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(54) **Title**: PROCESS FOR PREPARING LOW MOLECULAR WEIGHT WAX

(57) **Abstract**: Polyethylene wax having a number average molecular weight of from 1,000 to 10,000 and a molecular weight distribution of from 2 to 4 may be produced using a phosphinimine catalyst under "forced" solution polymerization conditions. The "forced" conditions include high polymerization temperatures; comparatively low catalyst efficiencies and very high ethylene conversions. These "forced" conditions may be achieved by operating the reactor at a temperature of between 190° C and 250° C, using a high catalyst concentration and high ethylene conversion. Using these conditions, polyethylene wax may be produced in the absence of hydrogen.

PROCESS FOR PREPARING LOW MOLECULAR WEIGHT WAX

TECHNICAL FIELD

This invention relates to the preparation of polyethylene waxes having a narrow molecular weight distribution in a solution polymerization process using a phosphinimine catalyst.

BACKGROUND ART

Polyethylene waxes are readily available items of commerce and are used to prepare such products as paints, inks, cleaning waxes and polishes.

These waxes are prepared by the polymerization of ethylene (and, optionally, a comonomer such as butene, hexene or octene) in the presence of a catalyst. Conventional Zeigler Natta catalysts may be used to prepare the waxes, but extremely high levels of hydrogen are generally required to produce low molecular weights.

U.S. patent 5,023,388 teaches the use of a metallocene catalyst to prepare polyethylene without using disproportionately large amounts of hydrogen.

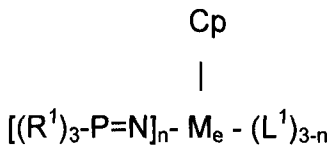
U.S. patent 6,063,879 (Stephan et al.) teaches the preparation of high molecular weight polyethylene in a solution polymerization process using a phosphinimine catalyst. We have now discovered that the phosphinimine catalyst disclosed in the Stephan et al. patent may also be used to prepare low molecular weight polyethylene waxes (even in the absence of hydrogen) when used at polymerization temperatures in excess of 190° C under polymerization conditions which allow greater than 90% ethylene conversion.

DISCLOSURE OF INVENTION

In one embodiment, the present invention provides:

A process to prepare polyethylene wax having a number average molecular weight of from 500 to 10,000 and a molecular weight distribution of from 2 to 4, said process comprising polymerizing ethylene and optionally, at least one C_3 to C_{10} alpha olefin, under solution polymerization conditions in a reactor in the presence of:

a) a catalyst defined by the formula:



wherein M_e is selected from the group consisting of Ti, Zr, and Hf; n is 1 or 2; Cp is a monocyclopentadienyl ligand which is unsubstituted or substituted by up to five substituents independently selected from the group consisting of a C_{1-10} hydrocarbyl radicals or two hydrocarbyl radicals taken together may form a ring which hydrocarbyl substituents or cyclopentadienyl radical are unsubstituted or further substituted by a halogen atom, a C_{1-8} alkyl radical, C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical; an amido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; silyl radicals of the formula -Si-$(R^2)_3$ wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals; germanyl radicals of the formula Ge-$(R^2)_3$ wherein R^2 is as defined above; each R^1 is independently selected from the group consisting of a hydrogen atom, a halogen atom, C_{1-10} hydrocarbyl radicals which are unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkyl radical, C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, a silyl radical of the formula -Si-$(R^2)_3$ wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, germanyl radical of the formula Ge-$(R^2)_3$ wherein R^2 is as defined above or two R^1 radicals taken together may form a bidentate C_{1-10} hydrocarbyl radical, which is unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkyl radical, C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, a silyl radical of the formula -Si-$(R^2)_3$ wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, germanyl radicals of the formula Ge-$(R^2)_3$ wherein R^2 is as defined above, provided that R_1 individually or two R_1 radicals taken together may not form a Cp ligand as defined above; each L^1 is independently selected from the group consisting of a hydrogen atom, of a halogen atom, a C_{1-10} hydrocarbyl radical a C_{1-10} alkoxy radical, a C_{5-10} aryl oxide radical, each of which said hydrocarbyl, alkoxy, and aryl oxide radicals may be unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkyl radical, C_{1-8} alkoxy radical, a C_{6-10} aryl or aryl oxy radical, an amido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals, provided that L^1 may not be a Cp radical as defined above; and

b) an activator,

with the provisos that:

1) said polymerization conditions are conducted at a temperature of from 190° C to 250° C;

2) at least 85 weight % of said ethylene is converted to polyethylene wax under said polymerization conditions; and

3) catalyst efficiency, Kp, is less than 300 but greater than 25 [mM × minutes]$^{-1}$, where mM is the concentration, expressed in millimoles, of said transition metal M_e within said reactor.

As used herein, the term "polyethylene wax" refers to a polymer of ethylene (and, optionally, an alpha olefin monomer) which has a number average molecular weight (Mn) of from about 500 to 10,000. The polyethylene waxes of this invention are further characterized by having a molecular weight distribution, Mw/Mn, of from 2 to 4 (where Mw is weight average molecular weight).

We have discovered that such waxes may be prepared at high polymerization temperatures under "forced" solution polymerization conditions. The term "forced" means that a very high ethylene conversion is achieved. In particular, the ethylene conversion must be greater than 85% (preferably greater than 90%) of the ethylene fed to the reactor. This forced condition can be achieved by using a very high level of catalyst (such that the catalyst efficiency, as quantified by the kinetic parameter "Kp" – discussed later) is less than 300. As will be shown in the Examples, wax may be produced using these conditions, even in the absence of hydrogen.

All three of these conditions (high temperature, high ethylene conversions and low catalyst efficiency) are required by the present invention. In other words, if only two of these conditions are used, the present catalyst system will generally provide a higher molecular weight polyethylene. Moreover, the catalyst efficiency (expressed as Kp, described below) is also strongly influenced by impurities. Specifically, impurities that are contained in the reactor feedstreams (for example, polar contaminants in the solvent or monomers) will typically reduce the catalyst efficiency without significantly changing the molecular weight of the polymer. While not wishing to be bound by theory, it is believed that such impurities interact with the catalyst in a manner that reduces or even eliminates the activity of the catalyst molecule that interacts with the impurity. The present invention requires comparatively high catalyst concentrations – even if all reactor feedstreams are highly purified. In other words, a given catalyst concentration that provides a high molecular weight thermoplastic polyethylene for given reaction conditions and a given ethylene conversion is "too low" for the process of

this invention. The molecular weight of the polymer can be reduced (so that wax is formed) by then increasing the catalyst concentration and ethylene conversion.

Finally, the Examples show that wax may be produced by the process of this invention even in the absence of hydrogen. The present invention does encompass the use of hydrogen. Hydrogen is a well known chain transfer agent and the use of hydrogen will generally allow the production of lower molecular weight polymer under less forced polymerization conditions.

BEST MODE FOR CARRYING OUT THE INVENTION

Part A. Catalyst

The catalyst used in this invention is a Group 4 metal complex of the formula:

$$[(R^1)_3\text{-}P{=}N]_n\text{-}\ M_e\ \text{-}\ (L^1)_{3-n}$$
with Cp

wherein M_e is selected from the group consisting of Ti, Zr, and Hf; n is 1 or 2; Cp is a monocyclopentadienyl ligand which is unsubstituted or substituted by up to five substituents independently selected from the group consisting of a C_{1-10} hydrocarbyl radicals or two hydrocarbyl radicals taken together may form a ring which hydrocarbyl substituents or cyclopentadienyl radical are unsubstituted or further substituted by a halogen atom, a C_{1-8} alkyl radical, C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical; an amido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; silyl radicals of the formula -Si-$(R^2)_3$ wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals; germanyl radicals of the formula Ge-$(R^2)_3$ wherein R^2 is as defined above; each R^1 is independently selected from the group consisting of a hydrogen atom, a halogen atom, C_{1-10} hydrocarbyl radicals which are unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkyl radical, C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, a silyl radical of the formula -Si-$(R^2)_3$ wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, germanyl radical of the formula Ge-$(R^2)_3$ wherein R^2 is as defined above or two R^1 radicals taken together may form a bidentate C_{1-10} hydrocarbyl radical, which is unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkyl radical, C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, a silyl radical of the formula -Si-$(R^2)_3$ wherein each R^2 is independently selected from the group consisting of hydrogen, a

C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, germanyl radicals of the formula $Ge-(R^2)_3$ wherein R^2 is as defined above, provided that R_1 individually or two R_1 radicals taken together may not form a Cp ligand as defined above; each L^1 is independently selected from the group consisting of a hydrogen atom, of a halogen atom, a C_{1-10} hydrocarbyl radical a C_{1-10} alkoxy radical, a C_{5-10} aryl oxide radical, each of which said hydrocarbyl, alkoxy, and aryl oxide radicals may be unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkyl radical, C_{1-8} alkoxy radical, a C_{6-10} aryl or aryl oxy radical, an amido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals, provided that L^1 may not be a Cp radical as defined above.

As used in this specification the term "cyclopentadienyl" refers to a 5-member carbon ring having delocalized bonding within the ring and typically being bound to the Group 4 metal (M) through covalent η^5 -bonds.

In the Group 4 metal complex preferably Cp is unsubstituted. However, if Cp is substituted preferred substituents include a fluorine atom, a chlorine atom, C_{1-6} hydrocarbyl radical, or two hydrocarbyl radicals taken together may form a bridging ring, an amido radical which is unsubstituted or substituted by up to two C_{1-4} alkyl radicals, a phosphido radical which is unsubstituted or substituted by up to two C_{1-4} alkyl radicals, a silyl radical of the formula $-Si-(R^2)_3$ wherein each R^2 is independently selected from the group consisting of a hydrogen atom and a C_{1-4} alkyl radical; a germanyl radical of the formula $-Ge-(R^2)_3$ wherein each R^2 is independently selected from the group consisting of a hydrogen atom and a C_{1-4} alkyl radical.

In the Group 4 metal complex preferably each R^1 is selected from the group consisting of a hydrogen atom, a halide, preferably fluorine or chlorine atom, a C_{1-4} alkyl radical, a C_{1-4} alkoxy radical, a silyl radical of the formula $-Si-(R^2)_3$ wherein each R^2 is independently selected from the group consisting of a hydrogen atom and a C_{1-4} alkyl radical; and a germanyl radical of the formula $-Ge-(R^2)_3$ wherein each R^2 is independently selected from the group consisting of a hydrogen atom and a C_{1-4} alkyl radical.

In the Group 4 metal complex preferably each L^1 is independently selected from the group consisting of a hydrogen atom, a halogen, preferably fluorine or chlorine atom, a hydrocarbyl such as a C_{1-6} alkyl radical, a C_{1-6} alkoxy radical, and a C_{6-10} aryl oxide radical.

Preferred catalysts are those in which M is titanium, each R^1 is an alkyl group (especially isopropyl or tertiary butyl) and there are 2 L ligands, each of which is preferably a halide (especially chlorine).

Part B. Activator

Preferred activators are selected from the groups consisting of aluminoxanes, ionic activators and mixtures of the two.

The aluminoxane activator may be of the formula $(R^4)_2AlO(R^4AlO)_mAl(R^4)_2$ wherein each R^4 is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and m is from 0 to 50, preferably R^4 is a C_{1-4} alkyl radical and m is from 5 to 30. Commercially available aluminoxanes (as described in the Examples) are preferably used for reasons of convenience, but aluminoxanes may be prepared by carefully reacting aluminum alkyls with small amounts of water.

Activation of a polymerization catalyst with aluminoxane generally requires a molar ratio of aluminum in the activator to Group 4 metal in the complex from 10:1 to 1000:1. The process of this invention preferably has an aluminum to Group 4 metal ratio of at least 50:1 (on a moler basis) most preferably from 50 to 500:1. High "absolute" amounts of aluminoxane are generally preferred. Without wishing to be bound by theory, it is believed that the high level of aluminum may lead to lower molecular weights (which is desired in the production of wax) by a chain transfer mechanism to aluminum. (Due to the high levels of transition metal catalyst that is preferably used in the process of this invention, the "absolute" levels of Al are also high even at relatively low Al/Ti ratios. For example, even at an Al/M ratio of 50/1, an increase of "X" millimoles of transition metal will increase the Al level by 50 X millimoles).

The "ionic activator" may be selected from the group consisting of:

(i) compounds of the formula $[R^5]^+ [B(R^7)_4]^-$ wherein B is a boron atom, R^5 is a cyclic C_{5-7} aromatic cation or a triphenyl methyl cation and each R^7 is independently selected from the group consisting of phenyl radicals which are unsubstituted or substituted with from 3 to 5 substituents selected from the group consisting of a fluorine atom, a C_{1-4} alkyl or alkoxy radical which is unsubstituted or substituted by a fluorine atom; and a silyl radical of the formula $-Si-(R^9)_3$; wherein each R^9 is independently selected from the group consisting of a hydrogen atom and a C_{1-4} alkyl radical; and

(ii) compounds of the formula $[(R^8)_t ZH]^+[B(R^7)_4]^-$ wherein B is a boron atom, H is a hydrogen atom, Z is a nitrogen atom or phosphorus atom, t is 2 or 3 and R^8 is selected

from the group consisting of C_{1-8} alkyl radicals, a phenyl radical which is unsubstituted or substituted by up to three C_{1-4} alkyl radicals, or one R^8 taken together with the nitrogen atom may form an anilinium radical and R^7 is as defined above; and

(iii) compounds of the formula $B(R^7)_3$ wherein R^7 is as defined above.

In the above compounds preferably R^7 is a pentafluorophenyl radical, and R^5 is a triphenylmethyl cation, Z is a nitrogen atom and R^8 is a C_{1-4} alkyl radical or R^8 taken together with the nitrogen atom forms an anilium radical which is substituted by two C_{1-4} alkyl radicals.

The "ionic activator" may abstract one or more L^1 ligands so as to ionize the Group 4 metal center into a cation but not to covalently bond with the Group 4 metal and to provide sufficient distance between the ionized Group 4 metal and the ionizing activator to permit a polymerizable olefin to enter the resulting active site.

Examples of ionic activators include the following compounds:

triethylammonium tetra(phenyl)boron,

tripropylammonium tetra(phenyl)boron,

tri(n-butyl)ammonium tetra(phenyl)boron,

trimethylammonium tetra(p-tolyl)boron,

trimethylammonium tetra(o-tolyl)boron,

tributylammonium tetra(pentafluorophenyl)boron,

tripropylammonium tetra (o,p-dimethylphenyl)boron,

tributylammonium tetra(m,m-dimethylphenyl)boron,

tributylammonium tetra(p-trifluoromethylphenyl)boron,

tributylammonium tetra(pentafluorophenyl)boron,

tri(n-butyl)ammonium tetra (o-tolyl)boron

N,N-dimethylanilinium tetra(phenyl)boron,

N,N-diethylanilinium tetra(phenyl)boron,

N,N-diethylanilinium tetra(phenyl)n-butylboron,

N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron

di-(isopropyl)ammonium tetra(pentafluorophenyl)boron,

dicyclohexylammonium tetra (phenyl)boron

triphenylphosphonium tetra)phenyl)boron,

tri(methylphenyl)phosphonium tetra(phenyl)boron,

tri(dimethylphenyl)phosphonium tetra(phenyl)boron,

tropillium tetrakispentafluorophenyl borate,

triphenylmethylium tetrakispentafluorophenyl borate,
benzene (diazonium) tetrakispentafluorophenyl borate,
tropillium phenyltris-pentafluorophenyl borate,
triphenylmethylium phenyl-trispentafluorophenyl borate,
benzene (diazonium) phenyltrispentafluorophenyl borate,
tropillium tetrakis (2,3,5,6-tetrafluorophenyl) borate,
triphenylmethylium tetrakis (2,3,5,6-tetrafluorophenyl) borate,
benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) borate,
tropillium tetrakis (3,4,5-trifluorophenyl) borate,
benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) borate,
tropillinum tetrakis (1,2,2-trifluoroethenyl) borate,
triphenylmethylium tetrakis (1,2,2-trifluoroethenyl) borate,
benzene (diazonium) tetrakis (1,2,2-trifluoroethenyl) borate,
tropillium tetrakis (2,3,4,5-tetrafluorophenyl) borate,
triphenylmethylium tetrakis (2,3,4,5-tetrafluorophenyl) borate, and
benzene (diazonium) tetrakis (2,3,4,5-tetrafluorophenyl) borate.
Readily commercially available ionic activators include:
N,N- dimethylaniliumtetrakispentafluorophenyl borate; triphenylmethylium tetrakispentafluorophenyl borate ("trityl borate"); and trispentafluorophenyl boron.

Part C. Monomers and Comonomers

Homopolymer polyethylene waxes are encompassed by this invention. However, preferred monomers are ethylene and C_{3-20} alpha olefins. Illustrative non-limiting examples of such alpha-olefins are one or more of propylene, 1-butene, 1-pentene, 1-hexene, 1-octene and 1-decene.

The polyethylene waxes which may be prepared in accordance with the present invention preferably comprise not less than 60, preferably not less than 70 weight % of ethylene and the balance of one or more C_{4-8} alpha olefins, most preferably selected from the group consisting of 1-butene, 1-hexene, 1-octene. The polyethylene waxes may contain large amounts of comonomer (and, as a result, have a very low density of less than 0.900 g/cc) or be ethylene homopolymers (having a density of greater than 0.955 g/cc) or copolymer waxes with intermediate levels of comonomer having an intermediate density.

As previously noted, the waxes of this invention have a number average molecular weight of from 500 to 10,000 (preferred range is from 500 to 2000). Comonomer may also be used to reduce the melting point of the wax.

Part D. Solution Polymerization

Solution polymerization processes for the preparation of polyethylene are well known in the art. These processes are conducted in the presence of a hydrocarbon solvent for the polymer, which solvent is typically a C_{5-12} hydrocarbon which may be unsubstituted or substituted by C_{1-4} alkyl group, such as pentane, hexane, heptane, octane, cyclohexane, methylcyclohexane and hydrogenated naphtha. An additional solvent is Isopar E (C_{8-12} aliphatic solvent, Exxon Chemical Co.).

Solution polymerizations for polyethylene are generally conducted at temperatures from about 80°C to about 250°C. The pressure of reaction may be as high as about 15,000 psig for the older high pressure processes or may range from about 100 to 4,500 psig. However, we have determined that high polymerization temperatures (especially greater than about 190° C) are preferable for the preparation of waxes.

In a solution polymerization the liquid monomers are dissolved/ dispersed in the solvent either prior to being fed to the reactor, or for gaseous monomers the monomer may be fed to the reactor so that it will dissolve in the reaction mixture. Prior to mixing, the solvent and monomers are generally purified to remove polar moieties. The polar moieties, or catalyst poisons include water, oxygen, metal impurities, etc. Preferably steps are taken before provision of such into the reaction vessel, for example by chemical treatment or careful separation techniques after or during the synthesis or preparation of the various components. The feedstock purification prior to introduction into the reaction solvent follows standard practices in the art, e.g. molecular sieves, alumina beds and oxygen removal catalysts are used for the purification of ethylene, alpha-olefin, and optional diene. The solvent itself as well (e.g. hexane and toluene) is similarly treated. In some instances, out of an abundance of caution excess scavenging activators may be used in the polymerization process.

The feedstock may be heated prior to feeding to the reactor. However, in many instances it is desired to remove heat from the reactor so the feed stock may be at ambient temperature to help cool the reactor.

Generally, the catalyst components may be premixed in the solvent for the reaction or fed as separate streams to the reactor. In some instances premixing is

desirable to provide a reaction time for the catalyst components prior to entering the reaction.

The reactor may comprise a tube or serpentine reactor used in the "high pressure" polymerizations or it may comprise one or more reactors or autoclaves. It is well known that the use in series of two such reactors each of which may be operated so as to achieve different polymer molecular weight characteristics. The residence time in the reactor system will depend on the design and the capacity of the reactor. Generally the reactors should be operated under conditions to achieve a thorough mixing of the reactants. On leaving the reactor system the solvent is removed and the resulting polymer is finished in a conventional manner.

EXAMPLES

Chemicals and Reagents

Purchased cyclohexane was dried and deoxygenated by passing it through a bed of deoxygenation catalyst (brand name R311 from BASF), an alumina bed (brand name Selexsorb COS/CD), and a molesieve (3A/13X) bed.

Purchased o-xylene was further purified by passing through the same purification beds as described for cyclohexane purification.

Ethylene was purchased from Praxair as polymer grade. The ethylene was purified and dried by passing the gas through a series of purification beds including alumina (brand: Selexsorb COS), molesieve (type: 13X), and a deoxygenation bed (brand: Oxiclear®).

Cyclopentadienyltitanium-(tri-tert-butylphosphinimino) dichloride was synthesized according the procedure disclosed in the publication (*Organometallics,* **2003**, *22*, 1937-1947) and confirmed with ^{1}H-NMR for 98.9% of purity.

Tritylborate was purchased from Albemarle with minimum 97% of purity.

Methylaluminoxane ("MAO") was purchased from Akzo Nobel under the trade name MMAO-7, reported to contain 13.0 wt% of Al.

4-ethyl-2,6-di-tert-butyl phenol ("Phenol 1") was purchased from Aldrich with 99% of purity.

Purchased 1-butene was dried by passing a series of columns containing 3A, COS and 13X.

Butene cyclohexane solution was prepared by passing pure 1-butene gas into butene absorption vessel containing cyclohexane. The concentration of 1-butene was determined by collecting a pressurized sample of 1-buene in cyclohexane using a

sample loop. The collected sample was then analyzed by gas chromatography (GC-FID) to obtain a weight % (wt%) of butene in the cyclohexene.

Purchased 1-hexene was dried by in a similar way as 1-butene.

Purchased isopropanol was used without further purification.

Analytical Methods

Polymer molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC). The instrument (Waters 150-C) was used at 140°C in 1,2,4-trichlorobenzene and was calibrated using polyethylene standards.

Polymer branch frequencies were determined by Fourier Transform-Infra Red (FT-IR). The instrument used was a Nicolet 750 Magna-IR spectrophotometer.

Butene content was determined by GC-FID. Composition was measured by split injection capillary gas chromatography with flame ionization detection. Sample injection was done with a pressurized liquid injection valve system. Component response factors were assumed to be unity. The GC-FID instrument used was HP 5890 Series 2.

Continuous Polymerization

Continuous polymerizations were conducted on a continuous polymerization unit (CPU). The CPU contained a 71.5 millilitre (mL) stirred reactor and was operated between 160-280 °C for the polymerization experiments. An upstream mixing reactor having a 20 mL volume was operated at 5° C lower than the polymerization reactor to a maximum 220° C. The mixing reactor was used to pre-heat the monomers and some of the solvent streams. Catalyst feeds and the rest of the solvent were added directly to the polymerization reactor as a continuous process. A total continuous flow of 27 mL/minute ("min") into the polymerization reactor was maintained. MAO and phenol 1 solutions were premixed prior to entering the reactor and the catalyst and the tritylborate were premixed before entering the reactor. The catalyst was activated in situ (in the polymerization reactor) at the reaction temperature in the presence of the monomers. Ethylene was supplied to the reactor by a calibrated thermal mass flow meter and was dissolved in the reaction solvent prior to the polymerization reactor. The comonomers were premixed with the ethylene before entering the polymerization reactor. Internal reaction temperature is monitored by a thermocouple in the polymerization medium and can be controlled at the required set point to ± 0.5° C. Ethylene and 1-hexene copolymer was made at 1-hexene / ethylene weight ratio of 0.75. 1 and 1.5. Ethylene and 1-butene copolymers were made at a 1-butene / ethylene weight ratio of 1. The ethylene was fed at a 2.0 g/min of ethylene to the

polymerization reactor for the 1-butene runs whereas at a 4.5 g/min of ethylene for the 1-hexene runs. The CPU system operated at a pressure of 10.5 Mega Pascals (MPa). The solvent, monomer and comonomer streams were all purified by the CPU systems before entering the reactor. Q is ethylene conversation (and determined by an online gas chromatograph (GC)) and polymerization activity Kp is defined as:

(Kp)(HUT)=Q((1-Q)(1/catalyst concentration)

wherein Q is the fraction of ethylene monomer converted; HUT is a reciprocal space velocity (hold up time) in the polymerization reactor expressed in minutes and maintained constant throughout the experimental program; and the catalyst concentration is the concentration in the polymerization reactor expressed in mmol of transition metal (Ti) per liter. Thus, the units for Kp are $[mM \times min]^{-1}$ where mM is the millimoler concentration of the transition metal in the catalyst (which is titanium in the Examples) and min is minutes. The concentration of catalyst used in each experiment is shown in Table 1 (expressed as the micromolar concentration of Ti). MAO was added with an Al/Ti aiming point of 80/1; tritylborate was added with a B/Ti aiming point of 1.2/1; phenol 1 was added with a phenol 1/Al aiming point of 0.3/1 (where all of these ratios are expressed on a moler basis).

Downstream of the reactor the pressure was reduced from the reaction pressure to atmospheric pressure. The solid polymer was then recovered as a slurry in the condensed solvent and was dried by evaporation and vacuum oven before analysis.

In this set of experiments, polymerization temperature and ethylene conversion were used to control the polymer molecular weights.

Mn (or number average molecular weight) is reported in Table 1. "PD" (or "polydispersity", also known as "molecular weight distribution"), which is calculated by dividing weight average molecular weight ("Mw") by Mn is also reported in Table 1.

INDUSTRIAL APPLICABILITY

A process for the preparation of very low molecular weight ethylene polymers having a narrow molecular weight distribution. These low molecular polymers are useful as waxes. The waxes are useful in the formulation of polishes and protective coatings and may also be used in blends with higher molecular weight polyethylenes.

TABLE 1

run #	polymerization temperature C	Comonomer to C2 ratio	C2 in feed	Ti concentration in reactor	Q %	Kp (1/mM*min)	comonomer content	comonomer type	Mn	Pd
			g /min	µM			wt %			
1	230	1	2	37.04	93.6	152.82	14.1	butene	1744	2.82
2	230	1	2	50.00	90.7	75.59	13.7	butene	1582	2.99
3	230	1	2	74.07	92.6	65.54	14.5	butene	1742	2.6
4	240	1	2	74.07	87.5	36.35	10	butene	1457	3.67
5	220	1	1.47	32.03	91.6	130.47	14.4	butene	1998	2.64
6	220	1.01	2	29.11	92.7	168.29	15.6	butene	2232	2.74
7	220	1.01	2	21.49	90.3	167.49	12.8	butene	2600	3.68
8	210	1.01	2	19.29	92.5	247.72	16	butene	3324	2.47
9	210	1.01	2	13.93	90.1	250.67	13.3	butene	3423	2.94
10	224.3	1.5	4.5	22.42	90.7	168.18	18.2	hexene	3185	3.53
11	220	0.7	4.5	14.90	90.9	258.57	9.5	hexene	5228	3.64
12	220	1	4.5	16.52	89.4	196.14	10.7	hexene	9288	2.17

C = Centigrade
C_2 = ethylene
Mn = number average molecular weight
Pd = Mw/Mn
mM = millimoles
µM = micromoles

CLAIMS

1. A process to prepare polyethylene wax having a number average molecular weight of from 500 to 10,000 and a molecular weight distribution of from 2 to 4, said process comprising polymerizing ethylene and optionally, at least one C_3 to C_{10} alpha olefin, under solution polymerization conditions in a reactor in the presence of:

a) a catalyst defined by the formula:

$$[(R^1)_3\text{-}P{=}N]_n\text{-}\ M_e\ \text{-}\ (L^1)_{3-n}$$
$$|$$
$$Cp$$

wherein M_e is selected from the group consisting of Ti, Zr, and Hf; n is 1 or 2; Cp is a monocyclopentadienyl ligand which is unsubstituted or substituted by up to five substituents independently selected from the group consisting of a C_{1-10} hydrocarbyl radicals or two hydrocarbyl radicals taken together may form a ring which hydrocarbyl substituents or cyclopentadienyl radical are unsubstituted or further substituted by a halogen atom, a C_{1-8} alkyl radical, C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical; an amido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; silyl radicals of the formula -Si-$(R^2)_3$ wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals; germanyl radicals of the formula Ge-$(R^2)_3$ wherein R^2 is as defined above; each R^1 is independently selected from the group consisting of a hydrogen atom, a halogen atom, C_{1-10} hydrocarbyl radicals which are unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkyl radical, C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, a silyl radical of the formula -Si-$(R^2)_3$ wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, germanyl radical of the formula Ge-$(R^2)_3$ wherein R^2 is as defined above or two R^1 radicals taken together may form a bidentate C_{1-10} hydrocarbyl radical, which is unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkyl radical, C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, a silyl radical of the formula -Si-$(R^2)_3$ wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, germanyl radicals of the formula Ge-$(R^2)_3$ wherein R^2 is as defined above, provided that R_1

individually or two R_1 radicals taken together may not form a Cp ligand as defined above; each L^1 is independently selected from the group consisting of a hydrogen atom, of a halogen atom, a C_{1-10} hydrocarbyl radical a C_{1-10} alkoxy radical, a C_{5-10} aryl oxide radical, each of which said hydrocarbyl, alkoxy, and aryl oxide radicals may be unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkyl radical, C_{1-8} alkoxy radical, a C_{6-10} aryl or aryl oxy radical, an amido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals, provided that L^1 may not be a Cp radical as defined above; and

b) an activator,

with the provisos that:

1) said polymerization conditions are conducted at a temperature of from 190° C to 250° C;

2) at least 85 weight % of said ethylene is converted to polyethylene wax under said polymerization conditions; and

3) catalyst efficiency, Kp, is less than 300 but greater than 25 [mM × minutes]$^{-1}$, where mM is the concentration, expressed in millimoles, of said transition metal M_e within said reactor.

2. The process of claim 1 wherein said M_e is titanium.

3. The process of claim 1 wherein said activator includes both an aluminoxane and an ionic activator.

4. The process of claim 1 wherein said catalyst is cyclopentadienyl titanium – (tri-tertiarybutyl phosphinimine) dichloride.

5. The process of claim 4 wherein said activator is a combination of methylaluminoxane and tritylborate.

6. The process of claim 5 wherein the moler ratio of aluminum contained in said methylaluminoxane to titanium contained in said catalyst is from 50:1 to 500:1.

7. The process of claim 6 wherein said number average molecular weight is from 500 to 2000.

8. The process of claim 1 which comprises polymerizing ethylene and one C_4 to C_8 alpha olefin.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2011/000168

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***C08F 4/6592*** (2006.01) , ***C08F 10/02*** (2006.01) , ***C08F 2/00*** (2006.01) , ***C08F 2/04*** (2006.01)

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: ***C08F 4/6592*** (2006.01) , ***C08F 10/02*** (2006.01) , ***C08F 2/00*** (2006.01) , ***C08F 2/04*** (2006.01)

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

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

Canadian Patent Database, WEST (PGPB, USPT, USOC, EPAB, JPAB), Scopus, EPOQUE (Epodoc); keywords: catalyst, phosphinimine?, *ethylene, wax, waxes, (low ADJ3 weight), temperature, solution.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,777,509 B2 (BROWN et al.) 17 August 2004 (17-08-2004) Col. 2, line 25 - Col. 4, line 1; Col. 6, lines 1-17, 32-48; Example 9; Table 1	1-8
A	US 6,355,744 B1 (von HACKEN SPENCE et al.) 12 March 2002 (12-03-2002) entire document	1-8
A	US 6,063,879 A (STEPHAN et al.) 16 May 2000 (16-05-2000) Cited by Applicant entire document	1-8

[ ] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent 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	Date of mailing of the international search report
07 April 2011 (07-04-2011)	6 May 2011 (06-05-2011)

Name and mailing address of the ISA/CA	Authorized officer
Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Samantha Drouin (819) 934-2324

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2011/000168

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)

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

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

2. [X] Claim Nos. : 1-8
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically :

See the extra sheet.

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

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows :

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos. :

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos. :

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

[ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

[ ] No protest accompanied the payment of additional search fees.

Extra Sheet.

Continuation of Box No. II.

The claimed subject-matter is based, in part, on the "catalyst efficiency, Kp", but there is considerable ambiguity surrounding the present definition of this parameter. As a result, the claims so lack clarity under PCT Article 6 that a precise search of the subject-matter as claimed cannot be performed. The search under PCT Article 17(2)(a) has therefore been carried out without regard for the parameter of "catalyst efficiency, Kp".

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