halogen is selected from chlorine, bromine and fluorine, and selected from fluorine and bromine in another embodiment, and the halogen is fluorine in yet another embodiment.

[00294] Non-limiting examples of heterocyclic compounds utilized in the activator of the invention include substituted and unsubstituted pyrroles, imidazoles, pyrazoles, pyrrolines, pyrrolidines, purines, carbazoles, and indoles, phenyl indoles, 2,5-dimethyl pyrroles, 3-pentafluorophenyl pyrrole, 4,5,6,7-tetrafluoroindole or 3,4-difluoropyrroles.

[00295] In one embodiment, the heterocyclic compound described above is combined with an alkylaluminum or an alumoxane to yield an activator compound which, upon reaction with a catalyst component, for example a metallocene, produces an active polymerization catalyst. Non-limiting examples of suitable alkylaluminums include trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, tri-iso-octylaluminum, triphenylaluminum, and combinations thereof.

[00296] Other activators include those described in WO 98/07515 such as tris (2, 2', 2''-nonafluorobiphenyl) fluoroaluminate. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations. Other activators include aluminum/boron complexes, perchlorates, periodates and iodates including their hydrates; lithium (2,2'-bisphenyl-ditrimethylsilicate)·4THF; silylium salts in combination with a non-coordinating compatible anion. Also, methods of activation such as using radiation, electro-chemical oxidation, and the like are also contemplated as activating methods for the purposes of rendering the neutral bulky ligand metallocene-type catalyst compound or precursor to a bulky ligand metallocene-type cation capable of polymerizing olefins. Other activators or methods for activating a bulky ligand metallocene-type catalyst compound are described in for example, US 5,849,852, 5,859,653 and 5,869,723 and WO 98/32775.

[00297] In general, the activator and catalyst component(s) are combined in mole ratios of activator to catalyst component from 1000:1 to 0.1:1, and from 300:1 to 1:1 in another embodiment, and from 150:1 to 1:1 in yet another embodiment, and from 50:1 to 1:1 in yet another embodiment, and from 10:1 to 0.5:1 in yet another embodiment, and from 3:1 to 0.3:1 in yet another embodiment, wherein a desirable range may include any combination of any upper mole ratio limit with any lower mole ratio limit described herein. When the activator is a cyclic or oligomeric poly(hydrocarbylaluminum oxide) (*e.g.*, "MAO"), the mole ratio of activator to catalyst component ranges from 2:1 to 100,000:1 in one embodiment, and from 10:1 to 10,000:1 in another embodiment, and from 50:1 to 2,000:1 in yet another embodiment. When the activator is a neutral or ionic ionizing activator such as a boron alkyl and the ionic salt of a boron alkyl, the mole ratio of activator to catalyst component ranges from 0.5:1 to 10:1 in one embodiment, and from 1:1 to 5:1 in yet another embodiment.

**Spray Drying Process**

[00298] Any spray-drying method known in the art may be used. For example, a suitable spray-drying method comprises atomizing a solution, suspension or dispersion of the catalyst and/or the activator, optionally together with a filler, and optionally with heating of the solution, suspension or dispersion. Atomization is preferably done by passing the slurry through the atomizer together with an inert drying gas, i.e., a gas which is nonreactive under the conditions employed during atomization, such as nitrogen for example. An atomizing nozzle or a centrifugal high speed disc can be employed to effect atomization, whereby there is created a spray or dispersion of droplets of the mixture. The volumetric flow of drying gas, if used, preferably considerably exceeds the volumetric flow of the slurry to effect atomization of the slurry and/or evaporation of the liquid medium. Ordinarily the drying gas is heated to a temperature as high as about 160°C to facilitate atomization of the slurry; however, if the volumetric flow of drying gas is maintained at a very high level, it is possible to employ lower temperatures. Atomization pressures of from about 1 psig to 200 psig are suitable. Some examples of suitable spray-drying methods include those disclosed in U.S. Pat. Nos. 5,290,745, 5,652,314, 4,376,062, 4,728,705, 5,604,172, 5,306,350 and 4,638,029.

[00299] Figure 1 is a schematic representation of an exemplary spray-drying apparatus. Referring to Figure 1, each mixture is drawn through silicone tubing from a reservoir attached at point C by a peristaltic pump D. As the mixture passes through nozzle F, it is mixed with

atomizing nitrogen gas, which enters the system at point E. The mist of catalyst composition thus formed in the drying chamber G is then dried in the presence of bath nitrogen gas, which enters the drying chamber at point A. The bath nitrogen bath is heated by heater B before entering. Particles of unacceptably large diameter catalyst composition are not entrained in the nitrogen flow and drop into oversize collection pot H. The remainder of the catalyst composition continues through chamber outlet I into the cyclone separator J, where the particulate catalyst composition is disengaged from the gas stream and dropped into a removable product collection pot K, from which the fully activated catalyst composition is recovered. The nitrogen gas is drawn through the aspirator L and removed from the system at point M.

[00300] Another type of suitable spray-drying method includes forming a liquid mixture of a nonvolatile materials fraction, a solvent fraction and at least one compressed fluid; and spraying the liquid mixture at a temperature and pressure that gives a substantially decompressive spray by passing the mixture through an orifice into an environment suitable for forming solid particulates by solvent evaporation. Such a method is disclosed in U.S. Pat. No. 5,716,558.

[00301] By adjusting the size of the orifices of the atomizer employed during spray-drying, it is possible to obtain particles having desired average particle size, e.g., from about 5 micrometers to about 200 micrometers. The particles recovered from the spray-drying can optionally be decarboxylated by heating the particles, e.g., as disclosed in U.S. Pat. No. 5,652,314.

[00302] Any solid particulate material which is inert to the other components of the catalyst system, and during subsequent polymerization, can be employed as the filler. Such materials can be organic or inorganic. Suitable fillers include fumed silica, non-fumed silica, boron nitride, titanium dioxide, zinc oxide, polystyrene, and calcium carbonate. Fumed hydrophobic silica is preferred because it imparts high viscosity to the slurry and good strength to the spray-dried particles. For example, Gasil™ or Cabosil™ may be used. The particulate material employed as filler should have an average particle size no greater than 50 micrometers, preferably no greater than 10 micrometers. The particulate material employed as filler should be dry, i.e., free of absorbed water.

[00303] Sufficient filler is preferably employed to produce a slurry suitable for spray-drying, i.e., a slurry containing such filler in an amount of from 0 percent by weight to about 15

percent by weight, preferably from about 2.5 percent by weight to about 10 percent by weight. When spray-dried, such slurry produces discrete catalyst particles in which filler is present in an amount of from 0 percent by weight to about 50 percent by weight, preferably from about 10 percent by weight to about 30 percent by weight. The spray-dried catalyst particles produced in this manner typically have an average particle size of from about 5 micrometers to about 200 micrometers, preferably from about 10 micrometers to about 30 micrometers.

**Polymerization Process**

[00304] The spray dried catalyst is suitable for use in any prepolymerization and/or polymerization process over a wide range of temperatures and pressures. The temperatures may be in the range of from –60°C to about 280°C, preferably from 50°C to about 200°C. In one embodiment, the polymerization temperature is above 0°C, above 50°C, above 80°C, above 100°C, above 150°C, or above 200°C. In one embodiment, the pressures employed may be in the range from 1 atmosphere to about 500 atmospheres or higher.

[00305] Polymerization processes include solution, gas phase, slurry phase, and a high pressure process, or a combination thereof. Particularly preferred is a gas phase or slurry phase polymerization of one or more olefin(s) at least one of which is ethylene or propylene.

[00306] In one embodiment, the process is a solution, high pressure, slurry or gas phase polymerization process of one or more olefin monomers having from 2 to 30 carbon atoms, preferably 2 to12 carbon atoms, and more preferably 2 to 8 carbon atoms. The invention is particularly well suited to the polymerization of two or more olefin monomers of ethylene, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene and 1-decene.

[00307] Other monomers useful include ethylenically unsaturated monomers, diolefins having 4 to 18 carbon atoms, conjugated or nonconjugated dienes, polyenes, vinyl monomers and cyclic olefins. Non-limiting monomers useful in the invention may include norbornene, norbornadiene, isobutylene, isoprene, vinylbenzocyclobutane, styrenes, alkyl substituted styrene, ethylidene norbornene, dicyclopentadiene and cyclopentene.

[00308] In another embodiment, a copolymer of ethylene is produced, where with ethylene, a comonomer having at least one alpha-olefin having from 4 to 15 carbon atoms, preferably from 4 to 12 carbon atoms, and most preferably from 4 to 8 carbon atoms, is polymerized in a gas phase process.

[00309] In another embodiment, ethylene or propylene is polymerized with at least two different comonomers, optionally one of which may be a diene, to form a terpolymer.

[00310] In one embodiment, the invention is directed to a polymerization process, particularly a gas phase or slurry phase process, for polymerizing propylene alone or with one or more other monomers including ethylene, and/or other olefins having from 4 to 12 carbon atoms.

[00311] Typically in a gas phase polymerization process, a continuous cycle is employed where in one part of the cycle of a reactor system, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. This heat is removed from the recycle composition in another part of the cycle by a cooling system external to the reactor. Generally, in a gas fluidized bed process for producing polymers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. The gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and fresh monomer is added to replace the polymerized monomer.

[00312] The reactor pressure in a gas phase process may vary from about 100 psig (690 kPa) to about 500 psig (3448 kPa), preferably in the range of from about 200 psig (1379 kPa) to about 400 psig (2759 kPa), more preferably in the range of from about 250 psig (1724 kPa) to about 350 psig (2414 kPa).

[00313] The reactor temperature in a gas phase process may vary from about 30°C to about 120° C, preferably from about 60°C to about 115°C, more preferably in the range of from about 70° C to 110°C, and most preferably in the range of from about 70°C to about 95°C. In another embodiment, the reactor temperature in a gas phase process is above 60°C.

[00314] Other gas phase processes include series or multistage polymerization processes. Gas phase processes may also include those described in U.S. Patent Nos. 5,627,242, 5,665,818 and 5,677,375, and European publications EP-A- 0 794 200 EP-B1-0 649 992, EP-A- 0 802 202 and EP-B- 634 421.

[00315] In another embodiment, the process may produce greater than 500 lbs of polymer per hour (227 Kg/hr) to about 200,000 lbs/hr (90,900 Kg/hr) or higher of polymer, preferably greater than 1000 lbs/hr (455 Kg/hr), more preferably greater than 10,000 lbs/hr (4540 Kg/hr), even more preferably greater than 25,000 lbs/hr (11,300 Kg/hr), still more preferably greater

than 35,000 lbs/hr (15,900 Kg/hr), still even more preferably greater than 50,000 lbs/hr (22,700 Kg/hr) and most preferably greater than 65,000 lbs/hr (29,000 Kg/hr) to greater than 100,000 lbs/hr (45,500 Kg/hr).

[00316] A slurry polymerization process generally uses pressures in the range of from about 1 to about 50 atmospheres and even greater and temperatures in the range of 0°C to about 120°C. In another embodiment, the slurry process temperature is above 100°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization diluent medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The suspension including diluent is intermittently or continuously removed from the reactor where the volatile components are separated from the polymer and recycled, optionally after a distillation, to the reactor. The liquid diluent employed in the polymerization medium is typically an alkane having from 3 to 7 carbon atoms, preferably a branched alkane. The medium employed should be liquid under the conditions of polymerization and relatively inert. When a propane medium is used the process must be operated above the reaction diluent critical temperature and pressure. Preferably, a hexane or an isobutane medium is employed.

[00317] In another embodiment, the polymerization technique is referred to as a particle form polymerization, or a slurry process where the temperature is kept below the temperature at which the polymer goes into solution. Such technique is well known in the art, and described in for instance U.S. Patent No. 3,248,179. Other slurry processes include those employing a loop reactor and those utilizing a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Also, other examples of slurry processes are described in U.S. Patent No. 4,613,484,.

[00318] In another embodiment, this process may produce greater than 2000 lbs of polymer per hour (907 Kg/hr), more preferably greater than 5000 lbs/hr (2268 Kg/hr), and most preferably greater than 10,000 lbs/hr (4540 Kg/hr). In another embodiment the slurry reactor may produce greater than 15,000 lbs of polymer per hour (6804 Kg/hr), preferably greater than 25,000 lbs/hr (11,340 Kg/hr) to about 100,000 lbs/hr (45,500 Kg/hr).

[00319] Examples of solution processes are described in U.S. Patent Nos. 4,271,060, 5,001,205, 5,236,998 and 5,589,555 and PCT WO 99/32525.

[00320] In one embodiment, the slurry or gas phase process is operated in the presence of the catalyst system described herein and in the absence of or essentially free of any scavengers, such as triethylaluminum, trimethylaluminum, tri-isobutylaluminum and tri-n-hexylaluminum and diethyl aluminum chloride, dibutyl zinc and the like. This process is described in PCT publication WO 96/08520 and U.S. Patent No. 5,712,352 and 5,763,543.

[00321] In another embodiment, the method provides for injecting the catalyst system described herein into a reactor, particularly a gas phase reactor. In one embodiment the catalyst system is used in the unsupported form, preferably in a liquid form such as described in U.S. Patent Nos. 5,317,036 and 5,693,727 and European publication EP-A-0 593 083. The polymerization catalyst in liquid form can be fed with an activator, and/or a support, and/or a supported activator together or separately to a reactor. The injection methods described in PCT publication WO 97/46599 may be utilized.

[00322] Where an unsupported catalyst system is used the mole ratio of the metal of the activator component to the metal of the catalyst compound is in the range of between 0.3:1 to 10,000:1, preferably 100:1 to 5000:1, and most preferably 500:1 to 2000:1.

**Polymer Products**

[00323] The polymers produced can be used in a wide variety of products and end-use applications. The polymers produced include polyethylene homopolymers and polyethylene co-polymers, including linear low density polyethylene, elastomers, plastomers, high density polyethylenes, medium density polyethylenes, low density polyethylenes, as well as polypropylene homopolymers and polypropylene co polymers.

[00324] The polymers, typically ethylene based polymers, have a density in the range of from 0.86g/cc to 0.97 g/cc, preferably in the range of from 0.88 g/cc to 0.965 g/cc, more preferably in the range of from 0.900 g/cc to 0.96 g/cc, even more preferably in the range of from 0.905 g/cc to 0.95 g/cc, yet even more preferably in the range from 0.910 g/cc to 0.940 g/cc, and most preferably greater than 0.915 g/cc, preferably greater than 0.920 g/cc, and most preferably greater than 0.925 g/cc. Density is measured in accordance with ASTM-D-1238.

[00325] The polymers produced typically have a molecular weight distribution, a weight average molecular weight to number average molecular weight ($M_w/M_n$) of greater than 1.5 to about 15, particularly greater than 2 to about 10, more preferably greater than about 2.2 to less

than about 8, and most preferably from 2.5 to 8. The polymers may have a narrow molecular weight distribution and a broad composition distribution or vice-versa, and may be those polymers described in U.S. Patent No. 5,798,427.

[00326] Also, the polymers typically have a narrow composition distribution as measured by Composition Distribution Breadth Index (CDBI). Further details of determining the CDBI of a copolymer are known to those skilled in the art. See, for example, PCT Patent Application WO 93/03093, published February 18, 1993. The polymers in one embodiment have CDBI's generally in the range of greater than 50% to 100%, preferably 99%, preferably in the range of 55% to 85%, and more preferably 60% to 80%, even more preferably greater than 60%, still even more preferably greater than 65%. In another embodiment, polymers produced using a catalyst system described herein have a CDBI less than 50%, more preferably less than 40%, and most preferably less than 30%.

[00327] The polymers in one embodiment have a melt index (MI) or ($I_2$) as measured by ASTM-D-1238-E (190/2.16) in the range from no measurable flow to 1000 dg/min, more preferably from about 0.01 dg/min to about 100 dg/min, even more preferably from about 0.1 dg/min to about 50 dg/min, and most preferably from about 0.1 dg/min to about 10 dg/min.

[00328] In one embodiment, the polymers have a melt index ratio ($I_{21}/I_2$) ($I_{21}$ is measured by ASTM-D-1238-F) (190/21.6) of from 10 to less than 25, more preferably from about 15 to less than 25. The polymers, in a preferred embodiment, have a melt index ratio ($I_{21}/I_2$) of from greater than 25, more preferably greater than 30, even more preferably greater that 40, still even more preferably greater than 50 and most preferably greater than 65. For example, the melt index ratio ($I_{21}/I_2$) may be of from 5 to 300, 10 to 200, 20 to 180, 30 to 160, 40 to 120, 50 to 100, 60 to 90, and a combination of any upper limit with any lower limit.

[00329] In yet another embodiment, propylene based polymers are produced. These polymers include atactic polypropylene, isotactic polypropylene, hemi-isotactic and syndiotactic polypropylene. Other propylene polymers include propylene block or impact copolymers. Propylene polymers of these types are well known in the art see for example U.S. Patent Nos. 4,794,096, 3,248,455, 4,376,851, 5,036,034 and 5,459,117.

[00330] The polymers may be blended and/or coextruded with any other polymer. Non-limiting examples of other polymers include linear low density polyethylenes, elastomers, plastomers,

high pressure low density polyethylene, high density polyethylenes, polypropylenes and the like.

[00331] The polymers produced and blends thereof are useful in such forming operations as film, sheet, and fiber extrusion and co-extrusion as well as blow molding, injection molding and rotary molding. Films include blown or cast films formed by coextrusion or by lamination useful as shrink film, cling film, stretch film, sealing films, oriented films, snack packaging, heavy duty bags, grocery sacks, baked and frozen food packaging, medical packaging, industrial liners, membranes, etc. in food-contact and non-food contact applications. Fibers include melt spinning, solution spinning and melt blown fiber operations for use in woven or non-woven form to make filters, diaper fabrics, medical garments, geotextiles, etc. Extruded articles include medical tubing, wire and cable coatings, pipe, geomembranes, and pond liners. Molded articles include single and multi-layered constructions in the form of bottles, tanks, large hollow articles, rigid food containers and toys, etc.

**Bimodal Polymer Product**

[00332] The polymers produced by the processes described herein, utilizing the mixed catalysts described herein, are preferably bimodal. The term "bimodal," when used to describe a polymer or polymer composition, e.g., polyolefins such as polypropylene or polyethylene, or other homopolymers, copolymers or terpolymers, means "bimodal molecular weight distribution," which term is understood as having the broadest definition persons in the pertinent art have given that term as reflected in printed publications and issued patents. For example, a single composition that includes polyolefins with at least one identifiable high molecular weight distribution and polyolefins with at least one identifiable low molecular weight distribution is considered to be a "bimodal" polyolefin, as that term is used herein. Preferably, other than having different molecular weights, the high molecular weight polyolefin and the low molecular weight polyolefin are essentially the same type of polymer, e.g., polypropylene or polyethylene.

[00333] The bimodal polymer products prepared using the mixed catalysts described herein can be used in a wide variety of products and end-use applications. The polymers produced by the process of the invention include linear low density polyethylene, elastomers, plastomers, high density polyethylenes, low density polyethylenes, medium density polyethylenes, polypropylene and polypropylene copolymers.

[00334] Polymers that can be made using the described processes can have a variety of compositions, characteristics and properties. At least one of the advantages of the catalysts is that the process utilized can be tailored to form a polymer composition with a desired set of properties. For example, it is contemplated that the polymers having the same properties as the bimodal polymer compositions in U.S. Patent No. 5,525,678 can be formed. Also, the bimetallic catalysts described herein can be used in polymerization processes to form polymers having the same properties as the polymers in the following patents, 6,420,580; 6,388,115; 6,380,328; 6,359,072; 6,346,586; 6,340,730; 6,339,134; 6,300,436; 6,274,684; 6,271,323; 6,248,845; 6,245,868; 6,245,705; 6,242,545; 6,211,105; 6,207,606; 6,180,735; and 6,147,173.

[00335] The polymers, typically ethylene based polymers, should have a density in the range of from 0.86g/cc to 0.97 g/cc, preferably in the range of from 0.88 g/cc to 0.965 g/cc, more preferably in the range of from 0.900 g/cc to 0.96 g/cc, even more preferably in the range of from 0.905 g/cc to 0.955 g/cc, yet even more preferably in the range from 0.910 g/cc to 0.955 g/cc, and most preferably greater than 0.915 g/cc, preferably greater than 0.920 g/cc, and most preferably greater than 0.925 g/cc.

[00336] The polymers can have a molecular weight distribution, a weight average molecular weight to number average molecular weight ($M_w/M_n$) of greater than 5 to about 80, particularly greater than 10 to about 60, more preferably greater than about 15 to less than about 55, and most preferably from 20 to 50.

[00337] The polymers made by the described processes can in certain embodiments have a melt index (MI) or ($I_2$) as measured by ASTM-D-1238-E in the range from 0.01 dg/min to 1000 dg/min, more preferably from about 0.01 dg/min to about 100 dg/min, even more preferably from about 0.02 dg/min to about 50 dg/min, and most preferably from about 0.03 dg/min to about 0.1 dg/min.

[00338] Polymers made by the described processes can in certain embodiments have a melt index ratio ($I_{21}/I_2$) ($I_{21}$ is measured by ASTM-D-1238-F) of from 40 to less than 500, more preferably from about 60 to less than 200.

[00339] Expressed differently, polymers made by the described processes can in certain embodiments have a melt index ratio ($I_{21}/I_2$) ($I_{21}$ is measured by ASTM-D-1238-F) of from preferably greater than 40, more preferably greater than 50, even more preferably greater that

60, still even more preferably greater than 65 and most preferably greater than 70. In one or more other embodiments, the polymer of the invention may have a narrow molecular weight distribution and a broad composition distribution or vice-versa, and may be those polymers described in U.S. Patent No. 5,798,427.

[00340] In certain embodiments, propylene based polymers can be produced using the processes described herein. These polymers include atactic polypropylene, isotactic polypropylene, hemi-isotactic and syndiotactic polypropylene. Other propylene polymers include propylene block or impact copolymers. Propylene polymers of these types are well known in the art see for example U.S. Patent Nos. 4,794,096, 3,248,455, 4,376,851, 5,036,034 and 5,459,117.

[00341] The polymers of the invention may be blended and/or coextruded with any other polymer. Non-limiting examples of other polymers include linear low density polyethylenes produced via conventional Ziegler-Natta and/or bulky ligand metallocene-type catalysis, elastomers, plastomers, high pressure low density polyethylene, high density polyethylenes, polypropylenes and the like.

[00342] Polymers produced by the process of the invention and blends thereof are useful in such forming operations as film, sheet, pipe and fiber extrusion and co-extrusion as well as blow molding, injection molding and rotary molding. Films include blown or cast films formed by coextrusion or by lamination useful as shrink film, cling film, stretch film, sealing films, oriented films, snack packaging, heavy duty bags, grocery sacks, baked and frozen food packaging, medical packaging, industrial liners, membranes, etc. in food-contact and non-food contact applications. Fibers include melt spinning, solution spinning and melt blown fiber operations for use in woven or non-woven form to make filters, diaper fabrics, medical garments, geotextiles, etc. Extruded articles include medical tubing, wire and cable coatings, geomembranes, and pond liners. Molded articles include single and multi-layered constructions in the form of bottles, tanks, large hollow articles, rigid food containers and toys, etc.

## EXAMPLES

[00343] In order to provide a better understanding of the foregoing discussion, the following non-limiting examples are offered. Although the examples may be directed to specific embodiments, they are not to be viewed as limiting the invention in any specific respect. All parts, proportions, and percentages are by weight unless otherwise indicated. All examples

were carried out in dry, oxygen-free environments and solvents. All molecular weights are weight average molecular weight unless otherwise noted. Molecular weights including weight average molecular weight ($M_w$), number average molecular weight ($M_n$), and z-average molecular weight (Mz) were measured by Gel Permeation Chromatography (GPC), also known as size exclusion chromatography (SEC).

**Example 1 (comparative):**

[00344] "HN3Zr" {Bis(phenylmethyl)[N'-(2,4,6-trimethylphenyl)-N-[2-[2,4,6-trimethyl phenyl)amino-kN]ethyl]-1,2-ethanediaminato(2-)kN,kN']zirconium} and "X" {(n-propylcyclopentadienyl)(tetramethylcyclopentadienyl) zirconium dichloride} were mixed at a 4.5 to 1 molar ratio and then activated with methyl alumoxane. This catalyst system was then supported on silica Cabosil TS 610 in a pilot scale spray dryer. The Cabosil TS 610 was sold by Cabot Corporation. The composition of the resulting spray dried catalyst was 2wt% HN3Zr/X, 32% methyl alumoxane, 66% cabosil TS610.

[00345] This catalyst was mixed with mineral oil (Hydrobrite® 550 manufactured by Crompton Company) to produce three slurries having 8%, 12% and 18% solids concentration in oil. Foaming was noticed for each slurry and the intensity of foaming was found to increase with the solids concentration of the slurry. The viscosity of each slurry was measured at 25°C using a Brookfield viscometer as a function of shear rate, and is reported in Table 1 below.

**Example 2:**

[00346] The catalyst of Example 1 was mixed with Hydrobrite® 550 oil along with 10% heptane to produce a slurry having 25% solids concentration. Even though the solids concentration was higher than the slurries of Example 1, foaming was found to be significantly less. The viscosity of this slurry was also measured using a Brookfield viscometer as a function of shear rate and reported in Table 1.

[00347] Table 1: Effect of solids concentration on viscosity at 25°C.

| Shear rate (1/sec) | EX 1: Viscosity of 8% solids (cP) | EX. 1: Viscosity of 12% solids, (cP) | EX. 1: Viscosity of 18% solids (cP) | EX. 2: Viscosity of 25% solids (cP) |
|---|---|---|---|---|
| 1.7 | 504 | 858 | 1014 | 402 |
| 3.4 | 453 | 762 | 990 | 411 |
| 5.1 | 442 | 724 | 980 | 406 |
| 6.8 | 435 | 700 | 973 | 402 |
| 8.5 | 439 | 684 | 967 | 394 |
| 10.2 | 440 | 674 | 966 | 387 |
| 11.9 | 441 | 668 | 962 | 379 |
| 13.6 | 439 | 658 | 958 | 375 |

[00348] As seen in Table 1, the viscosity of this slurry at 25% solids with heptane (Example 2) was less than the lower concentration slurries without any heptane present. This observation, was surprising and unexpected considering the Example 2 slurry contained as much as three times the amount of solids than the slurries of Example 1.

**Example 3 (comparative):**

[00349] A spray dried catalyst containing "HN5Zr" {Bis(phenylmethyl)[N'-(2,3,4,5,6-pentamethylphenyl)-N-[2-[2,3,4,5,6-pentamethylphenyl)amino-kN]ethyl]-1,2-ethane diaminato(2-)kN,kN']zirconium} and "X" {(n-propylcyclopentadienyl) (tetramethylcyclopentadienyl) zirconiumdichloride} were mixed at a 4.2 to 1 molar ratio, and activated using methyl alumoxane. This catalyst was then supported on silica Cabosil TS 610 in a pilot scale spray dryer. This catalyst was then mixed with Hydrobrite® 550 mineral oil, to produce a slurry having 18% solids concentration in oil. Significant foaming was noticed.

**Example 4:**

[00350] The catalyst of Example 3 was mixed with Hydrobrite® mineral oil to produce a slurry having a higher solids concentration (25wt%) along with 10% n-hexane. Again, foaming was significantly less. A side by side comparison showed a surprising reduction in the foam content of the 25% slurry with 10% hexane of Example 4 compared to the 18% slurry of Example 3.

**Example 5:**

[00351] A spray dried catalyst containing 2% by weight of HN5Zr/X mixed at 5:1 molar ratio, 32% by weight of methyl alumoxane and 66% by weight of Cabosil TS 610 was prepared in a pilot scale spray dryer. The particle size distribution of the catalyst as measured by Mastersizer Instrument made by Malvern Instruments Ltd, Malvern, U.K. is given below:

D90:42 micron;
D50:24 micron; and
D10: 13 micron.

[00352] A large scale slurry was prepared using this catalyst and n-hexane and another type of mineral oil (Kaydol® also manufactured by Crompton Company) to test the foaming and ease of handling. The slurry was made in a 125 gallon vessel fitted with a helical ribbon agitator. About 483 lbs. of degassed mineral oil was charged into the 125 gallon vessel, and 71 lbs. of n-hexane was added and mixed for 1 hour at 40°C. Then 156.4 lbs. of the spray dried catalyst was added over a period of two hours. The slurry in the 125 gallon vessel was mixed at 40°C for about 4 hours and discharged into a horizontal metal cylinder of 120 gallon size. The composition of the slurry was 22% catalyst, 10% hexane, and 68% oil.

[00353] There was no foaming observed. The solids were mixed well and discharged into the horizontal cylinder easily. The viscosity of the slurry was measured using a Brookfield viscometer and the viscosity was much lower than the 18% slurry of Example 1. The results are shown in Table 2 below.

[00354] Table 2. Viscosity of 22% slurry, 10% hexane and 68% oil (Kaydol®)

| Shear Rate (1/sec) | Viscosity (cP) |
|---|---|
| 1.40 | 600 |
| 2.80 | 564 |
| 4.20 | 524 |
| 5.60 | 492 |
| 7.00 | 466 |
| 8.40 | 446 |
| 9.80 | 428 |
| 11.20 | 415 |

[00355] The above slurry was stored in the 125 gallon horizontal cylinder for about 6 months at ambient temperature. After rolling the cylinder for 24 hours, the slurry was transferred to a catalyst feeder in a fluidized bed reactor. No problem in transfer was encountered. The slurry was fed to the fluidized bed reactor for about 15 hours and 80,000 lbs of bimodal HDPE was produced. The properties of the resin were as follows:

Flow index: 8.5 dg/min;

Melt Flow Ratio: 218; and

Density: 0.9489.

**Example 6:**

[00356] Another slurry using a different catalyst ratio (HN5Zr/X mixed at 5.5 to 1 ratio) was prepared similar to the Example 5. No foaming or handling problem was encountered with this slurry (22% catalyst, 10% n-hexane and 68% Kaydol® oil). The slurry was stored in the 125 gallon horizontal cylinder for about 9 months at ambient temperature. After rolling the cylinder for 24 hours, the slurry was transferred to a catalyst feeder in a fluidized bed reactor. No problem in transfer was encountered. The slurry was fed to the fluid bed reactor for about 15 hours and 80,000 lbs of bimodal HDPE was produced. The properties of the resin were as follows:

Flow index: 6.5 dg/min;

Melt Flow Ratio: 115; and

Density: 0.9481.

[00357] Unless otherwise indicated, all numbers expressing quantities of ingredients, properties, reaction conditions, and so forth, used in the specification and claims are to be understood as approximations based on the desired properties sought to be obtained by the present invention, and the error of measurement, etc., and should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and values setting forth the broad scope of the invention are approximations, the numerical values set forth are reported as precisely as possible.

[00358] All priority documents are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted. Further, all documents cited herein, including testing procedures, are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted.

[00359] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

**Claims:**

1. A spray dried catalyst slurry for olefin polymerization, comprising:
a catalyst system comprising one or more catalysts selected from the group consisting of metallocenes, non-metallocenes, and a combination thereof, wherein the catalyst system is spray dried;
mineral oil to form a slurry comprising the catalyst system; and
one or more liquid alkanes having three or more carbon atoms in an amount sufficient to reduce foaming and viscosity of the slurry.

2. The catalyst slurry of claim 1, wherein the catalyst system further comprises one or more activators.

3. The catalyst slurry of claims 1 or 2, wherein the slurry comprises up to 20 percent by weight of the one or more liquid alkanes.

4. The catalyst slurry of any one of the preceding claims, wherein the slurry comprises between about 2 percent by weight and 15 percent by weight of the one or more liquid alkanes.

5. The catalyst slurry of any one of the preceding claims, wherein the slurry comprises up to 50 percent by weight of the catalyst system.

6. The catalyst slurry of any one of the preceding claims, wherein the slurry comprises at least 10 percent by weight of the catalyst system.

7. The catalyst slurry of any one of the preceding claims, wherein the metallocene component is represented by the formula:

$$Cp^ACp^BMX_n$$

wherein:
M is selected from the group consisting of Groups 3 through 10 atoms;
$Cp^A$ and $Cp^B$ are each independently an unsubstituted or substituted cyclic ring group;

X is a leaving group; and
n is zero or an integer from 1 to 4.

8. The catalyst slurry of claim 7, wherein $Cp^A$ and $Cp^B$ are each independently selected from the group consisting of cyclopentadienyl, indenyl, combinations thereof, and derivatives thereof.

9. The catalyst slurry of any one of the preceding claims, wherein the non-metallocene component is represented by the formula:

$$\alpha_a\beta_b\gamma_gMX_n$$

wherein M is selected from the group consisting of Groups 3 through 10 atoms;
X is independently selected from the group consisting of halogen ions, hydrides, $C_1$ to $C_{12}$ alkyls, $C_2$ to $C_{12}$ alkenyls, $C_6$ to $C_{12}$ aryls, $C_7$ to $C_{20}$ alkylaryls, $C_1$ to $C_{12}$ alkoxys, $C_6$ to $C_{16}$ aryloxys, $C_7$ to $C_{18}$ alkylaryloxys, $C_1$ to $C_{12}$ fluoroalkyls, $C_6$ to $C_{12}$ fluoroaryls, $C_1$ to $C_{12}$ heteroatom-containing hydrocarbons, halogenated $C_6$ to $C_{16}$ aryloxys, and substituted derivatives thereof;
$\beta$ and $\gamma$ are groups that each comprise at least one Group 14 to Group 16 atom; wherein at least one of the Group 14 to Group 16 atoms are bound to M;
$\alpha$ is a linking moiety that forms a chemical bond to each of $\beta$ and $\gamma$; and
a, b, g, and n are each integers from 1 to 4.

10. A method for preparing the spray dried catalyst of any one of the preceding claims comprising:
preparing a catalyst system comprising one or more components selected from the group consisting of metallocenes, non-metallocenes, and activators;
adding mineral oil to the catalyst system to form a slurry; and
adding one or more liquid alkanes having three or more carbon atoms to the slurry in an amount sufficient to reduce foaming and viscosity of the slurry.

11. A method for olefin polymerization, comprising transferring the catalyst slurry of any one of the preceding claims to a gas phase reactor and combining with olefins.

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US05/01708

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : C08F 4/60, 4/602, 4/606
US CL : 502/103, 113, 152, 162; 526/ 113, 114, 160, 161
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)
U.S. : 502/103, 113, 152, 162; 526/ 113, 114, 160, 161

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 2002/0161141 (MAWSON et al) 31 October 2002 (31.10.2002), page 31, paragraphs [0452]-[0453]. | 1-11 |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent 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
24 May 2005 (24.05.2005)

Date of mailing of the international search report
06 JUN 2005

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Form PCT/ISA/210 (second sheet) (July 1998)

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US05/01708

## Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

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

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim 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. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of Item 2 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 an additional fee, this Authority did not invite payment of any additional fee.
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.

☐ No protest accompanied the payment of additional search fees.