**[0009]** Thus, knowledge about supported Ziegler-Natta (pro)catalyst systems is not necessarily predictive of, or applicable to, spray-dried Ziegler-Natta (pro)catalyst systems, and vice versa.

## SUMMARY

**[0010]** We provide an activated, titanium-based, spray-dried Ziegler-Natta catalyst system comprising a titanium-based Ziegler-Natta catalyst, a carrier material, and an effective amount of an activator mixture comprising triethylaluminum (TEAl) and diethylaluminum chloride (DEAC); or an activation reaction product thereof. The inventive catalyst system may be used to enhance the polymerization reaction rate of a chemical process for manufacturing a polyolefin composition. In such a process the effective amount may be a quantity of the activator mixture sufficient for obtaining a substantially uniform (substantially flat (gently sloping) plot of) comonomer composition distribution of ethylene/alpha-olefin copolymer compositions made therewith. When the activator mixture is used in such an effective amount, it unpredictably enables the inventive catalyst system to copolymerize ethylene and alpha-olefin comonomer so as to produce an ethylene/alpha-olefin copolymer composition having a substantially uniform comonomer composition distribution than that of a comparative ethylene/alpha-olefin copolymer produced with a comparative catalyst system that is the same as the inventive catalyst system except wherein the activator of the comparative catalyst system consists of triethylaluminum (TEAl) and is free of diethylaluminum chloride (DEAC). The substantially uniform comonomer composition distribution of the inventive ethylene/alpha-olefin copolymer composition is in the regime we recognized would be beneficial for making films having improved mechanical properties. Alternatively or additionally, the effective amount may be a quantity of the activator mixture sufficient for making an inventive ethylene/alpha-olefin copolymer composition having a higher fluidized bulk density (FBD) and/or higher settled bulk density (SBD) and/or higher dart impact (film form) relative to that/those of the comparative ethylene/alpha-olefin copolymer composition, made with the comparative catalyst system. In some examples the inventive FBD and/or inventive SBD of the inventive ethylene/alpha-olefin copolymer composition and/or inventive dart impact of a film of the inventive ethylene/alpha-olefin copolymer composition independently is/are higher by at least 5%, alternatively at least 10%; and, in some examples, at most 20%, than the FBD and/or SBD, respectively, of the comparative ethylene/alpha-olefin copolymer composition and/or the dart impact of a film of the comparative ethylene/alpha-olefin copolymer composition, respectively. We also provide a method of making the inventive catalyst system, a method of polymerizing olefin (co)monomer(s), polyolefins made by the method, and manufactured articles containing or

made from the polyolefins. The polymerization may be conducted in a gas phase or a liquid-phase.

**[0010a]** In one aspect, the present disclosure refers to an activated spray-dried Ziegler-Natta catalyst system comprising (A*) an activated Ziegler-Natta catalyst comprising an activated complex of $TiCl_3$ and $MgCl_2$, (B) a hydrophobic pre-treated fumed silica, and (C) an activator mixture of triethylaluminum (TEAl) and diethylaluminum chloride (DEAC) at a TEAl/DEAC weight/weight ratio of from 20:80 to 80:20.

**[0010b]** In another aspect, the present disclosure refers to a method of making the activated spray-dried Ziegler-Natta catalyst system as disclosed herein, the method comprising contacting a reduced spray-dried Ziegler-Natta catalyst system comprising ($A^{red}$) a reduced Ziegler-Natta catalyst comprising a chemical reduction product of chemically reducing a complex of $TiCl_3$ and $MgCl_2$ and (B) a hydrophobic pre-treated fumed silica, with the effective amount of (C) the activator mixture, thereby making the activated spray-dried Ziegler-Natta catalyst system.

**[0010c]** In another aspect, the present disclosure refers to a method of making a polyethylene composition, the method comprising contacting ethylene (monomer) and optionally zero, one, or more ($C_3$-$C_{20}$)alpha-olefin (comonomer(s)) with the activated spray-dried Ziegler-Natta catalyst system as disclosed herein, or such product of the method as disclosed herein, to give a polyethylene composition comprising a polyethylene homopolymer or ethylene/($C_3$-$C_{20}$)alpha-olefin copolymer, respectively, and the activated spray-dried Ziegler-Natta catalyst system, or a by-product thereof.

DRAWING(S)

**[0011]** Figure (FIG.) 1 contains line plots of changes in weight percent (wt%) comonomer content of ethylene/alpha-olefin copolymer compositions on y-axis versus changes in LogM (by GPC) of the ethylene/alpha-olefin copolymer compositions on x-axis for each of inventive examples (A) and (B) and comparative example (A).

DETAILED DESCRIPTION

**[0012]** The Introduction, Summary and Abstract are incorporated here by reference.

**[0013]** Certain inventive embodiments are described below as numbered aspects for easy cross-referencing. Additional embodiments are described elsewhere herein.

**[0014]** Aspect 1. An activated spray-dried Ziegler-Natta catalyst system comprising (A*) an activated Ziegler-Natta catalyst comprising an activated complex of $TiCl_3$ and $MgCl_2$, (B) a hydrophobic pre-treated fumed silica (substantially nonporous, alternatively completely nonporous), and an effective amount of (C) an activator mixture of triethylaluminum (TEAl) and diethylaluminum chloride (DEAC) at a TEAl/DEAC weight/weight ratio of from 20:80 to

80:20; or a activation reaction product thereof. The effective amount is a quantity sufficient for obtaining the substantially uniform comonomer composition distribution of ethylene/alpha-olefin copolymer compositions made therewith and for making a polyethylene composition, such as an ethylene/alpha-olefin copolymer composition, having a higher fluidized bulk density and/or higher settled bulk density relative to that/those of a comparative polyethylene composition, such as a comparative ethylene/alpha-olefin copolymer composition, produced with a comparative activated spray-dried Ziegler-Natta catalyst system activated with TEAl alone or DEAC alone and made to the same melt index value (I2) as measured by the Melt Index Test Method and same density value as measured by the Density Test Method, described later. The substantially uniform (narrower) comonomer composition distribution (CCD) of the inventive ethylene/alpha-olefin copolymer composition may be a significant reason for the composition's better physical properties.

**[0015]** Aspect 2. The activated spray-dried Ziegler-Natta catalyst system of aspect 1 wherein the effective amount of (C) activator mixture is a TEAl/DEAC weight/weight ratio of from 25:75 to 75:25, alternatively from 30.0:70.0 to 70.0:30.0, alternatively from 35:65 to 65:35, alternatively from 40.0:60.0 to 60.0:40.0, alternatively from 45:55 to 55:45, alternatively from 47:53 to 53:47, alternatively 50:50.

**[0016]** Aspect 3. A method of making an activated spray-dried Ziegler-Natta catalyst system, the method comprising contacting a chemically-reduced spray-dried Ziegler-Natta catalyst system comprising ($A^{red}$) a chemically-reduced Ziegler-Natta catalyst comprising a complex

CLAIMS

1. An activated spray-dried Ziegler-Natta catalyst system comprising (A*) an activated Ziegler-Natta catalyst comprising an activated complex of $TiCl_3$ and $MgCl_2$, (B) a hydrophobic pre-treated fumed silica, and (C) an activator mixture of triethylaluminum (TEAl) and diethylaluminum chloride (DEAC) at a TEAl/DEAC weight/weight ratio of from 20:80 to 80:20.

2. The activated spray-dried Ziegler-Natta catalyst system of claim 1 wherein the effective amount of (C) activator mixture is a TEAl/DEAC weight/weight ratio of from 25:75 to 75:25.

3. A method of making the activated spray-dried Ziegler-Natta catalyst system of claim 1 or 2, the method comprising contacting a reduced spray-dried Ziegler-Natta catalyst system comprising ($A^{red}$) a reduced Ziegler-Natta catalyst comprising a chemical reduction product of chemically reducing a complex of $TiCl_3$ and $MgCl_2$ and (B) a hydrophobic pre-treated fumed silica, with the effective amount of (C) the activator mixture, thereby making the activated spray-dried Ziegler-Natta catalyst system.

4. A method of making a polyethylene composition, the method comprising contacting ethylene (monomer) and optionally zero, one, or more ($C_3$-$C_{20}$)alpha-olefin (comonomer(s)) with the activated spray-dried Ziegler-Natta catalyst system of claim 1 or 2, or such product of the method of claim 3, to give a polyethylene composition comprising a polyethylene homopolymer or ethylene/($C_3$-$C_{20}$)alpha-olefin copolymer, respectively, and the activated spray-dried Ziegler-Natta catalyst system, or a by-product thereof.

5. The method of claim 4 comprising a gas phase polymerization in the presence of molecular hydrogen gas ($H_2$) and, optionally, an induced condensing agent (ICA) in one, two or more gas phase polymerization reactors under (co)polymerizing conditions, thereby making the polyethylene composition; wherein the (co)polymerizing conditions comprise a reaction temperature from 80° to 110° C.; a molar ratio of the molecular hydrogen gas to the ethylene from 0.001 to 0.050; and a molar ratio of the comonomer to the ethylene from 0.005 to 0.10.

6. The method of claim 4 or 5 comprising copolymerizing ethylene and one or more ($C_3$-$C_{20}$)alpha-olefin (comonomer(s)) to give the ethylene/($C_3$-$C_{20}$)alpha-olefin copolymer composition