

681147
AUSTRALIA

P/00/008b 12/11/91
Section 29 (1)
Regulation 3.1 (2)

Patents Act 1990

NOTICE OF ENTITLEMENT

(To be filed before acceptance)

We, EXXON CHEMICAL PATENTS INC., of 5200 Bayway Drive, Baytown, Texas 77520, United States of America, being the applicant in respect of Application No. 67127/94 state the following:-

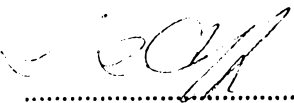
The Person nominated for the grant of the patent has entitlement from the actual inventors by assignment.

The Person nominated for the grant of the patent has entitlement from the applicant of the applications listed in the declaration under Article 8 of the PCT by assignment.

The basic applications listed in the declaration made under Article 8 of the PCT are the first applications made in a Convention country in respect of the invention.

EXXON CHEMICAL PATENTS INC.

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS


.....
Lynn P. Stafford
Registered Patent Attorney

2 April 1997



AU9467127

(12) PATENT ABRIDGMENT (11) Document No. AU-B-67127/94
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 681147

- (34) Title
PROCESS FOR POLYMERIZING MONOMERS IN FLUIDIZED BEDS
- (51)⁵ International Patent Classification(s)
C08F 010/00 C08F 002/34
- (21) Application No. : 67127/94 (22) Application Date : 25.04.94
- (87) PCT Publication Number : WO94/25497
- (30) Priority Data
- | | | |
|-------------|-----------|--|
| (31) Number | (32) Date | (33) Country |
| US 9303946 | 26.04.93 | WO WORLD INTELLECTUAL PROPERTY ORGANIZATION (WIPO) |
| 065250 | 20.05.93 | US UNITED STATES OF AMERICA |
- (43) Publication Date : 21.11.94
- (44) Publication Date of Accepted Application : 21.08.97
- (71) Applicant(s)
EXXON CHEMICAL PATENTS INC.
- (72) Inventor(s)
MARC LOUIS DEONELLIS; JOHN ROBERT GRIFFIN; MICHAEL ELROY MUHLE
- (74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122
- (57) Claim

1. A continuous gas phase polymerization process for polymerizing alpha-olefin(s) utilizing a metallocene catalyst in a gas phase fluidized bed reactor wherein a recycle stream having a liquid and a gas phase is introduced to the reactor such that the weight percent of liquid based on the total weight of the recycle stream is greater than 2.0 weight percent, and the recycle stream comprises a dew point increasing component in an amount greater than 2.0 mole percent.

28. A continuous process for the polymerization of ethylene and at least one copolymerizable alpha-olefin comonomer in a gas phase fluidized bed reactor operating in a condensed mode, said process comprising the steps of:

a) passing a recycle stream through a fluidized bed in said reactor, said recycle stream comprising a ratio of C_x/C_2 of less than 0.2, a dew point increasing component in an amount greater than 2.0 mole percent and optionally non-condensable inerts making up the balance of said recycle stream, where C_x and C_2 are the mole percent respectively of comonomer and ethylene;

b) introducing a metallocene catalyst under reactive conditions into said reactor to polymerize said recycle stream into a polymer product;

- c) withdrawing said recycle stream containing unreacted monomers from the reactor;
- d) introducing into said recycle stream additional monomers to replace monomers polymerized to maintain said ratio of said recycle stream;
- e) reintroducing said recycle stream into said reactor; and
- f) withdrawing said polymer product from said reactor.

35. A continuous process for the polymerization of ethylene and at least one copolymerizable alpha-olefin comonomer in a gas phase fluidized bed reactor, said process comprising the steps of:

- a) passing a recycle stream through said reactor, said recycle stream comprising a ratio of $(C_x + H_2)/C_2$ of less than 0.2, a dew point increasing component in an amount greater than 2.0 mole percent and non-condensable inerts making up the balance of said recycle stream, where C_x , H_2 and D_2 are the mole percent respectively of comonomer, hydrogen and ethylene;
- b) introducing a metallocene catalyst system under reactive conditions into said reactor to polymerize said recycle stream into a polymer product;
- c) withdrawing said recycle stream containing unreacted monomers from the reactor;
- d) compressing and cooling said recycle stream to form a liquid phase and a gas phase such that the weight percent of liquid based on the total weight of liquid in the recycle stream is greater than 2.0 and reintroducing said recycle stream into said reactor;
- e) introducing into said recycle stream additional monomers to replace monomers polymerized to maintain said ratio of said recycle stream, and
- f) withdrawing said polymer product from said reactor.

OPI DATE 21/11/94 APPLN. ID 67127/94
AOJP DATE 05/01/95 PCT NUMBER PCT/US94/04513



AU9467127

IN

(51) International Patent Classification ⁵ : C08F 10/00, 2/34		A1	(11) International Publication Number: WO 94/25497 (43) International Publication Date: 10 November 1994 (10.11.94)
(21) International Application Number: PCT/US94/04513 (22) International Filing Date: 25 April 1994 (25.04.94) (30) Priority Data: PCT/US93/03946 26 April 1993 (26.04.93) WO (34) Countries for which the regional or international application was filed: AT et al. 08/065,250 20 May 1993 (20.05.93) US (71) Applicant (for all designated States except US): EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): DECHELLIS, Marc, Louis [US/US]; 16702 Elm Park Way, Houston, TX 77058 (US). GRIFFIN, John, Robert [US/US]; 225 Pin Oak Drive, Baytown, TX 77520 (US). MUHLE, Michael, Elroy [US/US]; 5902 Leafy Aspen Court, Kingwood, TX 77345 (US). (74) Agents: SHER, Jaimes et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).		(81) Designated States: AU, CA, CN, JP, KR, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: PROCESS FOR POLYMERIZING MONOMERS IN FLUIDIZED BEDS			
(57) Abstract The invention is directed toward polymerizing alpha-olefins either alone or in combination with one or more other alpha-olefins utilizing a bulky ligand transition metal catalyst in a gas phase fluidized bed polymerization reactor operating in condensed mode.			

681147

- 1 -

**TITLE: PROCESS FOR POLYMERIZING MONOMERS IN
FLUIDIZED BEDS**

FIELD OF THE INVENTION

The present invention relates to a continuous process for the gas phase polymerization of olefins in a fluidized bed reactor. More particularly, the invention is directed to a gas phase polymerization process for polymerizing monomers in a fluidized bed reactor operating in a condensed mode. The invention is more specifically drawn to a condensed mode gas phase polymerization process utilizing as the catalyst a bulky ligand transition metal compound.

BACKGROUND OF THE INVENTION

It is widely known that gas phase fluidized bed polymerization processes produce a diverse array of polymers. In such a process a continuous cycle is employed where in one part of the cycle, 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 in another part of the cycle by a cooling system external to the reactor.

Generally in a gas fluidized bed process for producing polymer from monomers a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. This gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and new or fresh monomer is added to replace the polymerized monomer.

Conventionally in the past the temperature of the recycle stream entering the reactor could not be decreased below the dew point of the recycle stream. The dew point of the recycle stream is that temperature at which liquid condensate begins to form in the gaseous recycle stream. Later it was demonstrated as disclosed in U.S. Patent Nos. 4,543,399 and 4,588,790 to Jenkins, III, et al. that a recycle stream can be cooled to a temperature below the dew point in a fluidized bed polymerization process resulting in condensing a portion of the recycle stream. The resulting recycle stream containing entrained liquid is then returned to the reactor. U.S. Patent Nos. 4,543,399 and 4,588,790 to Jenkins, III, et al. are herein

- 2 -

fully incorporated by reference. For the purposes of this patent application the process of purposefully introducing a recycle stream having a liquid and a gas phase into a reactor such that the weight percent of liquid based on the total weight of the recycle stream is greater than about 2.0 weight percent is defined to be operating a gas phase polymerization process in a "condensed mode".

The catalyst system described in Jenkins, III, et al. is a TiCl_3 based traditional Ziegler-Natta catalyst system. Using this catalyst system in a condensed mode operation results inevitably in process and product constraints as all become apparent later in this specification. The process limitations limit production rates and significantly increase the cost of producing polymers. Also, as a direct consequence of using these traditional catalysts in this process the polymers available for production are restricted to certain densities and melt indices.

Polymer production rates and characteristics can be controlled to give a desired melt index and density in a gas phase fluidized bed reactor. In operation of a gas phase fluidized bed reactor, the process is a closed system. Changes in the process of one or more reactor conditions can lead to consequential changes elsewhere in the system. Therefore, great care is taken to avoid conditions which lead to chunking, sheeting, fluidized bed collapse, reaction termination and reactor shut-down. There are target values, determined by the polymer to be produced and the catalyst, for the operating temperature, the ratio of comonomer(s) to monomer and the ratio of hydrogen to monomer. Traditional catalyst systems and polymer produced therewith restrict these values, and as a direct consequence of this, drastically reduce production rates achievable for any given polymer being produced. Furthermore, these traditional catalysts and catalyst systems limit the type and characteristics of the polymer.

Therefore a need exists for a gas phase polymerization process that allows for the extension of the target values heretofore limited. Extending these values beyond that which was achievable in the past will allow for the operation of a gas phase fluidized bed polymerization reactor at significantly higher production rates and of the production of polymer grades at a significantly reduced cost not heretofore envisaged.

SUMMARY OF THE INVENTION

This invention relates to a continuous gas phase polymerization process for polymerizing alpha-olefins utilizing a bulky ligand transition metal catalyst, for

- 3 -

example a metallocene, in a gas phase fluidized bed reactor operating in a condensed mode.

This invention in another embodiment relates to a continuous process for the polymerization of alpha-olefin monomer and at least one copolymerizable alpha-olefin comonomer in a gas phase fluidized bed reactor. A recycle stream is passed through the reactor such that the recycle stream comprises a ratio of $(C_x + H_2)/C_y$ of less than about 0.2, a dew point increasing component in an amount greater than about 2.0 mole percent and non-condensable inerts making up the balance of the recycle stream, where C_x , H_2 and C_y are the mole percent respectively of comonomer, hydrogen and monomer. A catalyst is introduced under reactive conditions into the reactor to polymerize the recycle stream into a polymer product that is withdrawn from the reactor. The recycle stream containing unreacted monomers is also withdrawn from the reactor and additional monomers are introduced into the recycle stream to replace monomers polymerized so as to maintain the ratio of the recycle stream. In the preferred embodiment the recycle stream is compressed and/or cooled to form a liquid phase and a gas phase, which are reintroduced into the reactor.

In a preferred embodiment that alpha-olefin monomer is ethylene. In another preferred embodiment the comonomer is a C_5 or a higher alpha-olefin.

It is the an object of this invention to provide a process for polymerizing olefins in a gas fluidized bed polymerization reactor at significantly higher production rates. It is a related object of this invention to provide a process that results in the increased cooling capability of a recycle stream. It is further related object of this invention to provide a polymerization process for producing polymers having a broader range of densities and melt indices. It is yet another object of this invention to provide a polymerization process that provides for even greater savings in energy, raw materials and capital expenditure.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to the gas phase polymerization process for polymerizing olefins utilizing a metallocene in a gas phase fluidized bed polymerization reactor operating in a condensed mode. The invention provides for a significant increase in the production rate of polymer produced in a gas phase fluidized bed reactor. The invention further provides for the production of a broad range of polymers having improved characteristics at these significantly higher production rates. Traditional Ziegler-Natta catalysts are typically insoluble in

- 4 -

hydrocarbon solvents. For example, traditional Ziegler-Natta catalysts are typically isolated by precipitation in a hydrocarbon solvent, such as isopentene.

Surprisingly, a metallocene catalyst, being soluble in hydrocarbon solvents, polymerized olefins in a condensed mode process which utilizes a hydrocarbon solvent as the preferred condensable inert.

5 This invention is directed toward the gas phase polymerization or copolymerization reactions involving the polymerization of one or more of the alpha-olefin monomers having from 2 to 20 carbon atoms, preferably 2-15 carbon atoms. The invention is particularly well suited to the copolymerization reactions
10 involving the polymerization of one or more of the monomers, for example alpha-olefin monomers of ethylene, propylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1, octene-1, decene-1 and cyclic olefins such as styrene. Other monomers can include polar vinyl, dienes, norbornene, acetylene and aldehyde monomers. Preferably a copolymer of ethylene is produced such that the amount of ethylene
15 and comonomer is adjusted to produce a desired polymer product. Preferably the comonomer is an alpha-olefin having from 4 to 15 carbon atoms, more preferably 5 to 12 carbon atoms and most preferably 5 to 10 carbon atoms. In another embodiment ethylene is polymerized with at least two comonomers to form a terpolymer and the like.

20 The catalyst useful in the polymerization process of this invention are generally in the field of transition metal catalysis, which includes many transition metals of metallo-organic nature. Over the past few years a new catalyst technology has developed, which provides for the modification and/or control over the properties and characteristics of a polymer. This technology principally
25 involves the use of single-site catalysts to produce a broad range of polymers generally having a narrow molecular weight distribution and a narrow composition distribution. The art has focused on the type of catalyst and catalyst system employed and product attributes produced therefrom, however, the surprising and unexpected benefits derived from these catalysts in a condensed mode gas phase
30 polymerization process have gone unrecognized until now.

Selected metallo-organic catalysts and catalyst systems are suitable to produce polymer from selected gas compositions entering the reactor as the recycle stream. With reference to the catalyst, it is preferably a bulky ligand transition metal catalyst. The bulky ligand contains a multiplicity of bonded atoms,
35 preferably carbon atoms, forming a group which may be cyclic with one or more optional heteroatoms. The bulky ligand may be a cyclopentadienyl derivative

- 5 -

which can be mono- or poly-nuclear. One or more bulky ligands may be bonded to the transition metal atom. The transition metal atom is a Group IV, V or VI transition metal of the Periodic Table of Elements. Other ligands may be bonded to the transition metal, preferably detachable by a cocatalyst such as a hydrocarbyl or halogen leaving group. The catalyst is derivable from a compound represented by the formula:



wherein L is the bulky ligand; X is the leaving group, M is the transition metal and m and n are such that the total ligand valency corresponds to the transition metal valency. Preferably the catalyst is four co-ordinate such that the compound is ionizable to a 1⁺ valency state.

The ligands L and X may be bridged to each other and if two ligands L and/or X are present, they may be bridged. The metallocenes may be full-sandwich compounds having two ligands L which are cyclopentadienyl groups or half-sandwich compounds having one ligand L only which is a cyclopentadienyl group.

Certain types of metallocenes possess the necessary properties for the process of this invention. For the purposes of this patent specification the term "metallocene" is herein defined to contain one or more cyclopentadienyl moiety in combination with a transition metal of the Periodic Table of Elements. The metallocene catalyst component is represented by the general formula (Cp)_mMR_nR'_p wherein Cp is a substituted or unsubstituted cyclopentadienyl ring; M is a Group IV, V or VI transition metal; R and R' are independently selected halogen, hydrocarbyl group, or hydrocarboxyl groups having 1-20 carbon atoms; m = 1-3, n = 0-3, p = 0-3, and the sum of m + n + p equals the oxidation state of M. Various forms of the catalyst system of the metallocene type may be used in the polymerization process of this invention. Exemplary of the development of these metallocene catalysts for the polymerization of ethylene is found in the disclosure of U.S. Patent No. 4,937,299 to Ewen, et al. and EP-A-0 129 368 published July 26, 1989, both of which have been fully incorporated herein by reference. These publications teach the structure of the metallocene catalysts and includes alumoxane as the cocatalyst. There are a variety of methods for preparing alumoxane of which one described in U.S. Patent 4,665,208. Other cocatalysts may be used with metallocenes, such as trialkylaluminum compounds; or ionizing ionic activators or compounds such as, tri (n-butyl) ammonium tetra (pentafluorophenyl) boron, which ionize the neutral metallocene compound. Such ionizing compounds may contain an active proton, or some other cation associated

- 6 -

with but not coordinated or only loosely coordinated to the remaining ion of the ionizing ionic compound. Such compounds are described in EP-A-0 277 003 and EP-A-0 277 004 both published August 3, 1988 and are both herein fully incorporated by reference. Further, the metallocene catalyst component can be a
5 monocyclopentadienyl heteroatom containing compound. This heteroatom is activated by either an alumoxane or an ionic activator to form an active polymerization catalyst system to produce polymers useful in this present invention. These types of catalyst systems are described in, for example, PCT International Publications WO 92/00333 published January 9, 1992, U.S. Patent
10 Nos. 5,096,867 and 5,055,438, EP-A-0 420 436 and WO 91/ 04257 all of which are fully incorporated herein by reference. In addition, the metallocene catalysts useful in this invention can include non-cyclopentadienyl catalyst components, or ancillary ligands such as boroles or carbollides in combination with a transition metal. Additionally it is not beyond the scope of this invention that the catalysts
15 and catalyst systems may be those described in U.S. Patent No. 5,064,802 and PCT publications WO 93/08221 and WO 93/08199 published April 29, 1993 all of which are herein incorporated by reference. All the catalyst systems described above may be, optionally, prepolymerized or used in conjunction with an additive or scavenging component to enhance catalytic productivity.

20 Metallocenes selected to have a combination of good comonomer incorporation, hydrogen sensitivity and polymerization activity are preferred. The preferred metallocenes are those having two or more substituents on at least one cyclopentadienyl group such as the mono- or bis-substituted cyclopentadienyl zirconocenes, specifically, bis (1-methyl, 3-n-butyl cyclopentadienyl) zirconium
25 dichloride. Metallocene catalysts that are excessively hydrogen sensitive or generate hydrogen may restrict the process to the making of high melt index materials. Too low an activity leads to high ash levels and necessitates the use of higher levels of stabilizers. Too high an activity could induce fouling. Too poor a comonomer incorporation may impact on the range of low density materials
30 capable of being produced. A wide product range can be obtained by adjusting the feed gas stream or recycle stream composition for a particular metallocene. Mixtures of two or more different metallocenes can also be used.

 The catalyst may be supported on a suitable particulate material such as polymeric supports or inorganic-oxide such as silica, alumina or both. Methods of
35 supporting the catalyst of this invention are described in U.S. Patent Nos. 4,808,561, 4,897,455, 4,937,301, 4,937,217, 4,912,075, 5,008,228, 5,086,025 and

- 7 -

5,147,949 and U.S. Application Serial No. 898,255, filed June 15, 1992 and 885,170, filed May 18, 1992, all of which are herein incorporated by reference. The preferred support method is generally disclosed in U.S. Patent No. 4,937,301 and related U.S. patents which are cited above.

5 Depending on how well the catalyst incorporates comonomer certain levels of comonomer may yield certain levels of polymer density. For example, highly incorporating catalyst can produce a low density polymer with a low level of comonomer. Similarly, depending on how the catalyst responds to hydrogen, certain levels of melt indices may be obtained. For the preferred alpha-olefin
10 monomer ethylene, depending on the catalyst, the C_X/C_2 ratios are preferably less than about 0.2, and more preferably less than about 0.1, and as low as about 0.02 to provide a polymer having a density in the range of from about 0.86 g/cm³ to about 0.96 g/cm³, preferably about 0.88 g/cm³ to about 0.94 g/cm³ and most preferably between about 0.90 g/cm³ to about 0.935 g/cm³.

15 The advantages and benefits derived from this invention are equally seen in the polymers produced by this invention having a melt index of at least about 0.05 dg/min and less than about 1000 dg/min, preferably less than 100 dg/min.

Ethylene is the preferred monomer and depending on the catalyst, the H_2/C_2 ratios are less than about 10,000 ppm, preferably less than about 5000 ppm
20 and even more preferably less than about 1000 ppm and most preferably less than about 500 ppm to give a polymer with a melt index in the range of from about 0.05 dg/min to about 1000 dg/min, preferably about 0.05 dg/min to about 100 dg/min, more preferably greater than about 0.1 dg/min and most preferably greater than about 0.5 dg/min.

25 The reactivity ratios of the catalysts and catalyst systems of this invention are generally less than about 2, preferably less than about 1. Reactivity ratio is defined to be the mole ratio of comonomer to monomer in the recycle stream (C_X/C_Y) divided by the mole ratio of comonomer to monomer (C_X/C_Y) in the polymer produced, where C_X is the mole percent of comonomer and C_Y is the mole
30 percent of the monomer. The catalyst useful in this invention should preferably have a productivity of over 2000 grams of polymer per gram catalyst, preferably about 3000 grams of polymer per gram catalyst and most preferably greater than about 3500 grams of polymer per gram catalyst. The productivity is influenced by the ethylene partial pressure. The preferred mole percent of ethylene is from about
35 25 to about 75 mole percent and the monomer partial pressure is in the range of

- 8 -

from about 75 psia (517 kPaa) to about 240 psia (1655 kPaa). It is desirable that the catalyst combines the monomers efficiently to provide a low ash level.

In the preferred embodiment, composition of the recycle stream, used to fluidize the bed in the reactor, is maintained at a ratio of $(C_X + H_2)/C_Y$ of less than about 0.2, preferably less than about 0.1, where C_X , H_2 and C_Y are the mole percent respectively of the comonomer, the hydrogen and the alpha-olefin monomer. The recycle stream also contains in the range of from about 2.0 to about 6.0 mole percent, preferably at least about 2.5 mole percent and preferably greater than about 5.0 mole percent of a dew point increasing component, not exceeding an amount which would disrupt fluidization. In the preferred embodiment the balance of the feed stream is made up of non-condensable inerts for example, nitrogen (N_2). The preferred alpha-olefin is ethylene and the preferred comonomers are pentene-1, hexene-1 or octene-1.

By the combination of the catalyst and the recycle stream composition described above high reactor productivities become possible for lower density or higher melt index copolymers. The process of this invention requires significantly less comonomer and hydrogen and permits greater cooling by the recycle stream. The higher production rates result from the improved cooling capability or capacity of the recycle stream with the above described recycle stream compositions of the process of this invention. This relates to the increased gas density of the recycle stream and to the higher specific enthalpy change of the stream also referred to as the enthalpy change from the inlet to the reactor conditions.

The closer the dew point gets to the reactor temperature the likelihood of the polymers sticking together is substantially higher. Sticking can also be caused by the fusing of the polymer particles at too high reactor temperatures. As a result of polymer sticking together fluidization instabilities can occur. This may cause chunking and downstream activities, extrusion and the like, may become more difficult. There is generally no accepted view as to what precisely causes chunking or sheeting. Obviously some fusing together of the polymer particles is involved, possibly because of insufficient heat transfer caused by inadequate fluidization in the fluidized bed. However, no clear correlations have thus far been found between individual process settings and measurements and the occurrence of chunking and sheeting. However, in the preferred embodiment it is best to maintain greater than at least about 5°F (2.8°C), more preferably in the preferred embodiment at least about 10°F (5.6°C), temperature differential between the dew point temperature and the reactor temperature.

- 9 -

Also, a broader density and melt index range of polymer may be produced in an efficient and cost effective manner as a direct result of reduced comonomer in the process of this invention.

Using the process of the invention relatively high reactor temperatures may be used benefiting the catalyst activity as well as increasing the reactor productivity by higher levels of cooling. The combination of lower comonomer levels, lower amounts of polymerization reactants overall, and high reactor temperatures can help achieve significant improvements in the process.

The higher reactor temperatures are believed to be associated with lower stickiness of the polymer particles in the fluidized bed arising from lower levels of low molecular weight amorphous materials and lower levels of dissolved comonomer in the polymer. Lower stickiness improves resin flow ability which also benefits downstream handling.

Preferably, the catalyst selection should provide hexane extractability less than about 2 wt%, preferably less than about 1 wt%. Hexane extractables can be determined in detail by referring to 21 CFR 177.1520 (d)(3)(ii). The catalyst selection is preferably such that the composition distribution breadth index (CDBI) of the polymer produced is over 50%, preferably over 60%, most preferably in the range of 60% to about 80%. CDBI, its measurement and calculation, is explained in detail in PCT patent application WO 93/03093 published February 18, 1993. Essentially CDBI is a measure of compositional distribution. CDBI is defined as the weight percent of copolymer molecules having a comonomer content within 50% (that is, 25% on each side) of the median total molar comonomer content.

The lower stickiness is also reflected in the improved ability of this process to make high melt index or low density polymers. Also, because of the lower stickiness the reactor temperature can be significantly increased above that achievable in the past such that the even further cooling capabilities are achievable.

The term "dew point increasing component" is used herein to exclude polymerizable monomers, including those which raise the dew point. For the purposes of this patent specification the term "dew point increasing component" includes saturated or non-polymerizable unsaturated hydrocarbons. Examples of suitable dew point increasing components are readily volatile liquid hydrocarbons, which may be selected from saturated hydrocarbons containing from 3 to 10 carbon atoms. Some suitable saturated hydrocarbons are propane, n-butane, isobutane, n-pentane, isopentane, neopentane, n-hexane, isohexane, and other saturated C₆ hydrocarbons, n-heptane, n-octane and other saturated C₇ and C₈

- 10 -

hydrocarbons or mixtures thereof. The preferred hydrocarbons are C₄ to C₆ saturated hydrocarbons. The preferred dew point increasing components are pentanes. Preferably, the stream contains from about 5 to about 60 mole percent of a dew point increasing component, preferably with the component having one
5 carbon atom less than the comonomer or at least one carbon atom less than the comonomer. This may assist in achieving high reactor productivities. The dew point itself is calculated from the feed gas composition as analyzed for example by gas chromatography. In combination with actual recycle gas temperatures and pressures, the weight percent of condensed liquid in the recycle stream is also
10 calculated.

The preferred method for measuring fluidized bed stability is by monitoring the fluidized bulk density, pressure measurements along the upper part of the fluidized bed or detecting formation of chunks in the reactor. The fluidized bulk density (FBD) is the ratio of the measured pressure drops upward across a
15 centrally fixed portion of the reactor to the height of this fixed portion. It should be understood that under certain conditions known to those skilled in the art, a mean value may be measured which is greater or less than the actual bed bulk density. Fluidized bed stability is influenced by but difficult to link with particular operating conditions. Generally operating temperatures should be below the
20 melting point and below the temperature at which the particles become sticky as explained previously. Using the invention it is believed that high reactor temperatures can be maintained at low densities, high melt index, with higher olefin comonomers and high levels of dew point raising components. In the preferred embodiment, it is important that no more condensable components should be
25 added which would raise the dew point to such a level that the evaporation inside the reactor becomes incomplete. Applicants have discovered that as the concentration of the condensable component is increased in the gaseous stream flowing through the bed it is important that the ratio of the FBD to the settled bulk density is maintained above 0.59.

30 In practice of the process of this invention the weight percent of liquid in the recycle stream based on the total weight of the recycle stream is in the range of about 2 to about 50 weight percent, preferably greater than about 10 weight percent, and more preferably greater than about 15 weight percent and even more preferably greater than 20 weight percent and most preferable in the range between
35 about 25 to about 40 weight percent.

- 11 -

In one preferred embodiment of this present invention, the entry point for the recycle stream is preferably below the fluidized bed so as to provide a uniform flow of the recycle stream to maintain the fluidized bed in a suspended condition and to ensure uniformity of the recycle stream passing upwardly throughout the fluidized bed. In another embodiment of the present invention, the recycle stream can be divided into two or more separate streams, one or more of which can be introduced directly into the fluidized bed provided that the gas velocity below and through the fluidized bed is sufficient to keep the bed suspended. For example, the recycle stream can be divided into a liquid and a gas stream which can then be separately introduced into the reactor.

The reactor pressure may vary from about 100 psig (689.7 kPag) to about 500 psig (3448.3 kPag), preferably in the range of about 200 psig (1379.3 kPag) to about 400 psig (2758.6 kPag) and most preferably in the range of about 250 psig (1724.1 kPag) to about 350 psig (2413.8 kPag). Increasing catalyst activities combined with good comonomer incorporation and hydrogen sensitivity may enable lowering of the pressure overall or of the ethylene partial pressure. Typically reactor temperatures are in the range of about 130°F (54.4°C) to about 250°F (121.1°C), preferably in the range of about 140°F (60°C) to about 220°F (104.4°C), more preferably in the range of about 145°F (62.7°C) to about 215°F (101.7°C), even more preferably in the range of about 155°F (68.3°C) to about 200°F (93.3°C) and most preferably in the range of about 165°F (73.9°C) to about 185°F (85°C). It is preferable that the difference between the dew point temperature and the inlet temperature is less than 40°C, preferably less than 30°C, even more preferably less than 20°C and most preferably in the range of 5°C, preferably 10°C, to about 15°C. The superficial gas velocity of the gas flow through the reactor generally exceeds the minimum flow required for fluidization which is typically from about 0.2 ft/sec (0.061 m/s) to 0.5 ft/sec (0.153 m/s). Preferably, the superficial gas velocity is maintained not less than about 0.7 ft/sec (0.214 m/s), and even more preferably not less than 1.0 ft/sec (0.305 m/s). The superficial gas velocity should preferably not exceed 5.0 ft/sec (1.5 m/s).

EXAMPLES

In order to provide a better understanding of the present invention including representative advantages and limitations thereof, the following examples are offered.

- 12 -

EXAMPLE 1

In the examples different catalysts are used. For the actual comparative run C-1 and extrapolated data run C-1A of Table 1 a titanium based catalyst is used similar to that in U.S. Patent No. 4,543,399. The catalyst used is a complex of tetrahydrofuran, magnesium chloride and titanium chloride reduced with diethyl aluminum chloride (diethyl aluminum chloride-to-tetrahydrofuran molar ratio of 0.42) and tri-n-hexyl aluminum (tri-n-hexyl aluminum-to-tetrahydrofuran molar ratio of 0.28) impregnated on triethyl aluminum treated silicon dioxide. The activator is triethyl aluminum (TEAL).

For the actual runs 2A and 8A of Table 3 and extrapolated data runs 2-6 of Table 1, runs 8-13 of Table 3 and runs 14-18 of Table 4 the catalyst was based on a metallocene with a di-substituted cyclopentadienyl rings as follows:

To a clean, dry N₂ mixer were added 800 grams of silica dehydrated at 200°C with an LOI (OH content) of approximately 3 wt%. 2000 ml of toluene is rapidly added to the vessel. 1060 ml of 30 wt% MAO based on the Al-content is added to the vessel while mixing. The jacket temperature is increased such that the internal temperature is 155°F. The mixture is held at this temperature for 4 hours while mixing. Then there is added rapidly to the reactor with mixing, 23 grams of bis(1-methyl, 3-n-butyl Cp)ZrCl₂ dissolved in approximately 500 ml of toluene. The reactor temperature is again held at 155°F for 1 hour while continuing mixing. Finally the catalyst solids are dried with nitrogen under vacuum at 155°F until the solids are free-flowing and have a volatile content of 10 wt% or less.

The catalyst for actual run 7A of Table 3 and extrapolated data run 7 of Table 1 was prepared as follows:

All steps are performed in a dry box using dry, degassed solvents. Accordingly there is added to a clean, dry, 1 liter round bottom flask 300 ml of a 25 wt% solution of triethyl aluminum in heptane. 300 g of silica dehydrated at 800°C is added over a period of 15 minutes while stirring. The silica is Davison 948. The solvent is then removed in vacuo to obtain a free flowing solid. 12.0 g of tetrakis perfluorophenyl boron dimethylanilinium salt is then dissolved in 800 ml of hot (100°C) toluene in a 2 liter round bottom flask while stirring. This is added via a cannula to a 3 liter round bottom flask containing 300 g TEAL treated silica as obtained above slurried with a mechanical overhead stirrer in 500 ml of hot (100°C) toluene. The mixture is allowed to cool to room temperature and 1200 ml of pentane is added while stirring with a mechanical overhead stirrer. The solvent is decanted and residual solvent removed in vacuo to obtain a free flowing solid.

- 13 -

The supported activator prepared above is then slurried in 500 ml pentane, then 5.43 g of bis(n-butylcyclopentadienyl) dimethyl zirconium is added, dissolved in 200 ml pentane. The solvent is decanted and residual solvent is removed in vacuo to obtain a free flowing solid.

- 5 Runs C-1 of Table 1 and 2A, 7A and 8A of Table 3 are based on actual tests. The data shown by runs C-1A, 2, 3, 4, 5, 6 and 7 of Table 1, runs 8-13 of Table 2 and runs 14-18 of Table 4 were prepared by extrapolating information from actual operations by using thermodynamic equations well known in the art to project actual conditions and production rates. Each run is explained below:

TABLE 1

RUN	C-1	C-1A	2	3	4	5	6	7
Ml (dg/min)	3.39	3.39	1.61	1.61	1.61	1.61	1.61	18.7
Density (g/cm ³)	0.9168	0.9168	0.9175	0.9175	0.9175	0.9175	0.9175	0.9222
Temp (°C)	78.9	78.9	78.9	78.9	78.9	78.9	78.9	79.4
Temp (°F)	174	174	174	174	174	174	174	175
Pressure (kPag)	2110	2110	2110	2110	2110	2110	2110	2110
Pressure (psig)	306	306	306	306	306	306	306	306
C ₂ Pressure (kPaa)	719	719	881	881	881	881	881	665
C ₂ Pressure (psia)	104.2	104.2	127.7	127.7	127.7	127.7	127.7	96.4
Comonomer	Hexene	Hexene	Hexene	Hexene	Hexene	Hexene	Hexene	Hexene
Cx/C2	0.132	0.132	0.0157	0.0157	0.0157	0.0157	0.0157	0.0152
H2/C2								
mole/mole	0.364	0.364	-	-	-	-	-	-
mole ppm/mole	-	-	2.4	2.4	2.4	2.4	2.4	3.95
Ethylene (mole%)	32.5	32.5	39.8	39.8	39.8	39.8	39.8	30.1
iC5 (mole %)	1.0	10.3	1.6	8.5	11	13.5	21.1	14
H2 (mole %)	11.8	11.8	0.010	0.010	0.010	0.010	0.010	0.012
N2 (mole %)	48.6	39.5	56.9	50.1	47.6	45.1	37.6	54.3
Cx (mol%)	4.3	4.3	0.6	0.6	0.6	0.6	0.6	0.5
Prod Rate (lb/hr)	57400	95500	30500	50000	65000	80000	131400	80000
Prod Rate (tons/hr)	26.1	43.2	13.9	22.7	30.0	36.4	59.7	36.4
% Condensed	11.6	23.05	0.00	4.70	10.20	15.47	30.59	15.66
T inlet (°C)	40.4	40.6	40.4	40.6	40.5	40.7	40.6	40.4
T Inlet (°F)	104.8	105.0	104.8	105.0	104.9	105.3	105.0	104.8
T dew (°C)	64.3	73.3	18.4	46.9	53.7	59.4	73.4	59.4
T dew (°F)	147.7	164.0	65.1	116.4	128.6	139.0	164.2	139.0
Gas Velocity (ft/sec)	2.33	2.33	2.33	2.33	2.33	2.33	2.33	2.33
Gas Velocity (m/sec)	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71
Catalyst Productivity g PE per g Cat	3500	3500	3850	3850	3850	3850	3850	3490
Gas Density (lb/ft ³)	1.32	1.57	1.37	1.57	1.64	1.71	1.93	1.70
Gas Density (kg/m ³)	21.1	25.1	22.0	25.1	26.3	27.4	30.9	27.2
Spec. Enthalpy (Btu/lb)	45.7	64.6	23.5	34.0	42.4	50.3	73.5	50.6
Spec. Enthalpy (Cal/g)	25.4	35.9	13.0	18.9	23.6	27.9	40.8	28.1

Run C-1

- 5 Run C-1 of Table 1 is actual plant data in which substantially the same process and catalyst systems as disclosed in U.S. Patent Nos. 4,543,399 and 4,588,790.

Run C-1A

- 10 Run C-1A of Table 1 contains data extrapolated from run C-1 above. This run illustrates for this particular grade material the preferred dew point limit is

- 15 -

reached. That is the difference between the reactor temperature and the dew point temperature is about 10°F (5.6°C). At this point increasing the dew point to approach reactor temperature any further may result in instabilities in the fluidized bed, possibly sheeting and chunking as a result.

5

Run 2 and 2A

Run 2 of Table 1 contains data extrapolated from run 2A of Table 3. Run 2A is actual pilot plant data. Run 2 illustrates this data when scaled up to the reactor used in run C-1. The catalyst used is as described previously.

10 As one can see the C_X/C_2 and H_2/C_2 ratios are extremely low as compared with runs C-1 and C-1A.

Runs 3-6

15 Runs 3-6 illustrate extrapolated data where the level of dew point increasing component, in this particular example, isopentane (i-C₅) is used, is increased within the recycle stream composition. The amount of i-C₅ increases from 1.6 mole % in run 2 to 21.1 mole % in run 6. In so doing the dew point steadily increases such that the dew point limit of 10°F (5.6°C) is reached while the production rate for the same polymer grade is dramatically increased. This
20 figure is well above the limit of run C-1A. Note that the reactor and inlet temperature, pressure and gas velocity remain constant. Also note that the gas densities are much higher for the runs illustrating the process of this invention as are the cycle gas enthalpy changes. If the reactor temperature were raised to 185°F (85°C) and the dew point raised to 174.7°F (79.3°C), a further increase in
25 production rate up to 167,000 lb/hr (76.0 tons/hr) could be obtained.

Runs 7 and 7A

Run 7 of Table 1 contains data extrapolated from actual pilot plant run data shown in run 7A of Table 3. The catalyst system has been changed as described
30 previously. As the results show, the increases in production rate are achievable with different metallocene catalyst systems.

- 16 -

TABLE 2

RUN	8	9	10	11	12	13
MI (dg/min)	1.05	1.05	1.05	1.05	1.05	1.05
Density (g/cm ³)	0.918	0.918	0.918	0.918	0.918	0.918
Temp (°C)	78.9	78.9	78.9	78.9	78.9	78.9
Temp (°F)	174	174	174	174	174	174
Pressure (kPag)	2069	2069	2069	2069	2069	2069
Pressure (psig)	300	300	300	300	300	300
C ₂ Pressure (kPaa)	1090	1090	1090	1090	1090	870
C ₂ Pressure (psia)	158.1	158.1	158.1	158.1	158.1	126.2
Comonomer	Octene	Octene	Octene	Octene	Octene	Octene
C _x /C ₂	0.009	0.009	0.009	0.009	0.009	0.009
H ₂ /C ₂						
mole/mole	-	-	-	-	-	-
mole ppm/mole	2.00	2.00	2.00	2.00	2.00	2.00
Ethylene (mole%)	50.2	50.2	50.2	50.2	50.2	40.1
iC ₅ (mole %)	1	7.5	10.5	13	16	17.5
H ₂ (mole %)	0.010	0.010	0.010	0.010	0.010	0.008
N ₂ (mole %)	47.4	41.0	38.0	35.5	32.6	41.1
C _x (mol%)	0.5	0.5	0.5	0.5	0.5	0.4
Prod Rate (lb/hr)	37400	50600	63800	79200	96800	103400
Prod Rate (tons/hr)	16.8	23.0	29.0	36.0	44.0	47.0
% Cond	1.10	4.94	9.89	15.24	21.14	23.28
T Inlet (°C)	40.1	40.8	40.9	40.4	40.9	40.6
T Inlet (°F)	104.1	105.5	105.7	104.8	105.6	105.1
T dew (°C)	49.9	60.8	65.4	69.2	73.4	73.5
T dew (°F)	121.9	141.4	149.8	156.5	164.1	164.3
Gas Velocity (ft/sec)	2.33	2.33	2.33	2.33	2.33	2.33
Gas Velocity (m/sec)	0.71	0.71	0.71	0.71	0.71	0.71
Cat Activity gPE per g cat	3630	3630	3630	3630	3630	2900
Gas Density (lb/ft ³)	1.34	1.54	1.62	1.68	1.77	1.78
Gas Density (Kg/m ³)	21.4	24.6	25.9	27.0	28.4	28.6
Spec. Enthalpy (Btu/lb)	29.8	35.3	42.5	50.7	59.1	62.7
Spec. Enthalpy (cal/g)	16.6	19.6	23.6	28.2	32.8	34.8

Runs 8-13

5 Run 8 contains data extrapolated from the actual pilot plant data shown in run 8A of Table 3. The catalyst system used is the same as used in runs 2-6 of Table 1. However, the comonomer for runs 8A and 8-13 is octene-1.

Again, as the amount of the dew point increasing component increased the production rate is increased steadily such that at the preferred dew point limit the
10 rate of production is 103,400 lb/hr (47.0 tons/hr).

TABLE 3

RUN	2A	7A	8A
REACTOR PROPERTIES			
Melt Index (dg/min)	1.61	18.7	1.05
Density (g/cm ³)	0.9175	0.9222	0.9180
MIR	18.8	20.2	18.1
PHYSICAL PROPERTIES			
Bulk Density (lb/ft ³)	29.8	24.6	29.1
Bulk Density (kg/m ³)	477	394	466
Avg Particle Size (Inch)	0.0281	0.0331	0.0308
Avg Particle Size (cm)			
Fines (%) thru 120 mesh	0.15	1.14	0.58
Ash (ppm)	243	343	186
REACTOR CONCENTRATIONS			
Ethylene (mole %)	39.8	30.05	50.2
Octene (mole %)	--	--	0.452
Hexene (mole %)	0.62	0.46	--
Hydrogen (mole %)	0.0096	0.0118	0.0100
Nitrogen (mole %)	58.7	68.1	47.8
C6/C2 Mole Ratio	0.0157	0.0152	--
C8/C7 Mole Ratio	--	--	0.0090
H2/C2 Mole Ratio	0.00024	0.00039	0.00020
TEAL (ppm)	78	38	78
REACTOR CONDITIONS			
Production Rate (lb/hr)	59.8	43.8	57.0
Production Rate (kg/hr)	27.2	19.9	25.9
Reactor Temp (°C)	78.7	79.7	78.9
Reactor Temp (°F)	173.6	175.4	174.1
Catalyst Prod (Lb/Lb) (Kg/Kg)	3850	3490	3630
Bed Weight (Kg)	140	122	108
Bed Weight (lb)	307	268	237
Reactor Res Time (hr)	5.1	6.1	4.1
Gas Velocity (m/sec)	0.51	0.52	0.52
Gas Velocity (ft/sec)	1.67	1.7	1.7
Pressure (kPag)	2069	2069	2069
Pressure (psig)	300	300	300

The range of polymers which have in the past been so obtained is limited.

- 5 At a density below about 0.910 g/cm³ the polymer granules in the reactor become sticky and the reactor temperatures may have to be lowered, the same can be said for polymer granules at a density greater than 0.910 g/cm³ and a melt index greater than about 100 dg/min, preferably greater than 200 dg/min, even further limiting the scope for adding a dew point increasing component thus, resulting in
- 10 decreased reactor production rates. Of course one could lower the ethylene partial pressure to compensate for this but then the catalyst activity is lowered by the

- 18 -

effect of lower ethylene partial pressures. Similar constraints are encountered when seeking to raise the melt index.

EXAMPLE 2

- 5 Now referring to Table 4, run 14 is actual plant data using the condensed mode process with a metallocene catalyst prepared from 200°C silica having a water content of 4.1 weight percent. This catalyst was prepared by mixing 229 pounds of silica with 310 pounds of a 30 percent by weight toluene solution of methyl alumoxane. An additional 450 pounds of toluene were added and the
- 10 mixture held at 146°F for 2 hours after which 6.20 pounds of the bis-(n-butyl cyclopentadienyl) zirconium dichloride was added and allowed to mix for one hour. The catalyst was decanted and solvent exchanged with hexane several times. It was then dried at 150°F to a free flowing powder. The final catalyst weight was 340 pounds. The final catalyst had a zirconium loading of 0.37% and aluminum
- 15 loading of 12.5%.

- 19 -

Polymerization ConditionsTABLE 4

RUN	14
MI (dg/min)	0.85
Density (g/cc)	0.9208
Temp (°C)	73.9
Temp (°F)	165
Pressure (kPag)	2207
Pressure (psig)	320
C2 Pressure (kPaa)	719
C2 Pressure (psia)	204.5
Comonomer	Hexene
Cx/C2	0.020
H2/C2	
mole/mole	--
mole ppm/mole	1.19
Ethylene (mole %)	61.1
iC5 (mole %)	12.9
H2 (mole %)	0.0073
N2 (mole %)	25.9
Cx (mole %)	1.23
Prod Rate (lb/hr)	50040
Prod Rate (tons/hr)	22.7
Pct Condensed	19.3
T inlet (°C)	39.7
T inlet (°F)	103.4
T dew (°C)	55.9
T dew (°F)	132.6
Gas Velocity (ft/sec)	1.98
Gas Velocity (m/sec)	0.60
Catalyst Productivity g PE/g Cat	2880
Gas Density (lb/ft ³)	1.84
Gas Density (kg/m ³)	29.4
Spec Enthalpy (BTU/lb)	53.1
Spec Enthalpy (Cal/g)	29.5

5

EXAMPLE 3

Now referring to Table 5, extrapolated data for runs 15-19. The same catalyst and setup was used as for run 2 of Example 1. This example illustrates the effect of a particular dew point increasing component. Different components were used to raise the dew point to 10°F (5.6°C) below the reactor temperature. The cooling capacity of the recycle stream and reactor productivity were then compared. It can be seen that the lower molecular weight condensable

10

- 20 -

hydrocarbons tend to permit higher reactor production rates. This may also be coupled with lower solubility in the polymer particles of these hydrocarbons and less effect on the polymer melting point which could impact on the fluidized bed stability at a high reactor operating temperature.

5

TABLE 5

RUN	15	16	17	18	19
MI (dg/min)	1.61	1.61	1.61	1.61	1.61
Density (g/cm ³)	0.9175	0.9175	0.9175	0.9175	0.9175
Temp (°C)	78.9	78.9	78.9	78.9	78.9
Temp (°F)	174	174	174	174	174
Pressure (kPag)	2110	2110	2110	2110	2110
Pressure (psig)	306	306	306	306	306
C ₂ Pressure (kPaa)	881	881	881	881	881
C ₂ Pressure (psia)	127.7	127.7	127.7	127.7	127.7
Comonomer	Hexene	Hexene	Hexene	Hexene	Hexene
Catalyst Prod (lb/lb)	3850	3850	3850	3850	3850
Cx/C2	0.0157	0.0157	0.0157	0.0157	0.0157
H2/C2					
mole/mole	--	--	--	--	--
mole ppm/mole	2.4	2.4	2.4	2.4	2.4
Ethylene (mol%)	39.8	39.8	39.8	39.8	39.8
Nitrogen (mol%)	37.6	21.1	41.9	51.6	49.9
Hexene (mol%)	0.6	0.6	0.6	0.6	0.6
Hydrogen (mol%)	0.010	0.010	0.010	0.010	0.010
Condensable	Isopentane	Isobutane	Pentane	Hexane	Isohexane
Cond Conc (mol%)	21.1	40.2	15.7	5.8	7.5
Prod Rate (lb/hr)	131400	187709	113500	70840	78760
Prod Rate (tons/hr)	59.7	85.3	51.6	32.2	35.8
% Cond	30.59	41.80	25.68	13.90	16.78
T inlet (°C)	40.6	40.6	40.6	40.7	40.5
T inlet (°F)	105.0	105.0	105.0	105.2	104.9
T dew (°C)	73.4	73.3	73.2	73.2	73.2
T dew (°F)	164.2	164.0	163.7	163.8	163.8
Gas Density (lb/ft ³)	1.93	2.06	1.80	1.57	1.63
Gas Density (kg/m ³)	30.9	32.9	28.9	25.2	26.0
Specific Enthalpy (Btu/lb)	73.4	80.0	67.9	48.4	52.1
Specific Enthalpy (cal/g)	40.8	44.4	37.7	26.9	28.9

While the present invention has been described and illustrated by reference to particular embodiments thereof, it will be appreciated by those of ordinary skill in the art that the invention lends itself to variations not necessarily illustrated herein. For example, it is not beyond the scope of this invention to reduce the temperature of a recycle stream by employing refrigerator units or operating two

10

- 21 -

or more reactors in series with the same or different catalyst. For this reason, then, references should be made solely to the appended claims for purposes of determining the true scope of the present invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A continuous gas phase polymerization process for polymerizing alpha-olefin(s) utilizing a metallocene catalyst in a gas phase fluidized bed reactor wherein a recycle stream having a liquid and a gas phase is introduced to the reactor such that the weight percent of liquid based on the total weight of the recycle stream is greater than 2.0 weight percent, and the recycle stream comprises a dew point increasing component in an amount greater than 2.0 mole percent.
2. The process in accordance with claim 1 wherein a recycle stream passing through a fluidized bed in said reactor comprises a dew point increasing component in an amount of 5 to 60 mole percent.
3. The process of claims 1 or 2 wherein said dew point increasing component having at least one carbon less than the highest alpha-olefin monomer in the stream.
4. The process in accordance with claims 2 or 3 wherein said recycle stream composition contains a comonomer.
5. The process of claim 4 wherein said comonomer is maintained at a ratio of C_x/C_y of less than 0.2, where C_x and C_y are the mole percent respectively of comonomer and monomer.
6. The process of any one of claims 2 to 5 wherein said recycle stream comprises from 5 to 40 mole percent of the dew point increasing component.
7. The process in accordance with any one of claims 4 to 6 wherein the recycle stream further comprises hydrogen (H_2) in a mole ratio of H_2/C_y is less than 0.01.



8. The process in accordance with claim 7 wherein said hydrogen (H_2) is in an amount of from 10 mole ppm to 10,000 mole ppm.
9. The process in accordance with any one of claims 4 to 8 wherein the composition of said recycle stream is at a ratio of $(C_x + H_2)/C_y$ of less than 0.2.
10. The process in accordance with claim 9 wherein said recycle stream is at a ratio of $(C_x + H_2)/C_y$ of less than 0.1.
11. The process in accordance with any one of the preceding claims wherein the weight percent of liquid based on the total weight of the recycle stream is greater than 2.5 percent.
12. The process in accordance with any one of the preceding claims wherein the weight percent of liquid based on the total weight of the recycle stream is greater than 20 percent.
13. The process in accordance with any one of the preceding claims wherein the weight percent of liquid based on the total weight of the recycle stream is 5 to 50 weight percent.
14. The process in accordance with any one of the preceding claims wherein the metallocene catalyst has a reactivity ratio of less than about 2.
15. The process in accordance with any one of the preceding claims wherein the metallocene catalyst productivity is greater than 2000 grams of polymer per gram of said catalyst.
16. The process in accordance with any one of the preceding claims wherein the mole percent of alpha-olefin monomer is from 10 to 90 percent.



17. The process in accordance with any one of the preceding claims wherein the mole percent of alpha-olefin monomer is from 20 to 80 mole percent.

18. The process in accordance with any one of the preceding claims wherein the mole percent of alpha-olefin monomer is from 25 to 75 mole percent.

19. The process in accordance with any one of the preceding claims wherein the monomer partial pressure is in the range of from 70 psia (482-8 kPaa) to 240 psia (1655-2kPaa).

20. The process in accordance with any one of claims 16 to 19 wherein the recycle stream further comprises nitrogen in an amount from 5 to 50 mole percent.

21. The process in accordance with any one of claims 16 to 19 wherein said polymer product has a CDBI greater than 50 percent.

22. The process in accordance with any one of claims 16 to 21 wherein said polymer product has a density in the range of from 0.850 g/cm³ to 0.970 g/cm³.

23. The process in accordance with any one of claims 16 to 22 wherein said polymer product has a melt index of at least 0.01 dg/min and less than 1000 dg/min.

24. The process in accordance with any one of claims 4 to 23 wherein said at least two alpha-olefin monomers are C₄ and C₂ alpha-olefins in the ratio of from 0.001 to 0.2.

25. The process in accordance with any one of claims 4 to 23 wherein said at least two alpha-olefin monomers are C₅ and C₂ alpha-olefins in the ratio of from 0.001 to 0.15.



26. The process in accordance with any one of claims 4 to 23 wherein said at least two alpha-olefin monomers are C_6 and C_2 alpha-olefins in the ratio of from 0.001 to 0.1.

27. The process in accordance with any one of claims 4 to 23 wherein said at least two alpha-olefin monomers are C_8 and C_2 alpha-olefins in the ratio of from 0.001 to 0.05.

28. A continuous process for the polymerization of ethylene and at least one copolymerizable alpha-olefin comonomer in a gas phase fluidized bed reactor operating in a condensed mode, said process comprising the steps of:

a) passing a recycle stream through a fluidized bed in said reactor, said recycle stream comprising a ratio of C_x/C_2 of less than 0.2, a dew point increasing component in an amount greater than 2.0 mole percent and optionally non-condensable inerts making up the balance of said recycle stream, where C_x and C_2 are the mole percent respectively of comonomer and ethylene;

b) introducing a metallocene catalyst under reactive conditions into said reactor to polymerize said recycle stream into a polymer product;

c) withdrawing said recycle stream containing unreacted monomers from the reactor;

d) introducing into said recycle stream additional monomers to replace monomers polymerized to maintain said ratio of said recycle stream;

e) reintroducing said recycle stream into said reactor; and

f) withdrawing said polymer product from said reactor.

29. The process in accordance with claim 28 wherein said at least one copolymerizable alpha-olefin comonomer has from 3 to 15 carbon atoms.

30. The process in accordance with claims 28 or 29 wherein said recycle stream comprises a ratio of C_x/C_2 of less than 0.1.



31. The process in accordance with any one of claims 28 to 30 wherein said metallocene catalyst is used with an alumoxane or an ionic activated complex.

32. The process in accordance with any one of claims 28 to 31 wherein the comonomer is hexene-1 and the reactivity ratio is less than 2, the density of the polymer product is in the range of 0.88 g/cm³ to 0.970 g/cm³ and a melt index of 0.1 dg/min to 1000 dg/min.

33. The process in accordance with any one of claims 28 to 31 wherein the comonomer is octene-1 and the reactivity ratio is less than 1, the density of the polymer product is in the range of 0.88 g/cm³ to 0.97 g/cm³ and a melt index of 0.1 dg/min to 1000 dg/min.

34. The process in accordance with any one of claims 28 to 33 wherein the recycle stream further comprises hydrogen (H₂) in a mole ratio of H₂/C₂ less than 0.01.

35. A continuous process for the polymerization of ethylene and at least one copolymerizable alpha-olefin comonomer in a gas phase fluidized bed reactor, said process comprising the steps of:

a) passing a recycle stream through said reactor, said recycle stream comprising a ratio of (C_x + H₂)/C₂ of less than 0.2, a dew point increasing component in an amount greater than 2.0 mole percent and non-condensable inerts making up the balance of said recycle stream, where C_x, H₂ and D₂ are the mole percent respectively of comonomer, hydrogen and ethylene;

b) introducing a metallocene catalyst system under reactive conditions into said reactor to polymerize said recycle stream into a polymer product;

c) withdrawing said recycle stream containing unreacted monomers from the reactor;

d) compressing and cooling said recycle stream to form a liquid phase and a gas phase such the weight percent of liquid based on the total



weight of liquid in the recycle stream is greater than 2.0 and reintroducing said recycle stream into said reactor;

e) introducing into said recycle stream additional monomers to replace monomers polymerized to maintain said ratio of said recycle stream, and

f) withdrawing said polymer product from said reactor.

36. The process in accordance with claim 35 wherein said at least one copolymerizable alpha-olefin comonomer has from 3 to 15 carbon atoms.

37. The process in accordance with claims 35 or 36 wherein the liquid and the gas phases are introduced separately into the reactor.

38. The process in accordance with any one of claims 35 to 37 wherein the polymer product has a density less than 0.910 g/cm³.

39. The process in accordance with any one of claims 35 to 38 wherein the polymer product has a melt index greater than 3 dg/min.

DATED this 2nd day of April, 1997.

EXXON CHEMICAL PATENTS INC.

WATERMARK PATENT & TRADEMARK ATTORNEYS
290 BURWOOD ROAD
HAWTHORN VICTORIA 3122
AUSTRALIA

LPS/ML DOC 11 AU6712794.WPC



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/04513

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08F10/00 C08F2/34

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification-symbols)
IPC 5 C08F

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 535 582 (IDEMITSU PETROCHEMICAL CO) 7 April 1993 see claims 1,2 see example 1 ---	1
Y	EP,A,0 241 947 (UNION CARBIDE CORPORATION) 21 October 1987 see claims 1-16 see example 1a see examples 1,4,5 ---	1
X A	& US,A,4 543 399 ---	13 2,3,5,6, 10,12
P,X	EP,A,0 593 083 (UNION CARBIDE CORPORATION) 20 April 1994 see page 5, line 29 - line 34 see page 6, line 7 - line 24 see table IX --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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 document but 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

19 August 1994

Date of mailing of the international search report

30.08.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Fischer, B

INTERNATIONAL SEARCH REPORT

Inter. Application No
PCT/US 94/04513

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,94 03509 (EXXON CHEMICALS PATENTS INC.) 17 February 1994 see page 23, line 31 - page 25, line 20 see example 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/04513

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0535582	07-04-93	JP-A-	5093015	16-04-93
		US-A-	5306790	26-04-94

EP-A-0241947	21-10-87	AU-A-	1268883	29-09-83
		AU-A-	7948791	26-09-91
		AU-A-	8214087	31-03-88
		CA-A-	1214000	11-11-86
		DE-A-	3382632	03-12-92
		EP-A, B	0089691	28-09-83
		JP-A-	58201802	24-11-83
		SU-A-	1473713	15-04-89
		US-A-	4543399	24-09-85
		US-A-	4588790	13-05-86

US-A-4543399	24-09-85	AU-A-	1268883	29-09-83
		AU-A-	7948791	26-09-91
		AU-A-	8214087	31-03-88
		CA-A-	1214000	11-11-86
		DE-A-	3382632	03-12-92
		EP-A, B	0089691	28-09-83
		EP-A, B	0241947	21-10-87
		JP-A-	58201802	24-11-83
		SU-A-	1473713	15-04-89
		US-A-	4588790	13-05-86

EP-A-0593083	20-04-94	US-A-	5317036	31-05-94
		AU-B-	4902893	28-04-94
		BR-A-	9304244	05-07-94
		CA-A-	2108528	17-04-94
		FI-A-	934579	17-04-94

WO-A-9403509	17-02-94	NONE		
