**ABSTRACT**

The present disclosure relates to a process for the preparation of an ultra-high molecular weight (UHMW) polyolefin using aged Ziegler Natta catalyst system. The polyolefin prepared in accordance with the process of the present disclosure is characterized by a molecular weight ranging between 3 and 13 million g/ mole, a bulk density ranging between 0.1 and 0.36 g/cc, an average particle size ranging between 150 and 250 microns, a molecular weight distribution ranging between 7and 12; and a crystallinity ranging between 55 and 60%.

**We claim,**

1. A process for the preparation of a polyolefin; said process comprising the following steps:

   A. preparing a heterogeneous Ziegler-Natta catalyst system comprising:

      a. at least one pro- catalyst comprising:

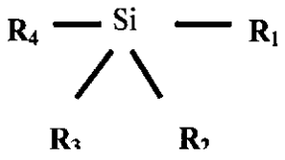
         i. at least one titanium halide as a catalyst; and

         ii. at least one magnesium compound as a base,

      b. at least one co-catalyst comprising at least one organo-aluminum compound,

      c. at least one hydrocarbon medium in an amount ranging between 0.4 and 0.6 L per 0.1 mmole of the catalyst,

      d. at least one external donor comprising at least one organo-silane compound of Formula I,




Formula I

wherein $R_1$, $R_2$, $R_3$ and $R_4$ of said organo-silane compound is at least one selected from the group consisting of $C_1$-$C_{14}$ branched or straight chain alkyl, $C_1$-$C_{14}$ branched or straight chain alkyl oxy, substituted or unsubstituted aryl, substituted or unsubstituted aryl oxy, $C_4$-$C_{14}$ cyclic alkyl and $C_4$-$C_{14}$ cyclic alkyl oxy,

said heterogeneous Ziegler-Natta catalyst system characterized in that:

i. the ratio of the elemental magnesium to the elemental titanium to halide in the pro-catalyst is 1: 1.3: 3.7;

ii the ratio of the elemental aluminum, present in said organo-aluminum compound to the elemental titanium, present in said pro-catalyst, ranges between 6:1 and 12: 1; and

iii. the ratio of the elemental silicon, present in said organo-silane compound to elemental titanium, present in said pro-catalyst, ranges between 1:10 and 10: 1,

B. ageing the heterogeneous Ziegler-Natta catalyst system at a temperature ranging from 10°C to 50 °C for a time period ranging between 1 and 11 days in presence of inert gas to obtain an aged heterogeneous Ziegler-Natta catalyst system; and

C. mixing the aged heterogeneous Ziegler-Natta catalyst system and at least one monomer at a temperature ranging between 30 °C and 125 °C, at a pressure ranging between 1 bar and 10 bars, followed by agitating at a speed ranging between 300 and 700 revolutions per minute to obtain a polyolefin, wherein the ratio of said catalyst system and said monomer ranges between 1:20 and 1:220,

said polyolefin being characterized by:

- a molecular weight ranging between 3 and 13 million g/ mole;
- a bulk density ranging between 0.1 and 0.36 g/cc;
- an average particle size ranging between 150 and 250 microns;
- a molecular weight distribution ranging between 7and 12; and
- a crystallinity ranging between 55 and 60%.

2. The process as claimed in claim 1, wherein the method step of preparing a heterogeneous Ziegler-Natta catalyst system comprises the following steps:

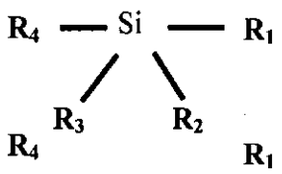
i. titanating at least one magnesium compound with at least one titanium halide, followed by allowing said titanium halide to bond with said magnesium compound, to obtain a mixture comprising at least one pro- catalyst; wherein

the ratio of the elemental magnesium to the elemental titanium to halide is 1: 1.3: 3.7;

ii. separating, washing said mixture to obtain a pro-catalyst;

iii. admixing said pro-catalyst and at least one organo-aluminum compound as a co-catalyst, in presence of at least one hydrocarbon medium, to obtain an activated catalyst, wherein the ratio of elemental aluminum, present in said organo-aluminum compound to elemental titanium, present in said pro-catalyst, ranges between 6: 1 and 12: 1; and

iv. adding, in a controlled manner, at least one organo-silane compound of Formula 1 as an external donor to said activated catalyst in presence of at least one hydrocarbon medium, under inert conditions, at a temperature ranging between 25°C and 35°C and over a time period ranging between 2 and 10 minutes to obtain a heterogeneous Ziegler-Natta catalyst system, wherein the ratio of elemental silicon, present in said organo-silane compound to elemental titanium, present in said procatalyst, ranges between 1: 10 and 10: 1,




Formula I

wherein, R1, R2, R3 and R4 of said organo-silane compound is at least one selected from the group consisting of C1-C14 branched or straight chain alkyl, C1-C14 branched or straight chain alkyl oxy, substituted or unsubstituted aryl, substituted or unsubstituted aryl oxy, C4-C14 cyclic alkyl and C4-C14 cyclic alkyl oxy.

3. The process as claimed in claim 1, wherein said titanium halide is at least one selected from the group consisting of titanium chloride, titanium bromide, titanium iodide and titanium fluoride.

4. The process as claimed in claim 1, wherein the titanium halide is titanium chloride.

5. The process as claimed in claim 1, wherein said magnesium compound is at least one selected from the group consisting of magnesium halide, magnesium oxide, magnesium hydroxyl halides, magnesium alkoxide and magnesium salts of inorganic oxygen containing acids.

6. The process as claimed in claim 1, wherein the magnesium compound is magnesium halide.

7. The process as claimed in claim 1, wherein said organo-aluminum compound is at least one selected from the group consisting of triethyl aluminum, tridecyaluminum, tri-n-butyl aluminum, tri-isopropyl aluminum, tri-isoprenyl aluminum, tri-isobutyl aluminum hydride, ethyl aluminumsesquichloride, diethyl aluminum chloride, di-isobutyl aluminum chloride, triphenyl aluminum, tri-n-octyl aluminum and tri-n-decyl aluminum.

8. The process as claimed in claim 1, wherein the organo-aluminum compound is triethyl aluminum.

9. The process as claimed in claim 1, wherein said hydrocarbon medium is at least one selected from the group consisting of pentane, hexane, cyclohexane, methyl cyclohexane, heptane, octane, decane, isopentane, and varsol.

10. The process as claimed in claim 1, wherein the hydrocarbon medium is varsol.

11. The process as claimed in claim 1, wherein said monomer is at least one selected from the group consisting of ethylene, propylene, butylene and alpha olefins.

12. The process as claimed in claim 1, wherein the monomer is ethylene.

13. The process as claimed in claim 1, wherein the mixing of the aged heterogeneous Ziegler-Natta catalyst system with at least one monomer is carried out at a temperature ranging between 70°C and 80°C.

Dated this 26th day of September, 2013

**MOHAN DEWAN**
**of R. K. DEWAN & CO.**
**APPLICANT'S PATENT ATTORNEY**

This application is a Divisional Patent Application to the Indian Patent Application No.3737/MUM/2012 field on 31st December, 2012 the entire contents of which are specifically incorporated herein by reference.

**FIELD OF THE DISCLOSURE**

The present disclosure relates to a process for the polymerization of an olefin using a heterogeneous Ziegler-Natta catalyst system.

**BACKGROUND**

Ultra-high molecular weight (UHMW) polyolefin, especially UHMW polyethylene, with a molecular weight of $1\times10^6$g/mol (gram per mole) or higher, is a commercially desired polymer because of its toughness and high impact strength, which is mainly influenced by the length of the molecular chain. The long molecular chain serves to transfer load more effectively to the polymer back-bone by strengthening the intermolecular interactions. Further, polymers with long molecular chains are highly resistant to corrosive chemicals with the exception of oxidizing acids, have extremely low moisture absorption capability and coefficient of friction, are self-lubricating and are highly resistant to abrasion. Based on the aforementioned unique properties, UHMW polyolefins have been employed for variety of important commercial uses such as protection fabrics, joint replacement materials and micro porous films.

Various conventional olefin polymerization processes are generally carried out in the presence of either homogenous or heterogeneous Ziegler-Natta catalyst systems. A heterogeneous Ziegler-Natta catalyst system is prepared by the activation of a Magnesium-Titanium (Mg-Ti) base by adding an organo- aluminum co-catalyst. To improve the activity of the catalyst and also to achieve and enhance polymer characteristics, either an internal electron donor compound is added to Mg support before the activation of the catalyst or an external electron donor compound is added after the activation of the catalyst. Both the

donors are mainly added to stabilize the geometry of the titanium ($Ti^{+3}$) ion which governs the molecular weight of the polymerized olefin besides controlling certain other polymer characteristics. In comparison, a homogeneous Single Site catalyst system includes a complex of different organic ligands with one of Titanium (Ti), Zirconium (Zr) and Hafnium (Hf) etc. which can result in metallocenes, where cyclopentadiene is used and non-metallocenes, where cyclopentadiene is absent. The homogeneous single site catalyst system further includes a co-catalyst such as methylaluminoxane (also known as methylalumoxane). However the use of methylaluminoxane as the co-catalyst results in fouling of the polymerization unit.

As Titanium ($Ti^{+3}$) ions play an important role in the polymerization process, efforts have been directed towards modification of Ziegler-Natta catalyst systems, especially by using electron donors which play an important role in the stabilization of $Ti^{+3}$ ions in an activated catalyst and facilitate an increase in the length of the polymer chain. A variety of compounds have been explored as internal and/ or external electron donors for modification of the heterogeneous Ziegler-Natta catalyst system.

US4962167, US6559249 and US2011/0159287 disclose catalyst compositions containing a Mg-ethoxide-Ti-tetrabutoxide base with an organoaluminum co-catalyst, with electron donor groups such as alcohols, ethers, esters, silanes and amines, for the preparation of UHMW polyethylene. The use of the catalyst compositions disclosed in these patent documents for the polymerization reaction result in increase in bulk density, intrinsic viscosity as well as molecular weight of the resulting UHMW polymer with a narrow molecular weight distribution.

CA2057688 discloses a process for the preparation of polyolefins, such as polyethylene, using a catalyst composition that includes a pro-catalyst based on a titanium compound and triethylaluminum as a co-catalyst and an organosilane compound as an external donor. The

catalyst is prepared by mixing triethylaluminum, organosilane compound as an external donor and anhydrous heptane followed by addition of the solid pro-catalyst.

WO2012119953 discloses a process for the preparation of UHMW polyethylene by blending two low molecular weight polyethylene resins, prepared by polymerization of ethylene in the presence of a Ziegler-Natta catalyst composition containing titanium compound supported on Mg-alkoxide along with triethylaluminum (TEAL) as a co-catalyst. The catalyst is prepared by the addition of halogenating/titanating agent in three successive addition steps followed by the addition of a co-catalyst.

EP607771 discloses a process for the preparation of polypropylene by polymerization of propylene using a Ziegler-Natta catalyst composition that includes Mg-Ti base, triethylaluminum as a co-catalyst and di-t-butyl dimethoxysilane as an external donor. The Ziegler-Natta catalytic composition is prepared by addition of a mixture comprising donor and said co-catalyst to the Mg-Ti base that is then added to the polymerization process.

EP1877450 discloses a process for the preparation of an olefinic polymer comprising contacting at least one olefinic monomer with a carbon chain consisting of more than three carbon atoms in the presence of Ziegler-Natta catalyst composition consisting of Titanium compound on Mg support, trialkylaluminum as a co-catalyst and a mixture of two silane compounds as an electron donor. The catalytic composition is prepared by the addition of the co-catalyst followed by the addition of the mixture comprising donors, to the Mg-Ti base.

WO1997043321 discloses a process for the preparation of polypropylene, in the presence of Ziegler-Natta catalyst composition comprising Ti supported on $MgCl_2$ base, (TEAL) as a co-catalyst and two or more external electron donors that consist of a mixture of at least two silane compounds. The catalyst composition is prepared by the addition of a co-catalyst

followed by the addition of a mixture comprising external donors to the Mg-Ti catalyst support.

IN231212 and IN239275 disclose processes for the preparation of polypropylene used for coating purposes by employing Ziegler-Natta catalyst composition that consists of titanium-containing solid components, an organo aluminum, magnesium or titanium compound as a co-catalyst and an external donor of formula R x R' y Si(MeO) 4-x-y'.

Most of the prior art reveals various polymerization processes using heterogeneous Ziegler-Natta catalyst systems. However, none of the aforementioned processes demonstrate any significant increase in the molecular weight and physicochemical properties of the resulting polyolefin. Further, these processes are not effective in reducing the intermolecular topological interactions or entanglements in the polyolefin. Therefore, there exists a need to develop a novel and economic heterogeneous Ziegler-Natta catalyst system having better control over the polymerization process in order to obtain an ultra-high molecular weight polyolefin having disentangled chain with a high degree of chain alignment without fouling of the reactor.

**DEFINITIONS**

As used in the present disclosure, the following words and phrases are generally intended to have the meaning as set forth below, except to the extent that the context in which they are used to indicate otherwise.

The term "ASTM scale" as used herein indicates a standard method (ASTM D-4020-01a) used to calculate molecular weight of polyolefin prepared by the polymerization process of the present disclosure based on the intrinsic viscosity of a 0.02% solution at a temperature of 135°C and using the equation $M=K[\acute{\eta}]^{\alpha}$; where $\acute{\eta}$ is the intrinsic viscosity, K = 53700 and $\alpha$ = 1.37.

The term 'titanating' as used herein indicates the incorporation of titanium in support materials like magnesium chloride through reaction with reagents like titanium halides.

**OBJECTS**

Some of the objects of the present disclosure, which at least one embodiment is able to achieve, are discussed herein below.

It is an object of the present disclosure to provide a process for the preparation of UHMW polyolefin.

It is another object of the present disclosure to provide a process for the preparation of UHMW polyolefin using a heterogeneous Ziegler-Natta catalyst system.

It is still another object of the present disclosure to provide a process for the preparation of UHMW polyolefin that is simple, economical and environment friendly.

It is yet another object of the present disclosure to provide a process for the preparation of UHMW polyolefin that obviates fouling of a polymerization unit.

It is a further object of the present disclosure to provide an UHMW polyolefin which is ductile.

It is still further object of the present disclosure to provide an UHMW polyolefin having disentangled chain with a high degree of chain alignment.

It is still further object of the present disclosure to provide an UHMW polyolefin having a porous and fibrous morphology.

It is still further object of the present disclosure to provide an UHMW polyolefin with low bulk density and enhanced crystallinity.

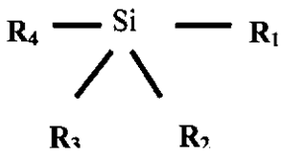
It is even further object of the present disclosure to ameliorate one or more problems of the prior art or to at least provide a useful alternative.

Other objects and advantages of the present disclosure will be more apparent from the following description which is not intended to limit the scope of the present disclosure.

**SUMMARY**

In accordance with one aspect of the present disclosure there is provided a process for the preparation of a polyolefin; said process comprising the following steps:

A. preparing a heterogeneous Ziegler-Natta catalyst system comprising:
   a. at least one pro- catalyst comprising:
      i. at least one titanium halide as a catalyst; and
      ii. at least one magnesium compound as a base,
   b. at least one co-catalyst comprising at least one organo-aluminum compound,
   c. at least one hydrocarbon medium in an amount ranging between 0.4 and 0.6 L per 0.1 mmole of the catalyst,
   d. at least one external donor comprising at least one organo-silane compound of Formula I,




Formula I

wherein $R_1$, $R_2$, $R_3$ and $R_4$ of said organo-silane compound is at least one selected from the group consisting of $C_1$-$C_{14}$ branched or straight chain alkyl, $C_1$-$C_{14}$ branched or straight chain alkyl oxy, substituted or unsubstituted aryl, substituted or unsubstituted aryl oxy, $C_4$-$C_{14}$ cyclic alkyl and $C_4$-$C_{14}$ cyclic alkyl oxy,

said heterogeneous Ziegler-Natta catalyst system characterized in that:

i. the ratio of the elemental magnesium to the elemental titanium to halide in the pro-catalyst is 1: 1.3: 3.7;

ii the ratio of the elemental aluminum, present in said organo-aluminum compound to the elemental titanium, present in said pro-catalyst, ranges between 6:1 and 12: 1; and

iii the ratio of the elemental silicon, present in said organo-silane compound to elemental titanium, present in said pro-catalyst, ranges between 1:10 and 10: 1,

B. ageing the heterogeneous Ziegler-Natta catalyst system at a temperature ranging from 10°C to 50 °C for a time period ranging between 1 and 11 days in presence of inert gas to obtain an aged heterogeneous Ziegler-Natta catalyst system; and

C. mixing the aged heterogeneous Ziegler-Natta catalyst system and at least one monomer at a temperature ranging between 30 °C and 125 °C, at a pressure ranging between 1 bar and 10 bars, followed by agitating at a speed ranging between 300 and 700 revolutions per minute to obtain a polyolefin, wherein the ratio of said catalyst system and said monomer ranges between 1:20 and 1:220,

said polyolefin being characterized by:

- a molecular weight ranging between 3 and 13 million g/ mole;
- a bulk density ranging between 0.1 and 0.36 g/cc;
- an average particle size ranging between 150 and 250 microns;
- a molecular weight distribution ranging between 7and 12; and
- a crystallinity ranging between 55 and 60%.

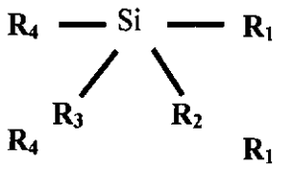
Typically, the method step of preparing a heterogeneous Ziegler-Natta catalyst system comprises the following steps:

i. titanating at least one magnesium compound with at least one titanium halide, followed by allowing said titanium halide to bond with said magnesium compound, to obtain a mixture comprising at least one pro- catalyst; wherein the ratio of the elemental magnesium to the elemental titanium to halide is 1: 1.3: 3.7;

ii. separating, washing said mixture to obtain a pro-catalyst;

iii. admixing said pro-catalyst and at least one organo-aluminum compound as a co-catalyst, in presence of at least one hydrocarbon medium, to obtain an activated catalyst, wherein the ratio of elemental aluminum, present in said organo-aluminum compound to elemental titanium, present in said pro-catalyst, ranges between 6: 1 and 12: 1; and

iv. adding, in a controlled manner, at least one organo-silane compound of Formula 1 as an external donor to said activated catalyst in presence of at least one hydrocarbon medium, under inert conditions, at a temperature ranging between 25°C and 35°C and over a time period ranging between 2 and 10 minutes to obtain a heterogeneous Ziegler-Natta catalyst system, wherein the ratio of elemental silicon, present in said organo-silane compound to elemental titanium, present in said procatalyst, ranges between 1: 10 and 10: 1




Formula I

wherein, R1, R2, R3 and R4 of said organo-silane compound is at least one selected from the group consisting of C1-C14 branched or straight chain alkyl, C1-C14 branched or straight chain alkyl oxy, substituted or unsubstituted aryl, substituted or unsubstituted aryl oxy, C4-C14 cyclic alkyl and C4-C14 cyclic alkyl oxy.

Typically, said titanium halide is at least one selected from the group consisting of titanium chloride, titanium bromide, titanium iodide and titanium fluoride.

In accordance with one of the embodiments of the present disclosure, the titanium halide is titanium chloride.

Typically, said magnesium compound is at least one selected from the group consisting of magnesium halide, magnesium oxide, magnesium hydroxyl halides, magnesium alkoxide and magnesium salts of inorganic oxygen containing acids.

In accordance with one embodiment of the present disclosure the magnesium compound is magnesium halide.

Typically, said organo-aluminum compound is at least one selected from the group consisting of triethyl aluminum, tridecyaluminum, tri-n-butyl aluminum, tri-isopropyl aluminum, tri-isoprenyl aluminum, tri-isobutyl aluminum hydride, ethyl aluminumsesquichloride, diethyl aluminum chloride, di-isobutyl aluminum chloride, triphenyl aluminum, tri-n-octyl aluminium and tri-n-decyl aluminum.

In accordance with one embodiment of the present disclosure the organo-aluminium compound is triethyl aluminium.

Typically, said hydrocarbon medium is at least one selected from the group consisting of pentane, hexane, cyclohexane, methyl cyclohexane, heptane, octane, decane, isopentane, and varsol.

In accordance with one embodiment of the present disclosure the hydrocarbon medium is varsol.

Typically, said monomer is at least one selected from the group consisting of ethylene, propylene, butylene and alpha olefins.

In accordance with one embodiment of the present disclosure the monomer is ethylene.

Typically, the mixing of the aged heterogeneous Ziegler-Natta catalyst system with at least one monomer is carried out at a temperature ranging between 70°C and 80°C.

**DETAILED DESCRIPTION**

Among the various heterogeneous catalysts, Ziegler-Natta catalyst system is a preferred catalyst for the preparation of polyolefins and particularly in the preparation of ultra-high molecular weight (UHMW) polyolefins for several reasons which include better control over the reaction, ability to produce polymers with a high molecular weight, improved bulk density, better adaptability in commercial plant set ups, lower specific consumption of costly co-catalysts and the like. However, currently available Ziegler-Natta catalyst systems when used for preparing the ultra-high molecular weight (UHMW) polyolefins produce highly entangled polyolefins which are difficult to process into high strength products like film, filaments, tapes and other molded articles.

Therefore, in order to obviate the problems regarding the intermolecular topological interactions and entanglements in the polyolefin, the inventors of the present disclosure developed a Ziegler Natta catalyst system containing a pro-catalyst, a co-catalyst and an external donor.

The inventors of the present disclosure observed that the external donor uniquely modify Ti catalyst and Mg support sites of the pro-catalyst to bring out unique electronic and geometrical environments. The inventors also observed that the co-catalyst present in the Ziegler Natta catalyst system reduces tetravalent Ti catalyst to trivalent Ti catalyst.

While conducting several experiments using the aforementioned Ziegler Natta catalyst system, the inventors surprisingly found that the polymerization of monomers using the aged Ziegler Natta catalyst system produces UHMW polyolefin with significant improvement in "chain disentanglement" and porosity.

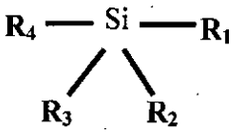
Accordingly, in the first aspect of the present disclosure there is provided a process for the preparation of a polyolefin using aged Ziegler Natta catalyst system.

In the first step, a heterogeneous Ziegler-Natta catalyst system comprising at least one pro-catalyst, at least one co-catalyst, at least one hydrocarbon medium and at least one external donor is prepared.

The pro-catalyst used in the preparation of the Ziegler-Natta catalyst system comprises at least one titanium halide as a catalyst and at least one magnesium compound as a base. The ratio of the elemental magnesium to the elemental titanium and to halide is maintained at 1: 1.3: 3.7.

The co-catalyst of the Ziegler-Natta catalyst system comprises at least one organo-aluminum compound and the ratio of elemental aluminum, present in the organo-aluminum compound to elemental titanium, present in the pro- catalyst, ranges between 6:1 and 12:1and.

The organo-silane compound of the Ziegler-Natta catalyst system is represented by Formula 1 and it acts as an external donor.




Formula I

wherein $R_1$, $R_2$, $R_3$ and $R_4$ of said organo-silane compound is at least one selected from the group consisting of $C_1$-$C_{14}$ branched or straight chain alkyl, $C_1$-$C_{14}$ branched or straight chain alkyl oxy, substituted or unsubstituted aryl, substituted or unsubstituted aryl oxy, $C_4$-$C_{14}$ cyclic alkyl and $C_4$-$C_{14}$ cyclic alkyl oxy.

The organo-silane compound is at least one selected from the group consisting of tetraethoxysilane, cyclohexylmethyldimethoxysilane, dicyclopentyldimethoxysilane, isobutylisopropyldimethoxysilane, n-propyltriethoxysilane, isobutyltriethoxysilane, phenyltriethoxysilane, diisopropyldimethoxysilane, diethyldimethoxysilane, diisobutyldimethoxysilane, aminopropyltriethoxysilane, diphenyldimethoxysilane and methyltrimethoxysilane.

The ratio of the elemental silicon, present in the organo-silane compound to the elemental titanium, present in the pro-catalyst, ranges between 1:10 and 10:1.

In the second step, the Ziegler-Natta catalyst system is subjected to ageing at a temperature ranging from 10 °C to 50 °C for a time period ranging between 1 and 11 days in presence of inert gas to obtain an aged heterogeneous Ziegler-Natta catalyst system.

In the third step, the aged Ziegler-Natta catalyst system is mixed with a monomer, at a temperature ranging between 30 °C and 125°C, at a pressure ranging between 1 bar and 10 bars with agitating at a speed ranging between 300 and 700 revolutions per minute to obtain a polyolefin. The aged Ziegler-Natta catalyst system is taken in such an amount that the ratio of the aged Ziegler-Natta catalyst system to the monomer is maintained in the range of 1:20 to 1:220.

In accordance with one of the embodiment of the present disclosure the aged Ziegler-Natta catalyst system is mixed with the monomer at a temperature ranging between 70 °C and 80 °C to obtain a polyolefin.

The monomer polymerized into polymer is at least one selected from the group consisting of ethylene, propylene, butylene and alpha olefins.

In accordance with one of the exemplary embodiments of the present disclosure the monomer is ethylene.

The polyolefin prepared by the process of the present disclosure is an ultra-high molecular weight polyolefin having:

- a molecular weight ranging between 3 and 13million g/ mole (on the ASTM basis),
- a porous and fibrous morphology,
- a bulk density ranging between 0.10 and 0.36g/cc ,
- a crystallinity ranging between 55 and 60%,
- an average particle size ranging between 150 and 250microns,
- a molecular weight distribution lowering by more than 20% , and ranging between 7 and 12.

In accordance with the present disclosure there is also provided a process for the preparation of a heterogeneous Ziegler-Natta catalyst system. The first step includes titanating one or more magnesium compounds with the titanium halide to obtain a mixture comprising at least one pro-catalyst. The mixture so obtained is then separated, washed to obtain a pro- catalyst. The ratio of the elemental magnesium to the elemental titanium and to halide in the pro-catalyst is 1: 1.3: 3.7.

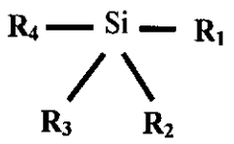
The titanium halide used for titanating the magnesium compound is at least one selected from the group consisting of titanium chloride, titanium bromide and titanium iodide.

The magnesium compound titanated in the first step is at least one selected from the group consisting of magnesium halide, a magnesium oxide, magnesium alkoxide, a magnesium hydroxyl halide and a magnesium salt of inorganic oxygen containing acids.

In the second step, the pro-catalyst is admixed with at least one organo-aluminum compound as a co-catalyst, and at least one hydrocarbon medium, to obtain an activated catalyst. The ratio of elemental aluminum, present in said organo-aluminum compound to the elemental titanium, present in said pro-catalyst, ranges between 6:1 and 12:1

The organo-aluminum compound used as a co-catalyst is selected from the group consisting of triethylaluminum, tridecyaluminum, tri-n-butyl aluminum, tri-isopropyl aluminum, tri-isoprenyl aluminum, tri-isobutyl aluminum hydride, ethyl aluminum sesquichloride, diethyl aluminum chloride, di-isobutyl aluminum chloride, triphenyl aluminum, tri-n-octyl aluminum, tri-n-decyl aluminum and combinations thereof.

In the third step, a mixture containing at least one organo-silane compound of Formula 1 as an external donor and at least one hydrocarbon medium is added to the activated catalyst, in a controlled manner, under inert conditions, at a temperature ranging between 25 and 35°C and over a time period ranging between 2 and 6 minutes to obtain a heterogeneous Ziegler-Natta catalyst system. The organo-silane compound is represented by Formula 1 and acts as an external donor.




Formula I

wherein $R_1$, $R_2$, $R_3$ and $R_4$ of said organo-silane compound is at least one selected from the group consisting of $C_1$-$C_{14}$ branched or straight chain alkyl, $C_1$-$C_{14}$ branched or straight chain alkyl oxy, substituted or unsubstituted aryl, substituted or unsubstituted aryl oxy, $C_4$-$C_{14}$ cyclic alkyl and $C_4$-$C_{14}$ cyclic alkyl oxy.

The organo-silane compound is at least one selected from the group consisting of tetraethoxysilane, cyclohexylmethyldimethoxysilane, dicyclopentyldimethoxysilane, isobutylisopropyldimethoxysilane, n-propyltriethoxysilane, isobutyltriethoxysilane, phenyltriethoxysilane, diisopropyldimethoxysilane, diethyldimethoxysilane, diisobutyldimethoxysilane, aminopropyltriethoxysilane, diphenyldimethoxysilane and methyltrimethoxysilane. The ratio of the elemental silicon, present in the organo-silane

compound to the elemental titanium, present in the base catalyst, ranges between 1: 10 and 10:1.

The hydrocarbon medium used in the second and third step of preparing the heterogeneous Ziegler-Natta catalyst system is at least one selected from the group consisting of pentane, hexane, cyclohexane, methyl cyclohexane, heptane, octane, nonane, decane, isopentane and and varsol.

The Ziegler-Natta catalyst system prepared in accordance with the present disclosure includes a pro-catalyst containing titanium chloride as a catalyst and magnesium halide as a base, triethyl aluminium as a co-catalyst, varsol as a hydrocarbon medium and organosilane compound of Formula I as an external donor.

The present disclosure will be discussed in the light of the following non-limiting embodiments:

**Example 1: Preparation of UHMW polyolefins using the Ziegler Natta catalyst system without external donor.**

0.185 mmole of the pro-catalyst (slurry in hexane) having a composition of Mg:Ti:Cl :: 1:1.3:3.7 was mixed with a mixture containing 2.04 mmole of co-catalyst, TEAL(10% solution in hexane), and 0.5 L of the hydrocarbon medium, varsol at a temperature of 28 to $35^0$ C and to obtain a Ziegler Natta catalyst system.

Polymerization of Ethylene monomer was carried out using freshly prepared Ziegler Natta catalyst system at pressure ranging between 2 to 7.5 bars, at a temperature of $75^OC$, agitation at 500 rpm for a time period of 2.25 hours. The results obtained are given below in Table 1(a) and Table 1(b).

Table 1(a)

| | Catalyst preparation | | | | | Polymerization | | | |
|---|---|---|---|---|---|---|---|---|---|
| SR. No. | Ti from catalyst (mmole) (A) | Al from TEAL (mmol) (B) | Silane donor (mmole) (C) | Mode of addition (D) | Ageing (Days) | Varsol (Liter) (E) | Al/TI | Si donor/Ti | Yield (g/g cat) |
| 1 | 0.185 | 2.04 | 0 (control) | E+B+A | 0 (control) | 0.5 | 11 | 0 (control) | 5469 |

Table 1(b)

| | UHMWPE characteristics | | | |
|---|---|---|---|---|
| SR. No. | Bulk density (g/cc) | IV (dl/g) | MW (M) [ASTM] | Morphology (by SEM) |
| 1 | 0.3534 | 21.5 | 3.6 | Dense solid particles |

**Example 2: Preparation of UHMW polyolefins using the Ziegler Natta catalyst system containing external donor.**

0.185 mmole of the pro-catalyst (slurry in hexane) having a composition of Mg:Ti:Cl :: 1:1.3:3.7 was mixed with a mixture containing 2.04 mmole of co-catalyst, TEAL(10% solution in hexane), and 0.5 L of the hydrocarbon medium, varsol at a temperature of 28 to 35$^0$ C to obtain an activated catalyst. 0.74 mmole of tetraethoxy silane (TEOS) (10% solution in hexane) was then added the activated catalyst to obtain a Ziegler Natta catalyst system.

Polymerization of Ethylene monomer using the freshly prepared Ziegler Natta catalyst system was carried out at pressure ranging between 2 to 2.5 bars, at a temperature of 75$^0$ C and at an agitation speed of 500 rpm for a time period of 2.25 hours. The results obtained are given below in Table 2(a) and Table 2(b).

Table 2(a):

| | Catalyst preparation | | | | | Polymerization | | | |
|---|---|---|---|---|---|---|---|---|---|
| SR. No. | Ti from catalyst (mmole) (A) | Al from TEAL (mmole) (B) | TEOS donor (mmole) (C) | Mode of addition (D) | Ageing (Days) | Varsol (L) (E) | Al/ TI | Si donor/Ti | Yield (g/g cat) |
| 1 | 0.185 | 0.01 | 0.74 | A+B+C to E containing 2.04 mmole of TEAL | 0 (control) | 0.5 | 11 | 4 | 2096 |

Table 2(b)

| | UHMWPE characteristics | | | |
|---|---|---|---|---|
| SR. No. | Bulk density (g/cc) | IV (dl/g) | MW (M) [ASTM] | Morphology (By SEM) |
| 1 | 0.3112 | 28.2 | 5.2 | Dense solid particles |

**Example 3:** Preparation of UHMW polyolefin using aged Ziegler Natta catalyst system.

0.185 mmole of the pro-catalyst (slurry in hexane) having a composition of Mg:Ti:Cl :: 1:1.3:3.7 was mixed with a mixture containing 2.04 mmole of co-catalyst, TEAL(10% solution in hexane), and 0.5 L of the hydrocarbon medium, varsol at a temperature of 28 to $35^0$ C to obtain an activated catalyst. 0.74 mmole of tetraethoxy silane (TEOS) (10% solution in hexane) was then added the activated catalyst to obtain a Ziegler Natta catalyst system.

The Ziegler Natta catalyst system so obtained was then aged for a time period of 1 to 11days at a temperature of 30°C in the presence of nitrogen gas to obtained aged Ziegler Natta catalyst system.

Polymerization of Ethylene monomer using the aged Ziegler Natta catalyst system was carried out at pressure ranging between 2 to 2.5 bars, at a temperature of 75° C and at an agitation speed of 500rpm for a time period of 2.25 hours. The results obtained are given below in Table 3(a) and Table 3(b).

Table 3(a)

| | Catalyst preparation | | | | | Polymerization | | | |
|---|---|---|---|---|---|---|---|---|---|
| SR. No. | Ti from catalyst (mmole) (A) | Al from TEAL (mmole) (B) | TEOS donor (mmole) (C) | Mode of addition (D) | Agein g (Days) | Varsol (L) (E) | Al/ TI | Si donor/Ti | Yield (g/g cat) |
| 1 | 0.185 | 0.01 | 0.74 | A+B+C to E containing 2.03 mmole of TEAL | 1 | 0.5 | 11 | 4 | 682 |
| 2 | 0.185 | 0.01 | 0.74 | A+B+C to E containing 2.03 mmole of TEAL | 11 | 0.5 | 11 | 4 | 101 |
| 3 | 0.173 | 1.90 | 0.69 | A+B+C to E containing 0.69 mmole of TEAL | 1 | 0.5 | 15 | 4 | 57 |
| 4 | 0.185 | 0.36 | 0.74 | A+B+C to E containing 1.3 mmole of TEAL | 1 | 0.5 | 9 | 4 | 270 |
| 5 | 0.185 | 0.01 | 0.18 | A+B+C to E containing 2.03 mmole of TEAL | 2 | 0.5 | 11 | 1 | 270 |
| 6 | 0.185 | 0.04 | 0.36 | A+B+C to E containing 2 mmole of TEAL | 2 | 0.5 | 11 | 2 | 81 |
| 7 | 0.185 | 0.02 | 0.09 | A+B+C to E containing 2.02 mmole of TEAL | 1 | 0.5 | 11 | 0.5 | 2568 |
| 8 | 0.185 | 0.36 | 0.18 | A+B+C to E containing 1.68 mmole of TEAL | 1 | 0.5 | 11 | 1 | 2298 |
| 9 | 0.370 | 0.72 | 1.48 | A+B+C to E containing 2.61 mmole of TEAL | 1 | 0.5 | 9 | 4 | 1054 |

Table 3(b)

| S.No. | Characteristics of UHMWPE | | | | |
|---|---|---|---|---|---|
| | Bulk density (g/cc) | Intrinsic viscosity IV (dl/g) | Molecular Weight (M) [ASTM] | % crystallinity by DSC (vs. 51.3% for control expt.) | Morphology (By SEM) |
| 1 | 0.2940 | 29.6 | 5.6 | 62.9 | Porous particles |
| 2 | 0.2095 | 31.7 | 6.1 | 62.7 | Porous particles |
| 3 | 0.1073 | 46.5 | 10.3 | 61.8 | Porous particles |
| 4 | 0.1211 | 29.6 | 5.6 | 56.3 | Porous particles |
| 5 | 0.1190 | 29.6 | 5.6 | 59 | Porous particles |
| 6 | 0.1096 | 35.9 | 7.3 | 60.3 | Porous particles |
| 7 | 0.2196 | 14.1 | 2.0 | 57.6 | Porous particles |
| 8 | 0.3398 | 23.9 | 4.2 | 57.4 | Porous particles |
| 9 | 0.2601 | 37,5 | 7.7 | 60.3 | Porous particles |

Example 4: Narrowing of molecular weight distribution (MWD) of UHMWPE using the Ziegler Natta catalyst system of the present disclosure.

The Ziegler Natta catalyst system prepared in accordance with the example 3 was aged for 2 days at a temperature of 30°C in the presence of nitrogen gas to obtained aged Ziegler Natta catalyst system.

Polymerization of Ethylene monomer using the aged Ziegler Natta catalyst system was carried out at pressure ranging between 2 to 2.5 bars, at a temperature of 75° C and at an

agitation speed of 500rpm for a time period of 2.25 hours. The molecular weight distribution of the polymer was found to be 20% lower with donor modified aged catalyst as compared to the Ziegler Natta catalyst system prepared in accordance with example 1. The results obtained are given below in Table 4.

Table 4

| | **ageing** | **MW of UHMWPE** | **MWD of UHMWPE** |
|---|---|---|---|
| Ziegler Natta catalyst system without donor | None | 4.09 Million | 14.91 |
| Ziegler Natta catalyst system with donor (D/Ti = 4.0) | 2 days | 4.47 Million | 11.90 |

Molecular weight distribution of UHMW polyethylene sample was determined using a Rheometric Dynamic Analyzer (RDA).

In the first step the melt rheology data for the UHMW polyethylene samples were obtained using the Rheometric Dynamic Analyzer maintained at a frequency ranging between 0.01 and 100 rad/s. The UHMW polyethylene samples used were maintained at a temperature of $19^0$ C and under strain of 2%. The melt rheology data so obtained was then used to determine the molecular weight and molecular weight distribution of the UHMW polyethylene samples, using Orchestrator software

The embodiments herein and the various features and advantageous details thereof are explained with reference to the non-limiting embodiments in the description. Descriptions of well-known components and processing techniques are omitted so as to not unnecessarily obscure the embodiments herein. The examples used herein are intended merely to facilitate

an understanding of ways in which the embodiments herein may be practiced and to further enable those of skill in the art to practice the embodiments herein. Accordingly, the examples should not be construed as limiting the scope of the embodiments herein.

The foregoing description of the specific embodiments will so fully reveal the general nature of the embodiments herein that others can, by applying current knowledge, readily modify and/or adapt for various applications such specific embodiments without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. Therefore, while the embodiments herein have been described in terms of preferred embodiments, those skilled in the art will recognize that the embodiments herein can be practiced with modification within the spirit and scope of the embodiments as described herein.

**TECHNICAL ADVANTAGES AND ECONOMIC SIGNIFICANCE**

The polyolefin prepared in accordance with the process of the present disclosure has very high molecular weight and intrinsic viscosity with lower bulk density due to disentanglement of the polymer chains

Further, the polyolefin prepared in accordance with the process of the present disclosure has lower molecular weight distribution.

Even further, the polyolefin prepared in accordance with the process of the present disclosure has disentangled chain with a high degree of chain alignment.

Even further, the polyolefin prepared in accordance with the process of the present disclosure has a unique fibrous and porous morphology.

Even further, the process of the present disclosure obviates the use of costly single site/ metallocene catalyst systems and methylalumoxane as activator to prepare UHMW polyolefin with porous morphology under cryogenic conditions, thereby making the process economical and environment friendly.

Still further, the use of the Ziegler-Natta catalyst prepared in accordance with the process of the present disclosure prevents fouling of the polymerization unit.

Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

The use of the expression "at least" or "at least one" suggests the use of one or more elements or ingredients or quantities, as the use may be in the embodiment of the invention to achieve one or more of the desired objects or results.

The numerical values given for various physical parameters, dimensions and quantities are only approximate values and it is envisaged that the values higher than the numerical value assigned to the physical parameters, dimensions and quantities fall within the scope of the invention and the claims unless there is a statement in the specification to the contrary.

While certain embodiments of the inventions have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the inventions. Variations or modifications in the process or compound or formulation or combination of this invention, within the scope of the invention, may occur to those skilled in the art upon reviewing the disclosure herein. Such variations or modifications are well within the spirit of this invention. The accompanying claims and their equivalents are intended to cover such forms or modifications as would fall within the scope and spirit of the invention.

**We claim,**

1. A process for the preparation of a polyolefin; said process comprising the following steps:

   A. preparing a heterogeneous Ziegler-Natta catalyst system comprising:

      a. at least one pro- catalyst comprising:

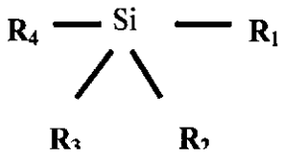
         i. at least one titanium halide as a catalyst; and

         ii. at least one magnesium compound as a base,

      b. at least one co-catalyst comprising at least one organo-aluminum compound,

      c. at least one hydrocarbon medium in an amount ranging between 0.4 and 0.6 L per 0.1 mmole of the catalyst,

      d. at least one external donor comprising at least one organo-silane compound of Formula I,




Formula I

wherein $R_1$, $R_2$, $R_3$ and $R_4$ of said organo-silane compound is at least one selected from the group consisting of $C_1$-$C_{14}$ branched or straight chain alkyl, $C_1$-$C_{14}$ branched or straight chain alkyl oxy, substituted or unsubstituted aryl, substituted or unsubstituted aryl oxy, $C_4$-$C_{14}$ cyclic alkyl and $C_4$-$C_{14}$ cyclic alkyl oxy,

said heterogeneous Ziegler-Natta catalyst system characterized in that:

i. the ratio of the elemental magnesium to the elemental titanium to halide in the pro-catalyst is 1: 1.3: 3.7;

ii the ratio of the elemental aluminum, present in said organo-aluminum compound to the elemental titanium, present in said pro-catalyst, ranges between 6:1 and 12: 1; and

iii. the ratio of the elemental silicon, present in said organo-silane compound to elemental titanium, present in said pro-catalyst, ranges between 1:10 and 10: 1,

B. ageing the heterogeneous Ziegler-Natta catalyst system at a temperature ranging from 10°C to 50 °C for a time period ranging between 1 and 11 days in presence of inert gas to obtain an aged heterogeneous Ziegler-Natta catalyst system; and

C. mixing the aged heterogeneous Ziegler-Natta catalyst system and at least one monomer at a temperature ranging between 30 °C and 125 °C, at a pressure ranging between 1 bar and 10 bars, followed by agitating at a speed ranging between 300 and 700 revolutions per minute to obtain a polyolefin, wherein the ratio of said catalyst system and said monomer ranges between 1:20 and 1:220,

said polyolefin being characterized by:

- a molecular weight ranging between 3 and 13 million g/ mole;
- a bulk density ranging between 0.1 and 0.36 g/cc;
- an average particle size ranging between 150 and 250 microns;
- a molecular weight distribution ranging between 7and 12; and
- a crystallinity ranging between 55 and 60%.

2. The process as claimed in claim 1, wherein the method step of preparing a heterogeneous Ziegler-Natta catalyst system comprises the following steps:

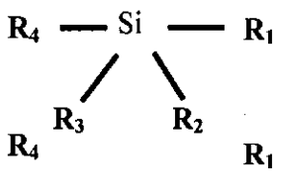
i. titanating at least one magnesium compound with at least one titanium halide, followed by allowing said titanium halide to bond with said magnesium compound, to obtain a mixture comprising at least one pro- catalyst; wherein

the ratio of the elemental magnesium to the elemental titanium to halide is 1: 1.3: 3.7;

ii. separating, washing said mixture to obtain a pro-catalyst;

iii. admixing said pro-catalyst and at least one organo-aluminum compound as a co-catalyst, in presence of at least one hydrocarbon medium, to obtain an activated catalyst, wherein the ratio of elemental aluminum, present in said organo-aluminum compound to elemental titanium, present in said pro-catalyst, ranges between 6: 1 and 12: 1; and

iv. adding, in a controlled manner, at least one organo-silane compound of Formula 1 as an external donor to said activated catalyst in presence of at least one hydrocarbon medium, under inert conditions, at a temperature ranging between 25°C and 35°C and over a time period ranging between 2 and 10 minutes to obtain a heterogeneous Ziegler-Natta catalyst system, wherein the ratio of elemental silicon, present in said organo-silane compound to elemental titanium, present in said procatalyst, ranges between 1: 10 and 10: 1,




Formula I

wherein, R1, R2, R3 and R4 of said organo-silane compound is at least one selected from the group consisting of C1-C14 branched or straight chain alkyl, C1-C14 branched or straight chain alkyl oxy, substituted or unsubstituted aryl, substituted or unsubstituted aryl oxy, C4-C14 cyclic alkyl and C4-C14 cyclic alkyl oxy.

3. The process as claimed in claim 1, wherein said titanium halide is at least one selected from the group consisting of titanium chloride, titanium bromide, titanium iodide and titanium fluoride.

4. The process as claimed in claim 1, wherein the titanium halide is titanium chloride.

5. The process as claimed in claim 1, wherein said magnesium compound is at least one selected from the group consisting of magnesium halide, magnesium oxide, magnesium hydroxyl halides, magnesium alkoxide and magnesium salts of inorganic oxygen containing acids.

6. The process as claimed in claim 1, wherein the magnesium compound is magnesium halide.

7. The process as claimed in claim 1, wherein said organo-aluminum compound is at least one selected from the group consisting of triethyl aluminum, tridecyaluminum, tri-n-butyl aluminum, tri-isopropyl aluminum, tri-isoprenyl aluminum, tri-isobutyl aluminum hydride, ethyl aluminumsesquichloride, diethyl aluminum chloride, di-isobutyl aluminum chloride, triphenyl aluminum, tri-n-octyl aluminum and tri-n-decyl aluminum.

8. The process as claimed in claim 1, wherein the organo-aluminum compound is triethyl aluminum.

9. The process as claimed in claim 1, wherein said hydrocarbon medium is at least one selected from the group consisting of pentane, hexane, cyclohexane, methyl cyclohexane, heptane, octane, decane, isopentane, and varsol.

10. The process as claimed in claim 1, wherein the hydrocarbon medium is varsol.

11. The process as claimed in claim 1, wherein said monomer is at least one selected from the group consisting of ethylene, propylene, butylene and alpha olefins.

12. The process as claimed in claim 1, wherein the monomer is ethylene.

13. The process as claimed in claim 1, wherein the mixing of the aged heterogeneous Ziegler-Natta catalyst system with at least one monomer is carried out at a temperature ranging between 70°C and 80°C.

Dated this 26th day of September, 2013

**MOHAN DEWAN**
**of R. K. DEWAN & CO.**
**APPLICANT'S PATENT ATTORNEY**