

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
17 February 2005 (17.02.2005)

PCT

(10) International Publication Number  
**WO 2005/014680 A1**

- (51) International Patent Classification<sup>7</sup>: **C08F 297/08**, C08L 23/00
- (21) International Application Number:  
PCT/EP2004/007897
- (22) International Filing Date: 16 July 2004 (16.07.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
0317012.3 21 July 2003 (21.07.2003) GB
- (71) Applicant (for all designated States except US): **BOREALIS TECHNOLOGY OY** [FI/FI]; P.O. Box 330, FIN-06101 Porvoo (FI).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **FELL, Hans, Jörg** [DE/NO]; Fagerlia 14, N-3960 Stathelle (NO). **WALTER, Philipp** [DE/DE]; Bruhlstrasse 3, 79540 Lörrach (DE).
- (74) Agent: **FRANK B. DEHN & CO.**; 179 Queen Victoria Street, London EC4V 4EL (GB).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**  
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



**WO 2005/014680 A1**

(54) Title: INJECTION MOULDING POLYMER

(57) Abstract: The use of a multimodal polyethylene composition comprising as comonomers to ethylene at least two C<sub>4-12</sub> alpha olefins in injection moulding.

Injection Moulding Polymer

This invention relates to a new polymer for  
5 injection moulding, in particular to a bimodal  
terpolymer composition which gives rise to a polymer  
having ideal properties for injection moulding,  
especially for moulding articles which will be used in  
contact with food.

10 Linear low density polyethylenes (LLDPE's) are  
widely used in the manufacture of packaging products  
which are typically produced by injection moulding.  
Conventional LLDPE's are made using Ziegler-Natta  
catalysis and therefore have broad molecular weight  
15 distributions.

In many applications, e.g. where food products are  
being packaged, it is essential that the injection  
moulded article, e.g. container or closure means  
therefor, does not contaminate the product. For these  
20 applications, an indication of the degree of  
contamination may be obtained from tests which  
determine the level of migration of the polymer  
material, e.g. when immersed in olive oil or hexane.  
Ziegler-Natta produced LLDPE polymers have been found  
25 to exhibit high levels of migration, i.e. foods in  
contact with Ziegler-Natta LLDPE's may become  
contaminated with polymer, and are therefore unsuitable  
for use in applications such as food and medical  
product packaging, especially where contact with fatty  
30 foods is made.

LLDPE's made using single site catalysis, in  
particular those produced using metallocenes  
(mLLDPE's), have been found to give rise to injection  
moulded articles having acceptable levels of migration  
35 due to their much narrower molecular weight  
distributions and molecular weight independent short  
chain branching distribution (SCBD). As discussed in  
WO01/96419 such LLDPE's are particularly useful for-

packaging fatty foods. However, mLLDPE's exhibit low shear thinning and do not therefore exhibit ideal processability.

When the mLLDPE is exposed to shear, e.g. during the screw and melting procedure prior to injection into the mould, its lack of shear thinning causes high pressure build up in the injection moulding machine, increased motor load, etc. Thus, the polymer is generally hard to process. This problem has been solved by the inclusion of long chain branches into the mLLDPE and these can be introduced by, for example, blending with high pressure polyethylene, post reactor treatment or *in situ* formation.

However, blending and post reactor treatment of the polymer are cost intensive procedures and the *in situ* formation of long chain branches requires particular single site catalysts and polymerisation conditions. Thus long chain branching inclusion is not favoured.

It is also known that mechanical properties, e.g. impact properties, can be generally improved by employing higher olefins. Thus whilst 1-butene is a commonly used comonomer, improved mechanical properties, e.g. impact properties, can be obtained relative to 1-butene using 1-hexene as comonomer.

The use of higher alpha-olefin comonomers, i.e. C<sub>4</sub> or greater alpha-olefins, however increases the cost of the polymer product and, generally, the efficiency of comonomer incorporation decreases as the carbon content of the comonomer increases, i.e. hexene is less efficiently incorporated than butene and octene is less efficiently incorporated than hexene, etc. For cost and efficiency reasons therefore, incorporation of higher alpha olefins is not always favoured.

There remains a need therefore to manufacture polymers for injection moulding which have low migration properties, excellent mechanical properties

as well as high shear thinning and hence acceptable processing properties. The polymers must also be cheap to manufacture to satisfy the packaging market.

We have now surprisingly found that by  
5 incorporating two different alpha-olefin comonomers into a polyethylene polymer, a multimodal polyethylene terpolymer product may be produced which has ideal properties for injection moulding compared to polyethylenes produced using either of the comonomers  
10 as the sole comonomer. The polyethylene terpolymers of the invention possess a multimodal molecular weight distribution therefore giving rise to improved processability and mechanical properties whilst migration is kept to a minimum by the different  
15 densities of the terpolymer component and the resulting reduction in short chain branching in the shorter chain components.

Thus, viewed from one aspect the invention provides the use of a multimodal, e.g. bimodal,  
20 polyethylene composition comprising as comonomers to ethylene at least two C<sub>4-12</sub> alpha olefins, preferably at least two alpha olefins selected from but-1-ene, hex-1-ene, 4-methyl-pent-1-ene, hept-1-ene, oct-1-ene, and dec-1-ene, particularly but-1-ene and hex-1-ene in  
25 injection moulding.

Viewed from another aspect the invention provides an injection moulded article produced from a multimodal polyethylene composition comprising as comonomers to ethylene at least two C<sub>4-12</sub> alpha olefins, preferably at  
30 least two alpha olefins selected from but-1-ene, hex-1-ene, 4-methyl-pent-1-ene, hept-1-ene, oct-1-ene, and dec-1-ene, particularly but-1-ene and hex-1-ene.

Typically, the polyethylene composition is a mixture of two or more polyethylenes, e.g. produced by  
35 blending or by two-or-more stage polymerization reactions. The constituent polyethylenes may be homopolymers, copolymers, terpolymers or polymers of

four or more comonomers; preferably however at least one polymer is a terpolymer or at least two polymers are copolymers, in particular in which one monomer, the major component, is ethylene and one or two comonomers, the minor components, are C<sub>4</sub> and/or C<sub>6</sub> alpha-olefins.

In an especially preferred embodiment, the polyethylene composition comprises an ethylene/1-butene copolymer fraction and an ethylene/1-butene/1-hexene terpolymer fraction.

It is especially preferred that the polymer be prepared in a two or more stage polymerization in which in an earlier stage the lower alpha-olefin comonomer (e.g. 1-butene) is incorporated and in which in a later stage the higher alpha-olefin comonomer is incorporated (e.g. 1-hexene). Nonetheless, it is within the scope of the invention to produce the polymer in a two stage polymerization reaction in which an ethylene homopolymer is produced in the first stage and an ethylene terpolymer is produced in the second stage or vice versa or in which an ethylene copolymer with the higher alpha-olefin comonomer is produced in the first stage and an ethylene copolymer with the lower alpha-olefin comonomer is produced in the second stage. Likewise, an ethylene copolymer may be produced in the first stage and an ethylene terpolymer in the second stage and vice versa. Terpolymers may also be produced in both stages although preferably a lower molecular weight higher density terpolymer is formed in a first stage with a higher molecular weight lower density terpolymer being formed in a second stage.

The expression "homopolymer" of ethylene used herein refers to a polyethylene that consists substantially, i.e. at least 98% by weight, preferably at least 99% by weight, more preferably at least 99.5% by weight, most preferably at least 99.8% by weight, of ethylene.

The ethylene polymers of the injection moulded articles of the invention can be produced using a Ziegler-Natta catalyst or a single site catalyst.

Preferably however, the polyethylene polymers of use in the invention are produced using a so-called single site catalyst, e.g. a catalyst comprising a metal coordinated by one or more  $\eta$ -bonding ligands. Such  $\eta$ -bonded metals are normally referred to as metallocenes and the metals are typically Zr, Hf or Ti, especially Zr or Hf. The  $\eta$ -bonding ligand is typically an  $\eta^5$ -cyclic ligand, i.e. a homo or heterocyclic cyclopentadienyl group optionally with fused or pendant substituents. Such metallocene catalysts have been widely described in the scientific and patent literature for about twenty years. Such metallocene catalysts are frequently used with catalyst activators or co-catalysts, e.g. alumoxanes such as methylaluminoxane, again as widely described in the literature.

Preferred metallocenes are optionally bridged bisindenyl or biscyclopentadienyl compounds with Hf, Zr or Ti. The  $\eta$ -ligands can carry typical substituents, preferably up to 5, e.g. 1 or 2,  $C_{1-6}$ -alkyl substituents as is known in the art. The metal ions conventionally are coordinated to sigma ligands, e.g. two chloride ligands. Bridges are typically ethylene or silyl based, e.g. dimethylsilyl.

The polymer used in the articles of the invention is multimodal, preferably bimodal, i.e. its molecular weight profile does not comprise a single peak but instead comprises the combination of two or more peaks (which may or may not be distinguishable) centred about different average molecular weights as a result of the fact that the polymer comprises two or more separately produced components. In this embodiment, a higher molecular weight component preferably corresponds to a

copolymer (or terpolymer etc.) of the higher alpha-olefin comonomer and a lower molecular weight component preferably corresponds to an ethylene homopolymer or a copolymer (or terpolymer etc.) of the lower alpha-olefin comonomer. Such bimodal ethylene polymers may be prepared for example by two or more stage polymerization or by the use of two or more different polymerization catalysts in a one stage polymerization. Preferably however they are produced in a two-stage polymerization using the same catalyst, e.g. a metallocene catalyst, in particular a slurry polymerization in a loop reactor followed by a gas phase polymerization in a gas phase reactor. A loop reactor - gas phase reactor system is marketed by Borealis A/S, Denmark as a BORSTAR reactor system.

Preferably, the lower molecular weight polymer fraction is produced in a continuously operating loop reactor where ethylene is polymerized in the presence of a polymerization catalyst as stated above and a chain transfer agent such as hydrogen. The diluent is typically an inert aliphatic hydrocarbon, preferably isobutane or propane. A C<sub>4</sub> to C<sub>12</sub> -olefin comonomer is preferably added to control the density of the lower molecular weight copolymer fraction.

Preferably, the hydrogen concentration is selected so that the lower molecular weight copolymer fraction has the desired melt flow rate.

In the case where the target density of the lower molecular weight copolymer fraction exceeds 955 kg/m<sup>3</sup>, it is advantageous to operate the loop reactor using propane diluent in so called supercritical conditions where the operating temperature exceeds the critical temperature of the reaction mixture and the operating pressure exceeds the critical pressure of the reaction mixture. A preferred range of temperature is then from 90 to 110°C and the range of pressures is from 50 to 80 bar.

The slurry is intermittently or continuously removed from the loop reactor and transferred to a separation unit where at least the chain transfer agents (e.g. hydrogen) are separated from the polymer. The polymer containing the active catalyst is then introduced into a gas phase reactor where the polymerization proceeds in the presence of additional ethylene, comonomer(s) and optionally chain transfer agent to produce the higher molecular weight copolymer fraction. The polymer is intermittently or continuously withdrawn from the gas phase reactor and the remaining hydrocarbons are separated from the polymer.

The conditions in the gas phase reactor are selected so that the ethylene polymer has the desired properties. Preferably, the temperature in the reactor is between 70 and 100°C and the pressure is between 10 to 40 bar. The hydrogen to ethylene molar ratio ranges from preferably 0 to 1 mol/kmol, more preferably 0 to 0.5 mol/kmol and the alpha-olefin comonomer to ethylene molar ratio ranges from preferably 1 to 100 mol/kmol, more preferably 5 to 50 mol/kmol and most preferably 5 to 30 mol/kmol.

The injected moulded article of the invention may be prepared using conventional injection moulding apparatus, e.g. a repetitive process in which plastic is melted and injected into a mould cavity where the article is cooled down. After cooling, the mould opens and the article is ejected.

The melt can be prepared conventionally in a screw set up which acts to melt and homogenise the polymer while slowly retracting to build up the melt reservoir necessary for the injection step. The screw can then be used as a plunger in a forward movement to inject the melt through the runner, optionally a manifold and the gate into the mould.

Whilst the polyethylene composition may be used to make any injection moulded article it is preferred if

the articles are for use in medical or food packaging in particular closure means such as lids or plastic storage containers or eating/drinking containers e.g. cups, bowls, dishes etc.

5 Viewed from a further aspect the invention provides a product (e.g. foodstuff, medical product etc) packaged within an injection moulded article as hereinbefore described. The articles of the invention are particularly suited to packaging fatty foods.

10 The article of the invention is preferably formed from either (I) a bimodal polyethylene composition comprising

15 a) a lower molecular weight homopolymer of ethylene and

b) a higher molecular weight terpolymer of ethylene, 1-butene and a C<sub>5</sub> to C<sub>12</sub> alpha-olefin (e.g. C<sub>6</sub> to C<sub>12</sub> alpha-olefin); or

20 (II) a bimodal polyethylene composition comprising

25 a) a lower molecular weight polymer which is a binary copolymer of ethylene and 1-butene or 1-hexene and

30 b) a higher molecular weight polymer different from a) which is either a binary copolymer of ethylene and 1-hexene, or a terpolymer of ethylene, 1-butene and a C<sub>5</sub> to C<sub>12</sub> alpha-olefin (e.g. C<sub>6</sub> to C<sub>12</sub> alpha-olefin); or

(III) a bimodal polyethylene composition comprising

35 a) a lower molecular weight polymer which is a terpolymer of ethylene, 1-butene and 1-hexene, and

- b) a higher molecular weight polymer which is a terpolymer of ethylene, 1-butene and 1-hexene.

5

The polymers used in the manufacture of these articles may themselves be new and hence form a still yet further aspect of the invention.

In a preferred embodiment the present invention provides an article of a bimodal polymer with a relatively narrow molecular weight distribution (MWD), good processability, and a low level of extractibles. The MWD is preferably 2 to 25, e.g. 2 to 10, more preferably 2.0 to 8.0, e.g. 2.0 to 6.0 or 3.0 to 8.0, especially 2.5 to 4.5.

The weight average molecular weight of the multimodal e.g. bimodal polymer is preferably between 15,000 and 250,000 g/mol, e.g. 20,000 to 180,000, preferably 30,000 to 140,000.

The molecular weight distribution of the polymer is further characterized by the way of its melt flow rate (MFR) according to ISO 1133 at 190°C. The final multimodal e.g. bimodal polymer preferably has a melt flow rate MFR<sub>2</sub> of 0.4 to 100 g/10min, more preferably of 0.8 to 80 g/10min, especially 1.5-40 g/10min. The lower molecular weight polymer fraction preferably has a melt index MFR<sub>2</sub> of 1 to 400 g/10min, more preferably of 10 to 200 g/10min, especially 50 to 150 g/10min.

The melt flow rate and the density of the material are decisive for strength properties.

The density of the final multimodal e.g. bimodal polymer is preferably 870 to 940 kg/m<sup>3</sup>, more preferably of 890 to 935 kg/m<sup>3</sup>, especially 905 to 930 kg/m<sup>3</sup>. The density of the lower molecular weight polymer fraction is preferably 905 to 975 kg/m<sup>3</sup>, more preferably 915 to 950 kg/m<sup>3</sup>, especially 920 to 945 kg/m<sup>3</sup>, e.g. 930 kg/m<sup>3</sup> or greater. The density of the lower molecular weight

35

fraction of the polyethylene composition should preferably be greater than that of the higher molecular weight composition.

The multimodal e.g. bimodal polymer according to the present invention preferably comprises 10 to 70%, more preferably 20 to 65% and most preferably 40 to 60% by weight of the lower molecular weight copolymer fraction with regard to the total composition.

The overall comonomer content in the polymer is preferably 0.1 to 10 mol%, preferably 0.5 to 7 mol% and in the lower molecular weight polymer the comonomer content is preferably 0 to 3.0 mol%, preferably 0 to 2.5 mol%. In the higher molecular weight polymer the comonomer content is preferably 0.1 to 10 mol%, preferably 0.1 to 7 mol%. Comonomer contents may be measured by NMR.

Further, the molecular weight of the higher molecular weight copolymer fraction should be such that when the lower molecular weight copolymer fraction has the melt index and density specified above, the final multimodal polymer has the melt index and density as discussed above.

The final multimodal e.g. bimodal polymer preferably has a tensile modulus (ISO527-2) of 10 to 500 MPa, preferably 30 to 450 MPa, especially 60 to 400 MPa.

The final multimodal e.g. bimodal polymer preferably has an Impact strength (ISO179 23°C) of at least 30 kJ/m<sup>2</sup>, preferably at least 40 kJ/m<sup>2</sup>, especially at least 50 kJ/m<sup>2</sup>.

The final multimodal e.g. bimodal polymer preferably has a hexane extractable fraction of less than 5, preferably less than 3, more preferably less than 2.5, especially less than 2 wt%.

The final multimodal polymer preferably has a low level of migration measured by immersion in olive oil

(as in Example 6) of less than 10, preferably less than 5, especially less than 3 mg/dm<sup>2</sup>.

It has surprisingly been found that for the same density the polymers of the invention exhibit high tensile modulus and high impact strength compared to conventional copolymers. In general, stiffness (tensile strength) and impact are intrinsically linked to crystallinity and thereby the density. So increasing density increases stiffness and decreases impact. However, in the polymers of the invention high stiffness and high impact strength are observed even at relatively high densities. This stiffness/impact balance allows the production of injected moulded articles with reduced wall thicknesses, i.e. lighter and cheaper injected moulded articles and also allows cycle times to be decreased, i.e. increase the number of injections per minute. Hence the polymers of the invention allow the production of more articles at less cost than is conventionally achieved.

In addition to the polymer itself, the composition and injection moulded article of the invention may also contain antioxidants, process stabilizers, pigments and other additives known in the art.

The present invention will now be illustrated further by the following non-limiting Examples:

#### **Experimental:**

##### **MFR**

MFR was measured according to ISO 1133 at 190°C. The load has been indicated as a subscript, i.e. MFR<sub>2</sub> denotes the measurement has been carried out under a load of 2.16 kg and MFR<sub>21</sub> denotes the measurement has been carried out under a load of 21.6 kg, respectively.

35

##### **M<sub>w</sub>, M<sub>n</sub> and MWD:**

The weight-average molecular weight M<sub>w</sub>, and the

molecular weight distribution ( $MWD = M_w/M_n$ , where  $M_n$  equals number-average molecular weight) is measured by a method based on ISO/TC61/SC5 N 5024. The difference between this method and the method used is the  
5 temperature; the ISO method being at room temperature while the method used being at 140°C. The ratio of  $M_w$  and  $M_n$  is a measure of the broadness of the distribution, since each is influenced by the opposite end of the "population".

10

**Density:**

Density is measured according to ISO 1183/D.

**1-butene and 1-hexene contents:**

15 1-butene and 1-hexene contents of the polymers were determined by  $^{13}\text{C}$  NMR.

**Extractables in hexane:**

Hexane extractions are carried out using ASTM D5227.

20

**Rheology:**

The rheological properties of the polymers were determined using Rheometrics RDA II Dynamic Rheometer. The measurements were carried out at 190°C under a  
25 nitrogen atmosphere. The measurement give storage modulus ( $G'$ ) and loss modulus ( $G''$ ) together with absolute value of complex viscosity ( $*$ ) as a function of frequency or absolute value of complex modulus ( $G^*$ ), where:

30

$$* = ((G'^2 + G''^2) / )^{1/2}$$

$$G^* = (G'^2 + G''^2)^{1/2}$$

In the present method, viscosity at low shear rates  
35 (0.05 rad/s) is plotted against viscosity at high shear rates (300 rad/s) as a measure of processability; a high viscosity at low shear rates combined with a low

viscosity at high shear rates giving superior processability.

### Catalyst Preparation

#### 5 Example 1:

134 grams of a metallocene complex (bis (n-butylcyclopentadienyl) hafnium dichloride supplied by Witco as TA02823, containing 0.36 % by weight Hf) and 9.67 kg of a 30% solution of methylalumoxane (MAO) in 10 toluene (supplied by Albemarle) were combined and 3.18 kg dry, purified toluene was added. The thus obtained complex solution was added on 17 kg silica carrier Sylopol 55 SJ by Grace. The complex was fed very slowly with uniform spraying during 2 hours. Temperature was 15 kept below 30°C. The mixture was allowed to react for 3 hours after complex addition at 30°C. The thus obtained solid catalyst was dried by purging it with nitrogen at 50°C for three hours and recovered.

#### 20 Polymerisation

##### Example 2:

A continuously operating loop reactor having a volume of 500 dm<sup>3</sup> was operated at 85°C temperature and 60 bar pressure. Into the reactor were introduced propane 25 diluent, ethylene, 1-butene comonomer, hydrogen and the polymerisation catalyst prepared according to Catalyst Preparation Example 1 in such amounts that the ethylene concentration in the liquid phase of the loop reactor was 7.2 % by mole, the ratio of hydrogen to ethylene 30 was 0.63 mol/kmol, the ratio of 1-butene to ethylene was 155 mol/kmol and the polymer production rate in the reactor was 30 kg/h. The thus formed polymer had a melt index MFR<sub>2</sub> of 120 g/10 min and a density of 936 kg/m<sup>3</sup>.

35 The slurry was intermittently withdrawn from the reactor by using a settling leg and directed to a flash tank operated at a temperature of about 50°C and a \_

pressure of about 3 bar.

From the flash tank the powder, containing a small amount of residual hydrocarbons, was transferred into a gas phase reactor operated at 75°C temperature and 20 bar pressure. Into the gas phase reactor were also introduced additional ethylene, 1-hexene comonomer and nitrogen as inert gas in such amounts that the ethylene concentration in the circulating gas was 19% by mol, the ratio of hydrogen to ethylene was about 1.0 mol/kmol, the ratio of 1-hexene to ethylene was 12 mol/kmol and the polymer production rate was 30 kg/h. The concentration of 1-butene was so low that it could not be detected by the on-line gas chromatograph which was used to monitor the gas composition.

The polymer collected from the gas phase reactor was stabilised by adding to the powder 400 ppm Irganox B561. The stabilised polymer was then extruded and pelletised under nitrogen atmosphere with a CIM90P extruder, manufactured by Japan Steel Works. The melt temperature was 200°C, throughput 280 kg/h and the specific energy input (SEI) was 200 kWh/t.

The production split between the loop and gas phase reactors was thus 50/50. The polymer pellets had a melt index MFR<sub>2</sub> of 20 g/10 min, a weight average molecular weight M<sub>w</sub> of 59600 g/mol, a number average molecular weight M<sub>n</sub> of 16900 g/mol and a z-average molecular weight M<sub>z</sub> of 134000 g/mol. Further, the polymer had a zero shear rate viscosity  $\eta_0$  of 460Pa·s, and a shear thinning index SHI<sub>0/100</sub> of 2.7.

30

### **Example 3 (Comparative):**

A continuously operating loop reactor having a volume of 500 dm<sup>3</sup> was operated at 85°C temperature and 60 bar pressure. Into the reactor were introduced propane diluent, ethylene, 1-butene comonomer, hydrogen and the polymerisation catalyst prepared according to Catalyst Preparation Example 1 in such amounts that the ethylene

35

concentration in the liquid phase of the loop reactor was 6.6 % by mole, the ratio of hydrogen to ethylene was 0.63 mol/kmol, the ratio of 1-butene to ethylene was 183 mol/kmol and the polymer production rate in the reactor was 25 kg/h. The thus formed polymer had a melt index MFR<sub>2</sub> of 120 g/10 min and a density of 936 kg/m<sup>3</sup>.

The slurry was intermittently withdrawn from the reactor by using a settling leg and directed to a flash tank operated at a temperature of about 50 °C and a pressure of about 3 bar.

From the flash tank the powder, containing a small amount of residual hydrocarbons, was transferred into a gas phase reactor operated at 75°C temperature and 20 bar pressure. Into the gas phase reactor were also introduced additional ethylene, 1-butene comonomer and nitrogen as inert gas in such amounts that the ethylene concentration in the circulating gas was 23% by mole, the ratio of hydrogen to ethylene was about 1.2 mol/kmol, the ratio of 1-butene to ethylene was 48 mol/kmol and the polymer production rate was 26 kg/h. The production split was thus 49/51. No 1-hexene was introduced into the gas phase reactor.

The polymer collected from the gas phase reactor was stabilised by adding to the powder 400 ppm Irganox B561. The stabilised polymer was then extruded and pelletised under nitrogen atmosphere with a CIM90P extruder, manufactured by Japan Steel Works. The melt temperature was 200 °C, throughput 280 kg/h and the specific energy input (SEI) was 200 kWh/t.

The production split between the loop and gas phase reactors was thus 49/51. The polymer pellets had a melt index MFR<sub>2</sub> of 10 g/10 min, a density of 916 kg/m<sup>3</sup>, a 1-butene content of 8.1 % by weight, a weight average molecular weight M<sub>w</sub> of 67800 g/mol, a number average molecular weight M<sub>n</sub> of 19600 g/mol and a z-average molecular weight M<sub>z</sub> of 140000 g/mol. Further, the polymer had a zero shear rate viscosity  $\eta_0$  of 800 Pa·s,

and a shear thinning index  $SHI_{0/100}$  of 2.4.

Polymerisation reactor conditions

Example	2	3
$C_2^=$ in loop, mol-%	7.2	6.6
$H_2/C_2$ in loop, mol/kmol	0.63	0.63
$C_4/C_2$ in loop, mol/kmol	155	183
$C_6/C_2$ in loop, mol/kmol	0	0
MFR <sub>2</sub> of loop polymer, g/10 min	120	120
Density of loop polymer, kg/m <sup>3</sup>	936	936
Production rate in loop, kg/h	30	25
$C_2^=$ in gpr, mol-%	19	23
$H_2/C_2$ in gpr, mol/kmol	1.0	1,2
$C_4/C_2$ in gpr, mol/kmol	*	48
$C_6/C_2$ in gpr, mol/kmol	12	0
Production rate in gpr, kg/h	30	26
Production split, Loop/gpr	50/50	49/51

\* indicates that the level was too low to be detected

5 by GC

Polymer properties

Example	2	3
MFR <sub>2</sub> , g/10 min	20	10
Density, kg/m <sup>3</sup>	915	915
$M_z/1000$	134	140
$M_w/1000$	59.6	67.8
$M_n/1000$	16.9	19.6
$\eta_0$ , Pa·s	460	800
$SHI_{0/100}$	2.7	2.4
$\eta_1$ , Pa·s	440	780
$SHI_{1/100}$	2.6	2.3
$G'_{5kPa}$ , Pa	810	630
$T_m$ , °C	117.3	115.8
Crystallinity, %	36.7	36.7

**Example 4: Tensile Modulus and Impact properties**

The tensile modulus and charpy impact were measured on injection moulded specimens. The results are given in table 3.

5

Table 3

Property	Standard	Unit	Example 2	Example 3
Comonomer			1-butene+1-hexene.	1-butene
Tensile Modulus	ISO 527-2	MPa	190	165
Charpy Impact; 23°C	ISO 179	kJ/m <sup>2</sup>	58	55
Density	ISO 1183-D	kg/m <sup>3</sup>	915,5	915,8

10 **Example 5****Comparative sample 1:**

The polymer was manufactured and sold by Borealis under trade name LE8030. This an ethylene butene copolymer formed by Z/N catalysis and has an MFR<sub>2</sub> of 28 g/10 min and density of 919 kg/m<sup>3</sup>.

15

**Comparative sample 2:**

The polymer manufactured and sold by Borealis under trade name MA8200. MA8200 is a LDPE for injection moulding. The polymer has an MFR<sub>2</sub> of 7.5 g/10 min, tensile modulus of 140 MPa and density of 920 kg/m<sup>3</sup>.

20

**Migration and extraction data for compression moulded samples**

25

2 mm thick compression moulded sheets of the polymer from example 2 and the comparative samples were prepared according to ISO1872-2 and subjected to migration tests by total immersion in olive oil at 40°C

for 10 days. Hexane extractions were carried out using ASTM D5227. The results are shown in Table 4.

Table 4

Polymer	Ex 2	LE8030	MA8200
Extractibles in hexane (%wt)	1,1	5,3	1,4
Migration (mg/dm <sup>2</sup> )	0	48,8	14

Claims

1. The use of a multimodal polyethylene composition comprising as comonomers to ethylene at least two C<sub>4-12</sub> alpha olefins in injection moulding.
2. Use as claimed in claim 1 wherein said at least two alpha olefins are selected from but-1-ene, hex-1-ene, 4-methyl-pent-1-ene, hept-1-ene, oct-1-ene, and dec-1-ene.
3. Use as claimed in claim 2 wherein said at least two alpha olefins are selected from but-1-ene and hex-1-ene.
4. Use as claimed in claim 3 wherein said polyethylene composition comprises an ethylene/1-butene copolymer fraction and either an an ethylene/1-hexene copolymer fraction or an ethylene/1-butene/1-hexene terpolymer fraction.
5. An injection moulded article produced from a multimodal polyethylene composition comprising as comonomers to ethylene at least two C<sub>4-12</sub> alpha olefins.
6. An article as claimed in claim 5 comprising a bimodal polyethylene composition comprising
- a) a lower molecular weight homopolymer of ethylene and
  - b) a higher molecular weight terpolymer of ethylene, 1-butene and a C<sub>5</sub> to C<sub>12</sub> alpha-olefin.
7. An article as claimed in claim 5 comprising a bimodal polyethylene composition comprising

5 a) a lower molecular weight polymer which is a binary copolymer of ethylene and 1-butene or 1-hexene and

b) a higher molecular weight polymer different from a) which is either a binary copolymer of ethylene and 1-hexene, or a terpolymer of ethylene, 1-butene and a C<sub>6</sub> to C<sub>12</sub> alpha-olefin.

10

8. An article as claimed in claim 5 comprising a bimodal polyethylene composition comprising

15 a) a lower molecular weight polymer which is a terpolymer of ethylene, 1-butene and 1-hexene, and

b) a higher molecular weight polymer which is a terpolymer of ethylene, 1-butene and 1-hexene.

20

9. An article as claimed in any one of claims 5 to 8 wherein the ratio of components a) to b) is 60:40 to 40:60% wt.

25

10. An article as claimed in any one of claims 5 to 9 wherein the bimodal polyethylene composition has a MWD of 2 to 8.

30

11. An article as claimed in any one of claims 5 to 10 wherein the bimodal polyethylene composition has a density of 905 to 930 kg/m<sup>3</sup>.

35 12. An article as claimed in any one of claims 5 to 11 wherein the bimodal polyethylene composition has an impact strength (ISO179 at 23°C) of at least 40 kJ/m<sup>2</sup>.

13. An article as claimed in any one of claims 5 to 12 wherein the bimodal polyethylene composition has a tensile modulus (ISO527-2) of 60 to 400 MPa.

5

14. An article as claimed in any one of claims 5 to 13 wherein the bimodal polyethylene composition has a hexane extractable fraction (ASTM D5227) of less than 3 wt%.

10

15. An article as claimed in any one of claims 5 to 14 wherein the bimodal polyethylene composition has a level of migration measured by immersion in olive oil of less than 10 mg/dm<sup>2</sup>.

15

16. An article as claimed in any one of claims 5 to 15 being medical or food packaging or a closure means.

17. A process for the preparation of an injection moulded article as claimed in any one of claims 5 to 16 comprising:

(I) polymerising ethylene and optionally at least one C<sub>4-12</sub> alpha olefin in a loop reactor in the presence of a metallocene catalyst:

(II) transferring the resulting polymer with the metallocene catalyst to a gas phase reactor and polymerising ethylene and at least one C<sub>4-12</sub> alpha olefin so as to form a multimodal polyethylene composition comprising as comonomers to ethylene at least two C<sub>4-12</sub> alpha olefins; and

(III) injection moulding said composition.

35

## INTERNATIONAL SEARCH REPORT

International Application No  
/EP2004/007897A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08F297/08 C08L23/00

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 7 C08F C08L

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)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 718 974 A (KMIIEC CHESTER J) 17 February 1998 (1998-02-17)	1-5, 7, 9
Y	column 1, line 23 - column 6, line 55	8, 10-17
X	US 6 103 807 A (COPPENS WIM ET AL) 15 August 2000 (2000-08-15)	1-3, 5
	column 3, line 63 - column 3, line 67; claim 19	
P, X	EP 1 359 191 A (SOLVAY) 5 November 2003 (2003-11-05)	1, 2, 5, 6
P, Y	claims 1, 2, 9-11	3, 4, 7-17
P, Y	EP 1 333 044 A (BOREALIS TECH OY) 6 August 2003 (2003-08-06)	3, 4, 7-17
	the whole document	
	-/--	

 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.

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

13 October 2004

Date of mailing of the international search report

20/10/2004

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

Van Golde, L

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP2004/007897

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 146 079 A (BOREALIS TECH OY) 17 October 2001 (2001-10-17) paragraph '0003!; claim 1 -----	1-17

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

.../EP2004/007897

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5718974	A	17-02-1998	AT 197603 T	15-12-2000
			AU 712189 B2	28-10-1999
			AU 3488897 A	14-01-1998
			BR 9710034 A	10-08-1999
			DE 69703549 D1	21-12-2000
			DE 69703549 T2	31-05-2001
			EP 0907682 A1	14-04-1999
			ES 2154049 T3	16-03-2001
			GR 3035325 T3	30-04-2001
			NZ 333096 A	28-01-2000
			PT 907682 T	30-04-2001
WO 9749764 A1	31-12-1997			
US 6103807	A	15-08-2000	AT 254644 T	15-12-2003
			BR 9901171 A	21-12-1999
			DE 69912871 D1	24-12-2003
			DE 69912871 T2	15-04-2004
			DK 943650 T3	29-03-2004
			EP 0943650 A1	22-09-1999
			ES 2212455 T3	16-07-2004
			JP 11323039 A	26-11-1999
			PT 943650 T	27-02-2004
EP 1359191	A	05-11-2003	EP 1359191 A1	05-11-2003
			WO 03093362 A1	13-11-2003
EP 1333044	A	06-08-2003	EP 1333044 A1	06-08-2003
			WO 03066698 A1	14-08-2003
			WO 03066699 A1	14-08-2003
EP 1146079	A	17-10-2001	EP 1146079 A1	17-10-2001
			AU 6379801 A	30-10-2001
			BR 0109973 A	22-07-2003
			CA 2405280 A1	25-10-2001
			WO 0179345 A1	25-10-2001
			HU 0300637 A2	28-06-2003
			JP 2003531233 T	21-10-2003
			TR 200202339 T2	21-01-2003
			US 2003096901 A1	22-05-2003
			ZA 200207931 A	17-11-2003