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(54) **Title:** BOTTLE CAP

(57) **Abstract:** A polyethylene cap/closure for a bottle that contains a carbonated beverage is provided. The cap has improved barrier properties and thereby lowers the rate at which carbon dioxide is transmitted through the cap.

BOTTLE CAP

TECHNICAL FIELD

This invention relates to caps for carbonated soft drinks. The caps of this invention are made from polyethylene and have improved barrier properties which reduce the permeation of carbon dioxide through the caps.

BACKGROUND ART

Polymer compositions useful for molding applications, specifically the manufacture of caps and closures for bottles are well known. Screw closures for example, are typically made from polypropylene (PP) in order to achieve the necessary cap strength, however, an inner liner composed of a soft polymer is required to provide necessary seal properties. The soft inner liner can be made from ethylene/vinyl acetate (EVA), polyvinyl chloride (PVC), butyl rubber or other suitable material. The two-part cap is costly, and single part constructions are preferred to reduce cost.

Accordingly, one-piece closures, such as screw caps have more recently been made from polyethylene resins. The use of high density resin is required if the closures are to have sufficient stiffness, while broader molecular weight distributions are desirable to impart good flow properties and to improve environmental stress crack resistance (ESCR).

One piece caps are now in widespread commercial use, especially for "still" (non-carbonated) beverages such as water and juice.

The design of a one piece cap for carbonated soft drinks (CSD) is more challenging because the carbon dioxide (CO_2) contained in these beverages can permeate through the cap, resulting in a "flat" beverage. A need exists to improve (reduce) the rate of CO2 transmission through one piece plastic caps. The present invention addresses this need.

DISCLOSURE OF INVENTION

In one embodiment, the present invention provides a bottle cap prepared from

I)   a bimodal polyethylene composition comprising:

(1)   10 to 70 wt% of a first ethylene polymer having a melt index, I_2, of less than 0.4 g/10 min; a molecular weight distribution, M_w/M_n, of less than 3.0; a CBDI >50 and a density of from 0.932 to 0.955 g/cm^3; and

(2)   90 to 30 wt% of a second ethylene polymer having a melt index, I_2, of from 20 to 1,000 g/l0min; and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm^3;

wherein the density of said second ethylene polymer is less than 0.035 g/cm^3 higher than the density of said first ethylene polymer; and wherein said polyethylene composition has a molecular weight distribution, Mw/M_n, of from 3 to 7; a density of more than 0.949 g/cm^3; a melt index of from 0.4 to 3 g/10 min and a comonomer content of less than 0.5 mol%; and

5   II)   an organic nucleating agent, wherein said bottle cap has a carbon dioxide transmission rate which is at least 10% lower than a bottle cap prepared in the absence of said nucleating agent.

In this embodiment, the first ethylene polymer is prepared with a single site catalyst and the second ethylene polymer may be prepared with a single site catalyst or a Ziegler-

10   Natta catalyst.

Thus, this invention requires a combination of a selected polyethylene composition and a selected nucleating agent to prepare a molding composition that is used to prepare a cap (also referred to as a closure) for a container that contains a carbonated beverage.

The caps of this invention have improved (low) rates of carbon dioxide

15   transmission. In an embodiment, the carbon dioxide transmission rate of a cap according to this invention is at least 10% lower than the carbon dioxide transmission rate of a comparative cap that is prepared without the nucleating agent.

The improved (lower) carbon dioxide transmission rate can increase the shelf life of carbonated beverages.

20   A general overview of three selected polyethylene compositions follows.

POLYETHYLENE COMPOSITION I

There are three species of Polyethylene Composition I, (namely Compositions 1.1, 1.2, and 1.3).

POLYETHYLENE COMPOSITION 1.1

25   In one embodiment, polyethylene 1.1 composition is a bimodal polyethylene composition comprising:

(1)   10 to 70 wt% of a first ethylene polymer having a melt index, I_2, of less than 0.4 g/lOmin; a molecular weight distribution, M_w/M_n, of less than 3.0; a CBDI >50 and a density of from 0.932 to 0.955 g/cm^3; and

30   (2)   90 to 30 wt% of a second ethylene polymer having a melt index, I_2, of from 20 to 1000 g/lOmin; a molecular weight distribution, M_w/M_n, of less than 3.0; a CBDI >50 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm^3;

wherein the density of said second ethylene polymer is less than 0.035 g/cm^3 higher than the density of said first ethylene polymer; and wherein said polyethylene composition has a molecular weight distribution, Mw/M_n, of from 3 to 7; a density of more than 0.949 g/cm^3; a melt index of from 0.4 to 3 g/10 min and a comonomer content of less than 0.5 mol%.

In an embodiment, polyethylene composition 1.1 has a molecular weight distribution, M_w/M_n, of from 4 to 7.

In an embodiment, polyethylene composition 1.1 has melt index, I_2, of from 0.4 to 2 g/10 min.

In an embodiment, the density of said second ethylene polymer in composition 1.1 is less than 0.030 g/cm^3 higher than the density of said first ethylene polymer in composition 1.1.

In an embodiment, polyethylene composition 1.1 has a hexane extractables level of less than 0.55 wt%.

POLYETHYLENE COMPOSITION 1.2

In another embodiment, polyethylene composition 1.2 comprises

(1)   20 to 60 wt% of a first ethylene polymer having a melt index, I_2, of less than 0.4 g/10 min; a molecular weight distribution, M_w/M_n, of less than 3.0; a CBDI >50 and a density of from 0.932 to 0.955 g/cm^3; and

(2)   80 to 40 wt% of a second ethylene polymer having a melt index, I_2, of from 20 to 1000 g/10 min; a molecular weight distribution, M_w/M_n, of less than 3.0; a CBDI >50 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm^3;

wherein the density of said second ethylene polymer is less than 0.035 g/cm^3 higher than the density of said first ethylene polymer; and

wherein said composition has a molecular weight distribution of from 3 to 7; a density of more than 0.949 g/cm^3; a melt index of from 0.4 to 3 g/10 min; and a comonomer content of less than 0.5 mol%, and

wherein said polyethylene composition 1.2 is prepared by contacting ethylene and 1-octene under solution polymerization conditions in at least two polymerization reactors.

POLYETHYLENE COMPOSITION 1.3

In yet another embodiment, composition 1.3 comprises

(1)   20-60 wt% of a first ethylene polymer having a Mw of at least 110,000; a molecular weight distribution, M_w/M_n, of less than 2.5 and a density of from 0.932 to 0.955 g/cm^3; and

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(2)   80-40 wt% of a second ethylene polymer having a **Mw** of at most 45,000; a molecular weight distribution, M_w/M_n, of less than 2.5 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm^3;

wherein the density of said second ethylene polymer is less than 0.035 g/cm^3 higher than the density of said first ethylene polymer; and

wherein said polyethylene composition has a hexane extractables level of less than 0.55 wt%; a shear viscosity at lOV ^{1} (240°C) of less than 50 (Pa.s) and satisfies the equations:

a)   the ratio of I_2 of the second ethylene polymer / I_2 of the first ethylene polymer > 50/1; and

b)   the ratio of I_2 of the second ethylene polymer / I_2 of the composition is from 6 to 2,500.

In an embodiment, composition 1.3 has a density of more than 0.949 g/cm^3.

In an embodiment, composition 1.3 has a molecular weight distribution, M_w/M_n, of 3 to 7.

In an embodiment, composition 1.3 has a melt index, I_2, of 0.4 to 3 g/lOmin.

POLYETHYLENE COMPOSITION II

In an embodiment, composition II comprises

(1)   10 to 70 wt% of a first ethylene copolymer having a melt index I_2, of from 0.1 to 10 g/10 min; a molecular weight distribution M_w/M_n, of less than 3.0; and a density of from 0.930 to 0.960 g/cm^3; and

(2)   90 to 30 wt% of a second ethylene copolymer having a melt index I_2, of from 50 to 10,000 g/10 min; a molecular weight distribution M_w/M_n, of less than 3.0; and a density higher than the density of the first ethylene copolymer, but less than 0.966 g/cm^3; wherein the density of the second ethylene copolymer is less than 0.037 g/cm^3 higher than the density of the first ethylene copolymer; the ratio (SCB 1/SCB2) of the number of short chain branches per thousand carbon atoms in the first ethylene copolymer (SCB1) to the number of short chain branches per thousand carbon atoms in the second ethylene copolymer (SCB2) is greater than 1.0; and

wherein the polyethylene composition has a molecular weight distribution M_w/M_n, of from 2 to 7; a density of at least 0.950 g/cm^3; a high load melt index I_2i, of from 150 to 400 g/10 min; a Z-average molecular weight **Mz,** of less than 300,000; a melt flow ratio I_2i/I_2, of from 22 to 50; a stress exponent of less than 1.40; and an ESCR Condition B (100% IGEPAL) of at least 3.5 hours.

In an embodiment, composition II has a TD/MD shrinkage ratio of from 0.90 to 1.15 when measured according to the Dimensional Stability Test (DST).

In an embodiment, composition II has an ESCR Condition B (100% IGEPAL) of from 3.5 to 15 hours.

In an embodiment, composition II has a melt index I_2, of greater than 5.0 to less than 20 g/10 min.

In an embodiment, composition II is made by polymerizing ethylene and an alpha olefin in the presence of a single site catalyst.

In an embodiment, the density of the second ethylene copolymer of composition II is less than 0.030 g/cm^3 higher than the density of the first ethylene copolymer of composition II.

In an embodiment, the first ethylene copolymer of composition II has a melt index I_2, of from 0.1 to 3.0 g/10 min.

In an embodiment, the second ethylene copolymer of composition II has a melt index I_2, of from 100 to 5,000 g/10 min.

In an embodiment, composition II has a melt index I_2, of from 6 to 12 g/10 min.

In an embodiment, composition II has a bimodal molecular weight distribution as determined by gel permeation chromatography.

In an embodiment, the ratio (SCB 1/SCB2) of the number of short chain branches per thousand carbon atoms in the first ethylene copolymer (SCB 1) of composition II to the number of short chain branches per thousand carbon atoms in the second ethylene copolymer (SCB2) of composition II is at least 1.5.

In an embodiment, composition II has a molecular weight distribution M_w/M_n, of from 3.5 to 6.

In an embodiment, the first ethylene copolymer of composition II has a density of from 0.936 to 0.952 g/cm^3.

In an embodiment, the second ethylene copolymer of composition II has a density of less than 0.965 g/cm^3.

In an embodiment, composition II has a density of from 0.952 to 0.960 g/cm^3.

In an embodiment, composition II has no long chain branching.

In an embodiment, the first and second ethylene copolymers of composition II have a M_w/M_n of less than 2.5.

In an embodiment, composition II has a composition distribution breadth index (CDBI(50)) of greater than 65 wt%.

In an embodiment, the first and second ethylene copolymers of composition II each have a composition distribution breadth index (CDBI(50)) of greater than 65 wt%.

In an embodiment, composition II comprises:

from 25 to 60 wt% of the first ethylene copolymer; and

from 75 to 40 wt% of the second ethylene copolymer.

In an embodiment, composition II has a comonomer content of less than 0.5 mol% as determined by ^{13}C NMR.

In an embodiment, the first and second ethylene copolymers of composition II are copolymers of ethylene and 1-octene.

In an embodiment, composition II is prepared by contacting ethylene and an alpha-olefin with a single site polymerization catalyst under solution polymerization conditions in a least two polymerization reactors.

POLYETHYLENE COMPOSITION III

In an embodiment, composition III comprises a bimodal polyethylene composition comprising:

(1)   10 to 70 wt% of a first ethylene copolymer having a melt index I_2, of less than 0.4 g/lOmin; a molecular weight distribution, M_w/M_n, of less than 3.0; and a density of from 0.920 to 0.955 g/cm^3; and

(2)   90 to 30 wt% of a second ethylene copolymer having a melt index I_2, of from 100 to 10,000 g/10 min; a molecular weight distribution M_w/M_n, of less than 3.0; and a density higher than the density of said first ethylene copolymer, but less than 0.967 g/cm^3; wherein the density of said second ethylene copolymer is less than 0.037 g/cm^3 higher than the density of said first ethylene copolymer; the ratio (SCB 1/SCB2) of the number of short chain branches per thousand carbon atoms in said first ethylene copolymer (SCB1) to the number of short chain branches per thousand carbon atoms in said second ethylene copolymer (SCB2) is greater than 0.5; and wherein said bimodal polyethylene composition has a molecular weight distribution, **Mw/Mn,** of from 3 to 11; a density of at least 0.949 g/cm^3; a melt index of from 0.4 to 5.0 g/10 min; an Mz of less than 400,000; a stress exponent of less than 1.50; and an ESCR Condition B (10% IGEPAL) of at least 20 hours.

In an embodiment, the ratio (SCB 1/SCB2) of the number of short chain branches per thousand carbon atoms in said first ethylene copolymer (SCB1) of composition III to the number of short chain branches per thousand carbon atoms in said second ethylene copolymer (SCB2) of composition III is at least 1.0.

In an embodiment, the ratio (SCB 1/SCB2) of the number of short chain branches per thousand carbon atoms in said first ethylene copolymer (SCB1) of composition III to the number of short chain branches per thousand carbon atoms in said second ethylene copolymer (SCB2) of composition III is at least 1.5.

In an embodiment, composition III has an ESCR Condition B (10% IGEPAL) of at least 60 hours.

In an embodiment, composition III has an ESCR Condition B (10% IGEPAL) of at least 120 hours.

In an embodiment, composition III has a molecular weight distribution, M_w/M_n, of from 4.5 to 9.5.

In an embodiment, composition III has melt index, I_2, of from 0.4 to 3.0 g/10 min.

In an embodiment, first ethylene copolymer of composition III has a density of from 0.925 to 0.950 g/cm^3.

In an embodiment, the second ethylene copolymer of composition III has a density of less than 0.965 g/cm^3.

In an embodiment, composition III has a density of from 0.951 to 0.957 g/cm^3.

In an embodiment, the density of said second ethylene copolymer of composition III is less than 0.03 1 g/cm^3 higher than the density of said first ethylene copolymer of composition III.

In an embodiment, the second ethylene copolymer of composition III has a melt index I_2, of greater than 1,500 g/10 min.

In an embodiment, the first and second ethylene copolymers of composition III have a M_w/M_n of less than 2.5.

In an embodiment, composition III has a comonomer distribution breadth index (CDBI) of greater than 65%.

In an embodiment, composition III comprises:

from 30 to 60 wt% of said first ethylene copolymer; and

from 70 to 40 wt% of said second ethylene copolymer.

In an embodiment, composition III has a comonomer content of less than 0.75 mol% as determined by ^{13}C NMR.

In an embodiment, composition III is prepared by contacting ethylene and 1-octene with a polymerization catalyst under solution polymerization conditions in a least two polymerization reactors.

BEST MODE FOR CARRYING OUT THE INVENTION

A general description of selected polyethylene compositions that are suitable for use in the present invention was provided above. A detailed description of preferred embodiments follows.

COMPOSITION I

Composition I is composed of at least two ethylene copolymer components: a first ethylene polymer and a second ethylene polymer.

The term "homogeneous" or "homogeneously branched polymer" as used herein is defined in US Patent 3,645,992. Accordingly, homogeneously branched polyethylene is a polymer that has a narrow composition distribution. That is, the comonomer is randomly distributed within a given polymer chain and substantially all of the polymer chains have same ethylene/comonomer ratio. The composition distribution of a polymer can be characterized by the short chain distribution index (SCDI) or composition distribution breadth index (CDBI). The CDBI is defined as the weight per cent of the polymer molecules having a comonomer content within 50 per cent of the median total molar comonomer content. The CDBI is determined using techniques well known in the art, particularly temperature rising elution fractionation (TREF) as described in Wild et al. *Journal of Polymer Science, Pol. Phys. Ed. Vol* 20, p 441 (1982) or in US Patent 4,798,081.

The First Ethylene Polymer of Composition I

In one embodiment, the first ethylene polymer of composition I is a homogeneous ethylene copolymer having a density of from about 0.932 g/cm^3 to about 0.955 g/cm^3; a melt index, I_2, of less than about 0.4 g/10 min; a molecular weight distribution, M_w/M_n, of below about 3.0 and a weight average molecular weight, M_w, that is greater than the M_w of the second ethylene polymer. Preferably, the weight average molecular weight of the first ethylene polymer is at least 110,000.

The density of the first ethylene polymer may be measured according to ASTM D792. The melt index, I_2, of the first ethylene polymer fraction may be measured according to ASTM D1238 (when conducted at 190°C, using a 2.16 kg weight).

The density and the melt index, I_2, of the first ethylene polymer can optionally be estimated from GPC-FTIR experiments and deconvolutions carried out on a bimodal polyethylene composition (see experimental section).

In another embodiment, the first ethylene polymer of composition I is a homogeneous ethylene copolymer having a weight average molecular weight, Mw, of at

least 110,000; a molecular weight distribution, M_w/M_n, of less than 2.5 and a density of from 0.932 to 0.955 g/cm^3.

In an embodiment, the first ethylene polymer of composition I is homogeneously branched ethylene copolymer and can have a CDBI of greater than about 30%, more preferably of greater than about 50%.

In addition, the first ethylene polymer can comprise between 10 and 70 weight percent (wt%) of the polyethylene composition, based on the total weight of the first and second ethylene polymers.

The comonomer content in the first ethylene polymer can be from about 0.01 to about 0.25 mol% as measured by NMR, or FTIR or GPC-FTIR methods. The comonomer content of the first ethylene polymer can also be determined by mathematical deconvolution methods applied to a bimodal polyethylene composition (see experimental section). The comonomer is one or more suitable alpha olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with 1-octene being preferred.

The Second Ethylene Polymer of Composition I

In an embodiment, the second ethylene polymer of composition I is a homogeneous ethylene copolymer having a density below 0.962 g/cm^3 but which is higher than the density of the first ethylene polymer; a melt index, I_2, of from about 20 to 1,000 g/10 min.; a molecular weight distribution, M_w/M_n, of below about 3.0 and a number average molecular weight that is less than the M_w of the first ethylene. Preferably, the weight average molecular weight, M_w, will be below 45,000.

The density of the second ethylene polymer may be measured according to ASTM D792. The melt index, I_2, of the second ethylene polymer may be measured according to ASTM D1238 (when conducted at 190°C, using a 2.16 kg weight).

The density and the melt index, I_2, of the second ethylene polymer of composition I can optionally be estimated from GPC-FTIR experiments and deconvolutions carried out on a bimodal polyethylene composition.

In another embodiment, the second ethylene polymer of composition I is a homogeneous ethylene copolymer having a weight average molecular weight, Mw, of at most 45000; a molecular weight distribution, M_w/M_n, of less than 2.5 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm^3.

In an embodiment, the second ethylene polymer is homogeneously branched ethylene copolymer and can have a CDBI of greater than about 30%, more preferably of greater than about 50%.

The second ethylene polymer can comprise between 90 and 30 wt% of the polyethylene composition, based on the total weight of the first and second ethylene polymers.

The comonomer content in the second ethylene polymer can be from about 0.01 to about 3 mol% as measured by NMR, or FTIR or GPC-FTIR methods. The comonomer content of the second ethylene polymer can also be determined by mathematical deconvolution methods applied to a bimodal polyethylene composition. The comonomer is one or more suitable alpha olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with the use of 1-octene being preferred.

In an embodiment, the second ethylene polymer has a density that is within about 0.035 g/cm^3 higher than the density of the first ethylene polymer.

In another embodiment, the I_2 of the second ethylene polymer is at least 10 times, preferably more than 25 times, the I_2 of the first ethylene polymer.

Overall Composition I

Composition I has a broad, bimodal or multimodal molecular weight distribution. Minimally, composition I will contain a first ethylene polymer and a second ethylene polymer.

In a specific embodiment, composition I is bimodal. The term "bimodal" means that the polyethylene composition comprises at least two components, one of which has a lower molecular weight and a higher density and another of which has a higher molecular weight and a lower density. Typically, a bimodal or multimodal polyethylene composition can be identified by using gel permeation chromatography (GPC). Generally, the GPC chromatograph will exhibit two or more component ethylene polymers, where the number of component ethylene polymers corresponds to the number of discernible peaks. One or more component ethylene polymers may also exist as a hump, shoulder or tail relative to the molecular weight distribution of the other ethylene polymer component.

Composition I has at least the following characteristics: a density of greater than or equal to 0.949 g/cm^3, as measured according to ASTM D792; a melt index, I_2, of from about 0.4 to about 5 g/10 min, as measured according to ASTM D1238 (when conducted at 190°C, using a 2.16 kg weight); a molecular weight distribution, M_w/M_n, of from about 3 to

about 9 and a comonomer content of less than 0.55 mol% as measured by FTIR or ^{13}C NMR methods, where the comonomer is one or more suitable alpha olefins such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with 1-octene being preferred. Alternatively, composition I has: a hexane extractables level of less than 0.55 wt%; a shear viscosity at 10^4 s^{-1} (240°C) of less than 50 (Pa.s) and satisfies the equations: a) the ratio of I_2 of the second ethylene polymer / I_2 of the first ethylene polymer $> 50/1$; and b) the ratio of I_2 of the second ethylene polymer / I_2 of composition I is from 6 to 2,500.

In an embodiment, composition I has a melt index, Is, of greater than about 1.1 g/10 min, as measured according to ASTM D1238 (when conducted at 190°C, using a 5 kg weight).

In an embodiment, composition I has a number average molecular weight, M_n, of below about 30,000.

In an embodiment, composition I has a melt flow ratio (MFR $_2$) defined as I_2i / I_2 of from 20 to 70.

In an embodiment, composition I has a melt flow (MFR5) defined as I_2i / I5 of less than 20.

In an embodiment, composition I has a shear viscosity at lOV ^{1} (240°C) of less than about 60 (Pa.s); and hexane extractables of below 0.55 wt%.

In an embodiment, composition I has a melt index, I_2, of between 0.4 and 3 g/10 min (especially less than 2 g/10 min).

In an embodiment, composition I has a MWD of between 4 and 7.

In an embodiment, composition I has at least one type of alpha-olefin that has at least 4 carbon atoms and its content is less than 0.5 mol % as determined by ^{13}C NMR.

In an embodiment, the shear viscosity ratio, SVR(io, 1000) at 240°C of composition I can be from about 5 to 25, preferably, 6 to 20. The shear viscosity ratio SVR(io, 1000) is determined by taking the ratio of shear viscosity at shear rate of 10s^{-1} and shear viscosity at shear rate of 1000 s^{-1} as measured with a capillary rheometer at constant temperature (e.g. 240°C), and a die with L/D ratio of 20 and diameter of 0.06".

In an embodiment, the shear thinning index, SHI(i, 100) of composition I is less than about 10; in another aspect the SHI(i, 100) will be less than about 7. The shear thinning index (SHI), was calculated using dynamic mechanical analysis (DMA) frequency sweep methods as disclosed in PCT applications WO 2006/048253 and WO 2006/048254.

The SHI value is obtained by calculating the complex viscosities eta(l) and eta(100) at a constant shear stress of 1 kPa and 100 kPa, respectively.

In an embodiment, the **SHI(i, ioo)** of composition I satisfies the equation: **SHI(i, ioo)** $< -10.58 \log(I_2)$ of polyethylene composition) + 12.94. In another embodiment, the **SHI(i, ioo)** of composition I satisfies the equation: **SHI(i, ioo)** $< -5.5 \log (I_2$ of polyethylene composition) + 9.66.

In an embodiment, the I_2 of the second ethylene polymer will be less than 200 times the I_5 of the overall composition I.

In an embodiment, a molded article made from composition I, has an environment stress crack resistance (ESCR) A10 of at least 20 hours as measured according to ASTM D1693 (at 10% IGEPAL and 50°C under condition A).

In an embodiment, a molded article made from composition I has an Izod impact strength of at least 50 kJ/m, as measured according to ASTM D256; a melt index, I_2, of from 1 to 3 g/10 min and a molecular weight distribution of from 5 to 8.

In another embodiment, a molded article made from composition I has a notched Izod impact strength of at least 100 kJ/m, as measured according to ASTM D256; a melt index, I_2, of from 0.4 to 1 g/10 min; and a molecular weight distribution of from 3 to 6.

In an embodiment, composition I has a density of between 0.950 and 0.953 g/cm^3; a melt index, I_2, of from 0.4 to 1 g/10 min; a molecular weight distribution of from 3 to 6; a number average molecular weight, M_n, of below 30,000; a shear viscosity at lOV^1 (240°C) of less than 50 (Pa.s) and hexane extractables of less than 0.55 % and a molded article made there from has a notched Izod impact strength of more than 100 kJ/m and an A 10 ESCR of at least 20 hours.

In another embodiment, composition I of the current invention has a density of between 0.950 and 0.953 g/cm^3; a melt index, I_2, of from 1 to 3 g/10 min; a molecular weight distribution of from 5 to 8; a number average molecular weight, M_n, of below 30,000; a shear viscosity at 10^4 s^{-1} (240°C) of less than 45 (Pa.s) and hexane extractables of less than 0.55 % and a molded article made there from has an Izod impact strength of more than 60 kJ/m and an ESCR of at least 20 hours.

Composition I can be made using any conventional blending method such as but not limited to physical blending and in-situ blending by polymerization in multi reactor systems. For example, it is possible to perform the mixing of the first ethylene polymer with the second ethylene polymer by molten mixing of the two preformed polymers.

Preferred are processes in which the first and second ethylene polymers are prepared in at least two sequential polymerization stages, however, both in-series, or an in-parallel dual reactor process are contemplated for use in the current invention. Gas phase, slurry phase or solution phase reactor systems may be used, with solution phase reactor systems being preferred.

In an embodiment, a dual reactor solution process is used as has been described in for example US Patent No. 6,372,864 and US Patent App. No. 20060247373A1 which are incorporated herein by reference.

The homogeneously branched ethylene polymers can be prepared using any catalyst capable of producing homogeneous branching. Generally, the catalysts will be based on a group 4 metal having at least one cyclopentadienyl ligand that is well known in the art. Examples of such catalysts which include metallocenes, constrained geometry catalysts and phosphinimide catalysts are typically used in combination with methylaluminoxanes, boranes or ionic borate salts and are further described in US Patents 3,645,992; 5,324,800; 5,064,802; 5,055,438; 6,689,847; 6,114,481 and 6,063,879. Such catalysts may also be referred to as "single site catalysts" to distinguish them from traditional Ziegler-Natta or Phillips catalysts which are also well known in the art. In general single site catalysts produce ethylene copolymers having a molecular weight distribution (**Mw/Mn**) of less than about 2.5 and a composition distribution breadth index (CDBI) of greater than about 30%, preferably greater than 50%.

In an embodiment, homogeneously branched ethylene polymers are prepared using an organometallic complex of a group 3, 4 or 5 metal that is further characterized as having a phosphinimide ligand.

In an embodiment, use of a single site catalyst that does not produce long chain branching (LCB) is preferred. Without wishing to be bound by any single theory, long chain branching can increase viscosity at low shear rates, thereby negatively impacting cycle times during the manufacture of caps and closures, such during the process of compression molding. Long chain branching is determined using ^{13}C NMR methods and can be quantitatively assessed using the method disclosed by Randall in Rev. Macromol. Chem. Phys. C29 (2 and 3), p. 285.

In an embodiment, composition I will contain fewer than 0.3 long chain branches per 100 carbon atoms. In another embodiment, composition I will contain fewer than 0.01 long chain branches per 1,000 carbon atoms.

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In an embodiment, a group IV phosphinimide catalyst system is used in a solution phase dual reactor system to prepare a bimodal polyethylene composition by polymerization of ethylene in the presence of 1-octene.

The production of the composition I will typically include an extrusion or compounding step. Such steps are well known in the art.

Composition I can comprise further polymer components in addition to the first and second ethylene polymers. Such polymer components include polymers made in situ or polymers added to the polymer composition during an extrusion or compounding step.

Optionally, additives can be added to the polyethylene composition. Additives can be added to the polyethylene composition during an extrusion or compounding step, but other suitable known methods will be apparent to a person skilled in the art. The additives can be added as is or as part of a separate polymer component (i.e. not the first or second ethylene polymers described above) added during an extrusion or compounding step. Suitable additives are known in the art and include but are not-limited to antioxidants, phosphites and phosphonites, nitrones, antacids, UV light stabilizers, UV absorbers, metal deactivators, dyes, fillers and reinforcing agents, nano-scale organic or inorganic materials, antistatic agents, lubricating agents such as calcium stearates, and slip additives such as erucimide.

DETAILED DESCRIPTION OF COMPOSITION II

It is well known that metallocene catalysts and other so called "single site catalysts" generally incorporate comonomer more evenly than traditional Ziegler-Natta catalysts when used for catalytic ethylene copolymerization with alpha olefins. This fact is often demonstrated by measuring the composition distribution breadth index (CDBI) for corresponding ethylene copolymers. The composition distribution of a polymer can be characterized by the short chain distribution index (SCDI) or composition distribution breadth index (CDBI). The definition of composition distribution breadth index (CDBI(50)) can be found in PCT publication WO 93/03093 and US Patent No. 5,206,075. The CDBI(50) is conveniently determined using techniques which isolate polymer fractions based on their solubility (and hence their comonomer content). For example, temperature rising elution fractionation (TREF) as described by Wild et al. J. Poly. Sci., Poly. Phys. Ed. Vol. 20, p.441, 1982 or in US Patent No. 4,798,081 can be employed. From the weight fraction versus composition distribution curve, the CDBI(50) is determined by establishing the weight percentage of a copolymer sample that has a comonomer content within 50% of the median comonomer content on each side of the median. Alternatively, the CDBI(25),

which is sometimes used in the art, is determined by establishing the weight percentage of a copolymer sample that has a comonomer content within 25% of the median comonomer content on each side of the median.

The First Ethylene Copolymer of Composition II

The first ethylene copolymer of the composition II has a density of from about 0.930 g/cm^3 to about 0.960 g/cm^3; a melt index, I_2, of more than 0.1 g/10 min; a molecular weight distribution, M_w/M_n, of below about 3.0 and a weight average molecular weight M_w, that is greater than the M_w of the second ethylene copolymer of composition II. Preferably, the weight average molecular weight M_w, of the first ethylene copolymer is at least 50,000 g/mol.

By the term "ethylene copolymer" it is meant that the copolymer comprises both polymerized ethylene and at least one polymerized alpha-olefin comonomer, with polymerized ethylene being the majority species.

In an embodiment, the first ethylene copolymer of composition II is made with a single site catalyst, such as for example a phosphinimine catalyst.

The comonomer (i.e. alpha-olefin) content in the first ethylene copolymer can be from about 0.05 to about 3.0 mol% as measured by ^{13}C NMR, or FTIR or GPC-FTIR methods, or as calculated from a reactor model (see the Examples section). The comonomer is one or more suitable alpha olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with 1-octene being preferred.

The short chain branching in the first ethylene copolymer can be from about 0.25 to about 15 short chain branches per thousand carbon atoms (SCBl/lOOOCs). In other embodiments, the short chain branching in the first ethylene copolymer of composition II can be from 0.25 to 10, or from 0.25 to 7.5, or from 0.25 to 5, or from 0.25 to 3 branches per thousand carbon atoms (SCBl/lOOOCs). The short chain branching is the branching due to the presence of alpha-olefin comonomer in the ethylene copolymer and will for example have two carbon atoms for a 1-butene comonomer, or four carbon atoms for a 1-hexene comonomer, or six carbon atoms for a 1-octene comonomer, etc. The comonomer is one or more suitable alpha-olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with 1-octene being preferred.

In an embodiment, the comonomer content in the first ethylene copolymer is greater than comonomer content of the second ethylene copolymer (as reported for example in mol%).

In an embodiment, the amount of short chain branching in the first ethylene copolymer of composition II is greater than the amount of short chain branching in the second ethylene copolymer (as reported in short chain branches, SCB per thousand carbons in the polymer backbone, 1OOOCs).

The melt index I_2 of the first ethylene copolymer can in an embodiment be from 0.1 to 10 g/lOmin and including narrower ranges within this range and any numbers encompassed by these ranges. For example, the melt index I_2 of the first ethylene composition can be from above 0.1 to below 10 g/10 min, or can be from 0.1 to 7.5 g/10 min, or from 0.1 to 5.0 g/10 min, or from 0.1 to 3.0 g/10 min, or from 0.1 to 2.5 g/10 min, or from 0.1 to 1.0 g/10 min.

In an embodiment, the first ethylene copolymer has a weight average molecular weight M_w of from about 50,000 to about 225,000 g/mol including narrower ranges and any numbers encompassed by these ranges. For example, in another embodiment, the first ethylene copolymer has a weight average molecular weight M_w of from about 75,000 to about 200,000. In further embodiments, the first ethylene copolymer of composition II has a weight average molecular weight M_w of from about 75,000 to about 175,000, or from about 85,000 to about 150,000, or from about 100,000 to about 150,000.

The density of the first ethylene copolymer of composition II is from 0.930 to 0.960 g/cm^3 or can be a narrower range within this range and any numbers encompassed by these ranges. For example, in further embodiments, the density of the first ethylene copolymer can be from 0.936 to 0.960 g/cm^3, or can be from 0.938 to 0.960 g/cm^3, or from 0.936 to 0.952 g/cm^3, or from 0.938 to 0.952 g/cm^3, or from 0.936 to 0.950 g/cm^3, or from 0.938 to 0.950 g/cm^3, or from 0.936 to 0.947 g/cm^3, or from 0.938 to 0.947 g/cm^3, or from 0.936 to 0.945 g/cm^3, or from 0.938 to 0.945 g/cm^3.

In embodiments, the first ethylene copolymer has a molecular weight distribution M_w/M_n of < 3.0, or ≤ 2.7, or < 2.7, or ≤ 2.5, or < 2.5, or ≤ 2.3, or from 1.8 to 2.3.

In an embodiment, the first ethylene copolymer of the polyethylene composition is produced with a single site catalyst and has a weight average molecular weight M_w, of at least 50,000 g/mol; a molecular weight distribution, M_w/M_n, of less than 3.0 and a density of from 0.936 to 0.950 g/cm^3.

In an embodiment, a single site catalyst which gives an ethylene copolymer having a CDBI(50) of at least 65% by weight, or at least 70%, or at least 75%, or at least 80%, or at

least 85%, during solution phase polymerization in a single reactor, is used in the preparation of the first ethylene copolymer.

In an embodiment, the first ethylene copolymer of composition II is ethylene copolymer which has a CDBI(50) of greater than about 60% by weight, or greater than about 65%, or greater than about 70%, or greater than about 75%, or greater than about 80%, or greater than about 85%.

The first ethylene copolymer of composition II can comprise from 10 to 70 weight percent (wt%) of the total weight of the first and second ethylene copolymers. In an embodiment, the first ethylene copolymer comprises from 20 to 60 weight percent (wt%) of the total weight of the first and second ethylene copolymers. In an embodiment, the first ethylene copolymer comprises from 25 to 60 weight percent (wt%) of the total weight of the first and second ethylene copolymers. In an embodiment, the first ethylene copolymer comprises from 30 to 60 weight percent (wt%) of the total weight of the first and second ethylene copolymers. In an embodiment, the first ethylene copolymer comprises from 40 to 50 weight percent (wt%) of the total weight of the first and second ethylene copolymers.

The Second Ethylene Copolymer of Composition II

The second ethylene copolymer of composition II has a density below 0.967 g/cm^3 but which is higher than the density of the first ethylene copolymer; a melt index I_2, of from about 50 to 10,000 g/10 min; a molecular weight distribution, M_w/M_n, of below about 3.0 and a weight average molecular weight M_w that is less than the M_w of the first ethylene copolymer. Preferably, the weight average molecular weight, M_w of the second ethylene copolymer will be below 45,000 g/mole.

By the term "ethylene copolymer" it is meant that the copolymer comprises both polymerized ethylene and at least one polymerized alpha-olefin comonomer, with polymerized ethylene being the majority species.

In an embodiment, the second ethylene copolymer of composition II is made with a single site catalyst, such as for example a phosphinimine catalyst.

The comonomer content in the second ethylene copolymer can be from about 0.05 to about 3 mol% as measured by ^{13}C NMR, or FTIR or GPC-FTIR methods, or as calculated from a reactor model. The comonomer is one or more suitable alpha olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with the use of 1-octene being preferred.

The short chain branching in the second ethylene copolymer of composition II can be from about 0.25 to about 15 short chain branches per thousand carbon atoms

(SCB 1/lOOOCs). In further embodiments, the short chain branching in the first ethylene copolymer can be from 0.25 to 10, or from 0.25 to 7.5, or from 0.25 to 5, or from 0.25 to 3 branches per thousand carbon atoms (SCBl/lOOOCs). The short chain branching is the branching due to the presence of alpha-olefin comonomer in the ethylene copolymer and will for example have two carbon atoms for a 1-butene comonomer, or four carbon atoms for a 1-hexene comonomer, or six carbon atoms for a 1-octene comonomer, etc. The comonomer is one or more suitable alpha olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with 1-octene being preferred.

In an embodiment, the comonomer content in the second ethylene copolymer is less than the comonomer content of the first ethylene copolymer (as reported for example in mol%).

In an embodiment, the amount of short chain branching in the second ethylene copolymer is less than the amount of short chain branching in the first ethylene copolymer (as reported in short chain branches, SCB per thousand carbons in the polymer backbone, lOOOCs).

The density of the second ethylene copolymer of composition II is less than 0.967 g/cm^3. In another embodiment, the density of the second ethylene copolymer is less than 0.966 g/cm^3. In another embodiment, the density of the second ethylene copolymer is less than 0.965 g/cm^3. In another embodiment, the density of the second ethylene copolymer is less than 0.964 g/cm^3. In an embodiment, the density of the second ethylene copolymer is from 0.952 to 0.967 g/cm^3 or can be a narrower range within this range, including all the number encompassed within these ranges.

The second ethylene copolymer of composition II has a density which is higher than the density of the first ethylene copolymer, but less than about 0.037 g/cm^3 higher than the density of the first ethylene copolymer. In an embodiment, the second ethylene copolymer has a density which is higher than the density of the first ethylene copolymer, but less than about 0.035 g/cm^3 higher than the density of the first ethylene copolymer. In another embodiment, the second ethylene copolymer of composition II has a density which is higher than the density of the first ethylene copolymer, but less than about 0.030 g/cm^3 higher than the density of the first ethylene copolymer. In still another embodiment, the second ethylene copolymer has a density which is higher than the density of the first ethylene copolymer, but less than about 0.027 g/cm^3 higher than the density of the first ethylene copolymer. In still another embodiment, the second ethylene copolymer of composition II

has a density which is higher than the density of the first ethylene copolymer, but less than about 0.025 g/cm^3 higher than the density of the first ethylene copolymer.

In an embodiment, the second ethylene copolymer of composition II has a weight average molecular weight M_w of less than 45,000 g/mol. In another embodiment, the second ethylene copolymer has a weight average molecular weight M_w of from about 7,500 to about 40,000. In further embodiments, the second ethylene copolymer has a weight average molecular weight M_w of from about 9,000 to about 35,000, or from about 10,000 to about 30,000, or from about 10,000 to 25,000.

In other embodiments, the second ethylene copolymer has a molecular weight distribution (M_w/M_n) of <3.0, or $\leq$ 2.7, or < 2.7, or $\leq$ 2.5, or < 2.5, or $\leq$ 2.3, or from 1.8 to 2.3.

In an embodiment, the melt index I_2 of the second ethylene copolymer can be from 50 to 10,000 g/10 min. In another embodiment, the melt index I_2 of the second ethylene copolymer can be from 100 to 5,000 g/10 min. In another embodiment, the melt index I_2 of the second ethylene copolymer can be from 50 to 3,500 g/10 min. In another embodiment, the melt index I_2 of the second ethylene copolymer can be from 100 to 10,000 g/10 min. In yet another embodiment, the melt index I_2 of the second ethylene copolymer can be from 1,000 to 7,000 g/10 min. In yet another embodiment, the melt index I_2 of the second ethylene copolymer can be from 1,200 to 10,000 g/10 min. In yet another embodiment, the melt index I_2 of the second ethylene copolymer can be from 1,200 to 7,000 g/10 min. In yet another embodiment, the melt index I_2 of the second ethylene copolymer can be greater than 1,200, but less than 5,000 g/10 min. In still yet another embodiment, the melt index I_2 of the second ethylene copolymer can be greater than 1000, but less than 3,000 g/l0min. In still yet another embodiment, the melt index I_2 of the second ethylene copolymer can be greater than 500, but less than 3,000 g/10 min. In still yet another embodiment, the melt index I_2 of the second ethylene copolymer can be greater than 250, but less than 2,700 g/10 min. In still yet another embodiment, the melt index I_2 of the second ethylene copolymer can be greater than 150, but less than 2,700 g/10 min.

In an embodiment, the melt index I_2 of the second ethylene copolymer is greater than 100 g/10 min. In an embodiment, the melt index I_2 of the second ethylene copolymer is greater than 200 g/10 min. In an embodiment, the melt index I_2 of the second ethylene copolymer is greater than 500 g/10 min. In an embodiment, the melt index I_2 of the second ethylene copolymer is greater than 1,000 g/10 min. In an embodiment, the melt index I_2 of

the second ethylene copolymer is greater than 1,200 g/10 min. In an embodiment, the melt index I_2 of the second ethylene copolymer is greater than 1,500 g/10 min.

In an embodiment, the second ethylene copolymer of the polyethylene composition is made with a single site catalyst and has a weight average molecular weight, Mw, of at most 45,000; a molecular weight distribution, M_w/M_n, of less than 3.0 and a density higher than the density of said first ethylene copolymer, but less than 0.967 g/cm^3.

In an embodiment, a single site catalyst which gives an ethylene copolymer having a CDBI(50) of at least 65% by weight, or at least 70%, or at least 75%, or at least 80%, or at least 85%, during solution phase polymerization in a single reactor, is used in the preparation of the second ethylene copolymer of composition II.

In an embodiment, the second ethylene copolymer has a CDBI(50) of greater than about 60% by weight, or greater than about 65%, or greater than about 70%, or greater than about 75%, or greater than about 80%, or greater than about 85%.

The second ethylene copolymer can comprise from 90 to 30 wt% of the total weight of the first and second ethylene copolymers. In an embodiment, the second ethylene copolymer comprises from 80 to 40 wt% of the total weight of the first and second ethylene copolymers. In an embodiment, the second ethylene copolymer comprises from 75 to 40 wt% of the total weight of the first and second ethylene copolymers. In an embodiment, the second ethylene copolymer comprises from 70 to 40 wt% of the total weight of the first and second ethylene copolymers. In an embodiment, the second ethylene copolymer comprises from 60 to 50 wt% of the total weight of the first and second ethylene copolymers.

In other embodiments, the melt index I_2 of the second ethylene copolymer is at least 50 times, or at least 100 times, or at least 1,000 times the melt index I_2 of the first ethylene copolymer.

Overall Polyethylene Composition II

Minimally, the composition II will contain a first ethylene copolymer and a second ethylene copolymer (as defined above).

In some embodiments, polyethylene composition II has a unimodal, broad unimodal, bimodal or multimodal molecular weight distribution as determined by gel permeation chromatography.

In another embodiment, polyethylene composition II which minimally comprises a first ethylene copolymer and a second ethylene copolymer (as defined above) will have a ratio (SCB 1/SCB2) of the number of short chain branches per thousand carbon atoms in the first ethylene copolymer (i.e. SCB1) to the number of short chain branches per thousand

carbon atoms in the second ethylene copolymer (i.e. SCB2) of greater than 1.0 (i.e. SCBl / SCB2 > 1.0).

In further embodiments, the ratio of the short chain branching in the first ethylene copolymer (SCBl) to the short chain branching in the second ethylene copolymer (SCB2) is at least 1.25. In still another embodiment, the ratio of the short chain branching in the first ethylene copolymer (SCBl) to the short chain branching in the second ethylene copolymer (SCB2) is at least 1.5.

In other embodiments, the ratio (SCB 1/SCB2) of the short chain branching in the first ethylene copolymer (SCBl) to the short chain branching in the second ethylene copolymer (SCB2) will be from greater than 1.0 to about 12.0, or from greater than 1.0 to about 10, or from greater than 1.0 to about 7.0, or from greater than 1.0 to about 5.0, or from greater than 1.0 to about 3.0.

In an embodiment, polyethylene composition II is bimodal as determined by GPC.

Typically, a bimodal or multimodal polyethylene composition can be identified by using gel permeation chromatography (GPC). A GPC chromatograph may exhibit two or more component ethylene copolymers, where the number of component ethylene copolymers corresponds to the number of discernible peaks. One or more component ethylene copolymers may also exist as a hump, shoulder or tail relative to the molecular weight distribution of the other ethylene copolymer component. By the phrase "bimodal as determined by GPC" it is meant that in addition to a first peak, there will be a secondary peak or shoulder which represents a higher or lower molecular weight component (i.e. the molecular weight distribution, can be said to have two maxima in a molecular weight distribution curve). Alternatively, the phrase "bimodal as determined by GPC" connotes the presence of two maxima in a molecular weight distribution curve generated according to the method of ASTM D6474-99.

Composition II has a density of greater than or equal to 0.950 g/cm^3, as measured according to ASTM D792; a melt index I_2, of from about 2 to about 22 g/10 min, as measured according to ASTM D1238 (when conducted at 190°C, using a 2.16 kg weight); a molecular weight distribution, M_w/M_n, of from about 2 to about 7, a Z-average molecular weight M_z, of less than 300,000; a stress exponent of less than 1.40; and an ESCR Condition B at 100% IGEPAL of at least 3 hours.

In certain embodiments, composition II has a comonomer content of less than 0.75 mol%, or less than 0.70 mol%, or less than 0.65 mol%, or less than 0.60 mol%, or less than

0.55 mol%, or less than 0.50 mol% as measured by FTIR or ^{13}C NMR methods, with ^{13}C NMR being preferred, where the comonomer is one or more suitable alpha olefins such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with 1-octene being preferred.

Composition II has a density of at least 0.950 g/cm^3. In further embodiments, composition II has a density of > 0.952 g/cm^3, or > 0.953 g/cm^3, or > 0.955 g/cm^3.

In an embodiment, composition II has a density in the range of 0.950 to 0.970 g/cm^3. In an embodiment composition II has a density in the range of 0.950 to 0.965 g/cm^3.

In an embodiment, composition II has a melt index I_2, of from 2 to 22 g/10 min according to ASTM D1238 (when conducted at 190°C, using a 2.16 kg weight) and including narrower ranges within this range and all numbers encompassed by these ranges. For example, composition II may have a melt index I_2, of greater than 2, but less than 22 g/10 min, or from 2 to 15.0 g/10 min, or from 3 to 12.5 g/10 min, or from 4 to 12.5 g/10 min, or from greater than 4 to less than 20 g/10 min, or from 4.5 to 10 g/10 min, or from 5 to 20 g/10 min, or from greater than 5.0 to less than 20 g/10 min, or from 3 to 15.0 g/10 min, or from 6.0 to 12.0 g/10 min, or from 6.0 to 10.0 g/10 min, or from about 5.0 to about 12.0 g/10 min, or from more than 5.0 to less than 10.0 g/10 min.

In an embodiment composition II has a "medium load" melt index Is, of at least 2.5 g/l0min according to ASTM D1238 (when conducted at 190°C, using a 5 kg weight). In another embodiment, composition II has a medium load melt index I_5, of greater than about 5.0 g/10 min, as measured according to ASTM D1238 (when conducted at 190°C, using a 5 kg weight). In further embodiments, polyethylene composition II has a medium load melt index I_5, of from about 5.0 to about 25.0 g/10 min, or from about 5.0 to about 20.0 g/10 min, or from about 5.0 to about 17.5 g/10 min, or from about 5.0 to about 15.0 g/10 min.

In an embodiment, composition II has a "high load" melt index I_2i of at least 100 g/10 min according to ASTM D1238 (when conducted at 190°C, using a 21 kg weight, especially from 150 to 450 g/10 min).

In an embodiment, polyethylene composition II has a number average molecular weight M_n, of below about 30,000 g/mol. In another embodiment, composition II has a number average molecular weight M_n, of below about 25,000 g/mol.

Composition II has a molecular weight distribution M_w/M_n, of from 2 to 7 or a narrower range within this range, including all the numbers encompassed within these ranges.

In an embodiment, composition II has a Z-average molecular weight Mz, of below 300,000 g/mole. In another embodiment, composition II has a Z-average molecular weight Mz, of below 250,000 g/mole. In yet another embodiment, composition II has a Z-average molecular weight Mz, of below 200,000 g/mole.

In other embodiments, composition II has a ratio of Z-average molecular weight to weight average molecular weight Mz/Mw, of from 2.0 to 4.0, or from 2.0 to 3.75, or from 2.25 to 3.75, or from 2.50 to 3.5.

In certain embodiments, composition II has a melt flow ratio defined as I_{21}/I_2, of from about 15 to about 50, or from about 20 to 50, or from about 22 to 50, or from about 25 to 45, or from about 30 to 45, or from about 30 to 50, or from 22 to 50, or from about 22 to less than 50.

In an embodiment, composition II has a melt flow rate defined as I_{21}/I_5, of less than 25.

In an embodiment, composition II has a shear viscosity at about $10V^{-1}$ (240°C) of less than about 10 (Pa.s). In other embodiments, composition II has a shear viscosity at about $10V^{-1}$ (240°C) of less than 7.5 Pa.s, or less than 6.8 Pa.s. Simultaneously, the polyethylene composition may have a shear viscosity at about $100s^{-1}$ (240°C) of less than about 600 Pa.s, a shear viscosity at about $200s^{-1}$ (240°C) of less than about 500 Pa.s and a shear viscosity at about $300s^{-1}$ (240°C) of less than about 400 Pa.s.

In an embodiment, composition II has at least one type of alpha-olefin that has at least 4 carbon atoms and its content is less than 0.75 mol% as determined by ^{13}C NMR. In an embodiment, composition II has at least one type of alpha-olefin that has at least 4 carbon atoms and its content is less than 0.55 mol% as determined by ^{13}C NMR. In an embodiment, composition II has at least one type of alpha-olefin that has at least 4 carbon atoms and its content is greater than 0.20 to less than than 0.55 mol% as determined by ^{13}C NMR.

In an embodiment, the shear viscosity ratio, SVR$_{(100,100000)}$ at 240°C of the composition II can be from 50 to 90, or can be from about 55 to 90, or from 55 to 85, or from 55 to 75. The shear viscosity ratio SVR(ioo,iooooo) is determined by taking the ratio of shear viscosity at shear rate of $100s^{-1}$ and shear viscosity at shear rate of 100000 s^{-1} as measured with a capillary rheometer at constant temperature (e.g. 240°C), and two dies with L/D ratio of 20 and diameter of 0.06" (from 3 to 1000 s^{-1}) and L/D ratio of 20 and diameter of 0.012" (from about 1000 to 100000 s^{-1}) respectively.

In an embodiment, the polyethylene composition or a molded article made from the polyethylene composition, has an environment stress crack resistance ESCR Condition B at 100% of at least 3 hours, as measured according to ASTM D1693 (at 50°C using 100% IGEPAL, condition B).

In an embodiment, composition II or a molded article made from the polyethylene composition, has an environment stress crack resistance ESCR Condition B at 100% of from 3.5 to 15 hours, as measured according to ASTM D1693 (at 50°C using 100% IGEPAL, condition B).

In an embodiment, composition II or a molded article made from the polyethylene composition has a notched Izod impact strength of at least 40 J/m, as measured according to ASTM D256.

In other embodiments, composition II has a TD/MD shrinkage ratio (for an injection molded disk at 48hrs post molding) of from 0.90 to 1.20, or from 0.90 to 1.15, or from 0.95 to 1.15, or from 0.90 to 1.10, or from 0.95 to 1.10, or from 0.95 to 1.05 when measured according to the Dimensional Stability Test (DST).

In other embodiments, composition II has a TD shrinkage - MD shrinkage (for an injection molded disk at 48 hour post molding time) of from 0.25 to -0.25, or from 0.20 to -0.20, or from 0.15 to -0.15, or from 0.10 to -0.10, or from 0.075 to -0.075, or from 0.05 to -0.05, when measured according to the Dimensional Stability Test (DST).

Dimensional Stability Test (DST): The dimensional stability of the polyethylene compositions was determined as follows: A 150-tonxl2-Oz Cincinnati Milacron injection molding machine (Hydradamp 150T 12oz PC- 111, serial #4001 A21/79-38) with a 2 inch (50.8 mm) screw was used to produce parts according to the conditions listed in Table 1. The mold was an ASTM test mold, which makes tensile test specimens with an overall length of 1.30 inches, an overall width of 0.75 inch, and a thickness of 0.12 inch; tensile test specimens with an overall length of 1.375 inch, an overall width of 0.375 inch, and a thickness of 0.12 inch; tensile test specimens with an overall length of 2.5 inch, an overall width of 0.375 inch, and a thickness of 0.12 inch; flexural modulus bars with a length of 5 inch, a width of 0.50 inch, and a thickness of either 0.12 inch or 0.75 inch, and an impact round disk with a diameter of 2 inch and a thickness of 0.12 inch. Immediately after molding, the injection-molded disk was removed from the runner (note: an injection molded disk with a 2 inch diameter and a thickness of 0.12 inches was used for measurements in the present invention). The diameters in both the machine (or in-flow)

direction (MD) and transverse-flow direction (TD) are then measured at room temperature

(23 ± 2°C) after 1, 24 and 48 hours of molding. Shrinkage at time t is defined as the

percentage change in dimension at measurement time from the original mold dimensions:

Shrinkage percent = (Mold dimension - Specimen dimension at time t) x 100 / Mold

dimension

Thus, MD shrinkage is the shrinkage measured on the disk in the flow direction, and

Transverse direction (TD) shrinkage is the shrinkage measured in the cross-flow direction.

Here, the isotropic shrinkage is defined as the equal shrinkage in both the flow direction (in-

flow) and the transverse direction. Differential shrinkage is defined as TD shrinkage minus

MD shrinkage (an indication of part planarity or flatness or the extent of part warpage).

The smaller the difference it is, the better the part planarity. A TD/MD shrinkage ratio, the

TD shrinkage divided by MD shrinkage, can also be used as a measure of the extent of

isotropic shrinkage (the closer to unity it is, the better the part planarity). The molding

parameters used are summarized in Table 1.

TABLE 1

Barrel Temperature (°C), feed Section	215.5
Barrel Temperature (°C), Trans. Section	237.8
Barrel Temperature (°C), Metering Section	237.8
Barrel Temperature (°C), Nozzle	237.8
Injection Time – High (s)	6
Injection Time – Low (s)	23
Cooling Time (s)	30
Decompression Time (s)	0.07
Clamp Open Time (s)	0.02
Mold Close Time (s)	60
Cycle Time (s)	62
Screw Speed (rpm)	20
Injection rate	Max
Shot size (inch)	1.5
Cushion (inch)	0.2
Injection Pressure – High (psi)	5250
Injection Pressure – Low (psi)	5000
Back Pressure (psi)	1000
Clamp Pressure – High (psi)	1850
Clamp Pressure – Low (psi)	1000
Mold Temperature (°C), represented by cooling water	11.7
Cycle	Auto

In an embodiment, composition II has a density of from 0.950 to 0.960 g/cm^3; a melt

index h, of from 3 to 12 g/10 min; a molecular weight distribution Mw/M_n, of from 2.0 to

7.0; a number average molecular weight M_n, of below 30,000; a shear viscosity at $10^5 s^{-1}$ (240°C) of less than 10 (Pa.s), a hexane extractables of less than 0.55%, a notched Izod impact strength of more than 40 J/m, and an ESCR B at 100% of at least 3.5 hours.

In an embodiment, composition II has a hexanes extractables of less than 0.55% or less than 0.35%.

In an embodiment, composition II has a stress exponent, defined as Logio[l6/l2]/Logio[6.48/2.16], which is ≤ 1.40, especially from 1.22 to 1.38, or from 1.24 to 1.36.

In an embodiment, composition II has a composition distribution breadth index (CDBI(50)), as determined by temperature elution fractionation (TREF), of ≥ 60 weight percent. In further embodiments, composition II will have a CDBI(50) of greater than 65%, or greater than 70%, or greater than 75%, or greater than 80%.

In an embodiment, composition II has a composition distribution breadth index (CDBI(25)), as determined by temperature elution fractionation (TREF), of ≥ 55 weight percent, especially from 55 to 75%, or from 60 to 75%.

Composition II can be made using any conventional blending method such as but not limited to physical blending and in-situ blending by polymerization in multi reactor systems. For example, it is possible to perform the mixing of the first ethylene copolymer with the second ethylene copolymer by molten mixing of the two preformed polymers. Preferred are processes in which the first and second ethylene copolymers are prepared in at least two sequential polymerization stages, however, both in-series, or an in-parallel dual reactor process are contemplated for use in the current invention. Gas phase, slurry phase or solution phase reactor systems may be used, with solution phase reactor systems being preferred.

Mixed catalyst single reactor systems may also be employed to make the polymer compositions of the present invention.

In an embodiment, a dual reactor solution polymerization process is used as has been described in for example US Patent No. 6,372,864 and US Patent Appl. No. 20060247373 A1 which are incorporated herein by reference.

Generally, the catalysts used in the current invention will be so called single site catalysts based on a group 4 metal having at least one cyclopentadienyl ligand. Examples of such catalysts which include metallocenes, constrained geometry catalysts and phosphinimine catalysts are typically used in combination with activators selected from

methylaluminoxanes, boranes or ionic borate salts and are further described in US Patent

Nos. 3,645,992; 5,324,800; 5,064,802; 5,055,438; 6,689,847; 6,114,481 and 6,063,879.

Such single site catalysts are distinguished from traditional Ziegler-Natta or Phillips

catalysts which are also well known in the art. In general, single site catalysts produce

ethylene copolymers having a molecular weight distribution (**Mw/Mn**) of less than about 3.0

and a composition distribution breadth index CDBI(50) of greater than about 65%.

In an embodiment, a single site catalyst which gives an ethylene copolymer having a

CDBI(50) of at least 65% by weight, or at least 70%, or at least 75%, or at least 80%, or at

least 85%, during solution phase polymerization in a single reactor, is used in the

preparation of each of the first and the second ethylene copolymers.

In an embodiment, homogeneously branched ethylene copolymers are prepared

using an organometallic complex of a group 3, 4 or 5 metal that is further characterized as

having a phosphinimine ligand. Such a complex, when active toward olefin polymerization,

is known generally as a phosphinimine (polymerization) catalyst. Some non-limiting

examples of phosphinimine catalysts can be found in US Patent Nos. 6,342,463; 6,235,672;

6,372,864; 6,984,695; 6,063,879; 6,777,509 and 6,277,931.

Some non-limiting examples of metallocene catalysts can be found in US Patent

Nos. 4,808,561; 4,701,432; 4,937,301; 5,324,800; 5,633,394; 4,935,397; 6,002,033 and

6,489,413, which are incorporated herein by reference. Some non-limiting examples of

constrained geometry catalysts can be found in US Patent Nos. 5,057,475; 5,096,867;

5,064,802; 5,132,380; 5,703,187 and 6,034,021, all of which are incorporated by reference

herein in their entirety.

In an embodiment, the use of a single site catalyst that does not produce long chain

branching (LCB) is preferred. Hexyl (C6) branches detected by NMR are excluded from

this definition of a long chain branch.

Without wishing to be bound by any single theory, long chain branching can

increase viscosity at low shear rates, thereby negatively impacting cycle times during the

manufacture of caps and closures, such as during the process of compression molding.

Long chain branching may be determined using ^{13}C NMR methods and may be

quantitatively assessed using the method disclosed by Randall in Rev. Macromol. Chem.

Phys. C29 (2 and 3), p. 285.

In an embodiment, composition II will contain fewer than 0.3 long chain branches

per 1000 carbon atoms. In another embodiment of the invention, the polyethylene

composition will contain fewer than 0.01 long chain branches per 1000 carbon atoms.

In an embodiment, composition II is prepared by contacting ethylene and at least one alpha-olefin with a polymerization catalyst under solution phase polymerization conditions in at least two polymerization reactors (for an example of solution phase polymerization conditions see for example US Patent Nos. 6,372,864; 6,984,695 and US Patent Appl. No. 20060247373 Al).

DETAILED DESCRIPTION OF COMPOSITION III

The terms "homogeneous" or "homogeneously branched polymer" as used herein define homogeneously branched polyethylene which has a relatively narrow composition distribution, as indicated by a relatively high composition distribution breadth index (CDBI). That is, the comonomer is randomly distributed within a given polymer chain and substantially all of the polymer chains have same ethylene/comonomer ratio.

It is well known that metallocene catalysts and other so called "single site catalysts" incorporate comonomer more evenly than traditional Ziegler-Natta catalysts when used for catalytic ethylene copolymerization with alpha olefins. This fact is often demonstrated by measuring the composition distribution breadth index (CDBI) for corresponding ethylene copolymers. The composition distribution of a polymer can be characterized by the short chain distribution index (SCDI) or composition distribution breadth index (CDBI). The definition of composition distribution breadth index (CDBI) can be found in US Patent No. 5,206,075 and PCT publication WO 93/03093. The CDBI is conveniently determined using techniques which isolate polymer fractions based on their solubility (and hence their comonomer content). For example, temperature rising elution fractionation (TREF) as described by Wild et al. J. Poly. Sci., Poly. Phys. Ed. Vol. 20, p.441, 1982 or in US Patent No. 4,798,081 can be employed. From the weight fraction versus composition distribution curve, the CDBI is determined by establishing the weight percentage of a copolymer sample that has a comonomer content within 50% of the median comonomer content on each side of the median. Generally, Ziegler-Natta catalysts produce ethylene copolymers with a CDBI of less than about 50%, consistent with a heterogeneously branched copolymer. In contrast, metallocenes and other single site catalysts will most often produce ethylene copolymers having a CDBI of greater than about 55%, consistent with a homogeneously branched copolymer.

The First Ethylene Copolymer of Composition III

The first ethylene copolymer of composition III has a density of from about 0.920 g/cm^3 to about 0.955 g/cm^3; a melt index, I_2, of less than about 0.4 g/10 min; a molecular weight distribution, M_w/M_n, of below about 3.0 and a weight average molecular weight, M_w,

that is greater than the M_w of the second ethylene copolymer. Preferably, the weight average molecular weight, M_w, of the first ethylene copolymer is at least 110,000. Preferably the first ethylene copolymer is a homogeneously branched copolymer.

In an embodiment, the first ethylene copolymer of composition III is made with a single site catalyst, such as for example a phosphinimine catalyst.

The comonomer (i.e. alpha-olefin) content in the first ethylene copolymer can be from about 0.05 to about 3.0 mol%. The comonomer content of the first ethylene polymer is determined by mathematical deconvolution methods applied to a bimodal polyethylene composition (see the Examples section). The comonomer is one or more suitable alpha olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with 1-octene being preferred.

The short chain branching in the first ethylene copolymer can be from about 0.25 to about 15 short chain branches per thousand carbon atoms (SCBl/lOOOCs). In further embodiments, the short chain branching in the first ethylene copolymer can be from 0.5 to 15, or from 0.5 to 12, or from 0.5 to 10, or from 0.75 to 15, or from 0.75 to 12, or from 0.75 to 10, or from 1.0 to 10, or from 1.0 to 8.0, or from 1.0 to 5, or from 1.0 to 3 branches per thousand carbon atoms (SCBl/lOOOCs). The short chain branching is the branching due to the presence of alpha-olefin comonomer in the ethylene copolymer and will for example have two carbon atoms for a 1-butene comonomer, or four carbon atoms for a 1-hexene comonomer, or six carbon atoms for a 1-octene comonomer, etc. The number of short chain branches in the first ethylene copolymer is determined by mathematical deconvolution methods applied to a bimodal polyethylene composition. The comonomer is one or more suitable alpha olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with 1-octene being preferred.

In an embodiment, the comonomer content in the first ethylene copolymer of composition III is substantially similar or approximately equal (e.g. within about ± 0.05 mol%) to the comonomer content of the second ethylene copolymer (as reported for example in mol%).

In an embodiment, the comonomer content in the first ethylene copolymer is greater than comonomer content of the second ethylene copolymer (as reported for example in mol%).

In an embodiment, the amount of short chain branching in the first ethylene copolymer is substantially similar or approximately equal (e.g. within about ± 0.25 SCB/lOOOCs) to the amount of short chain branching in the second ethylene copolymer (as

reported in short chain branches, SCB per thousand carbons in the polymer backbone, lOOOCs).

In an embodiment, the amount of short chain branching in the first ethylene copolymer is greater than the amount of short chain branching in the second ethylene copolymer (as reported in short chain branches, SCB per thousand carbons in the polymer backbone, lOOOCs).

The melt index of the first ethylene copolymer of composition III can be above 0.01 g/10 min, but below 0.4 g/10 min.

The density of the first ethylene copolymer of composition III is from 0.920 to 0.955 g/cm^3 or can be a narrower range within this range.

In other embodiments, the first ethylene copolymer has a molecular weight distribution M_w/M_n of < 3.0, or ≤ 2.7, or < 2.7, or ≤ 2.5, or < 2.5, or ≤ 2.3, or from 1.8 to 2.3.

The density and the melt index, I_2, of the first ethylene copolymer can be estimated from GPC (gel permeation chromatography) and GPC-FTIR (gel permeation chromatography with Fourier transform infra-red detection) experiments and deconvolutions carried out on the bimodal polyethylene composition using conventional teachings, as disclosed in CA Patent 2,752,407.

In an embodiment, the first ethylene copolymer of composition ΙΙΙ is a homogeneously branched ethylene copolymer having a weight average molecular weight, Mw, of at least 110,000; a molecular weight distribution, M_w/M_n, of less than 2.7 and a density of from 0.925 to 0.948 g/cm^3.

In an embodiment, the first ethylene copolymer is homogeneously branched ethylene copolymer and has a CDBI of greater than about 50%, preferably of greater than about 55%. In further embodiments, the first ethylene copolymer has a CDBI of greater than about 60%, or greater than about 65%, or greater than about 70%.

The first ethylene copolymer of composition III can comprise from 10 to 70 weight percent (wt%) of the total weight of the first and second ethylene copolymers. In an embodiment, the first ethylene copolymer comprises from 20 to 60 weight percent (wt%) of the total weight of the first and second ethylene copolymers. In an embodiment, the first ethylene copolymer comprises from 30 to 60 weight percent (wt%) of the total weight of the first and second ethylene copolymers. In an embodiment, the first ethylene copolymer

comprises from 40 to 50 weight percent (wt%) of the total weight of the first and second ethylene copolymers.

The Second Ethylene Copolymer of Composition III

The second ethylene copolymer of composition III has a density below 0.967 g/cm^3 but which is higher than the density of the first ethylene copolymer; a melt index, I_2, of from about 100 to 10,000 g/10 min; a molecular weight distribution, M_w/M_n, of below about 3.0 and a weight average molecular weight M_w that is less than the M_w of the first ethylene copolymer. Preferably, the weight average molecular weight, M_w of the second ethylene copolymer will be below 45,000. Preferably the second ethylene copolymer is homogeneously branched copolymer.

In an embodiment, the second ethylene copolymer is made with a single site catalyst, such as for example a phosphinimine catalyst.

The comonomer content in the second ethylene copolymer of composition III can be from about 0.05 to about 3 mol% as measured by ^{13}C NMR, or FTIR or GPC-FTIR methods. The comonomer content of the second ethylene polymer can also be determined by mathematical deconvolution methods applied to a bimodal polyethylene composition as disclosed in CA Patent 2,752,407. The comonomer is one or more suitable alpha olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with the use of 1-octene being preferred.

The short chain branching in the second ethylene copolymer can be from about 0.25 to about 15 short chain branches per thousand carbon atoms (SCB2/1000Cs). In further embodiments, the short chain branching in the first ethylene copolymer can be from 0.25 to 12, or from 0.25 to 8, or from 0.25 to 5, or from 0.25 to 3, or from 0.25 to 2 branches per thousand carbon atoms (SCB2/1000Cs). The short chain branching is the branching due to the presence of alpha-olefin comonomer in the ethylene copolymer and will for example have two carbon atoms for a 1-butene comonomer, or four carbon atoms for a 1-hexene comonomer, or six carbon atoms for a 1-octene comonomer, etc. The number of short chain branches in the second ethylene copolymer can be measured by ^{13}C NMR, or FTIR or GPC-FTIR methods. Alternatively, the number of short chain branches in the second ethylene copolymer can be determined by mathematical deconvolution methods applied to a bimodal polyethylene composition (see the Examples section). The comonomer is one or more suitable alpha olefin such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with 1-octene being preferred.

In an embodiment, the comonomer content in the second ethylene copolymer of composition III is substantially similar or approximately equal (e.g. within about ± 0.05 mol%) to the comonomer content of the first ethylene copolymer.

In an embodiment, the comonomer content in the second ethylene copolymer is less than the comonomer content of the first ethylene copolymer.

In an embodiment, the amount of short chain branching in the second ethylene copolymer is substantially similar or approximately equal (e.g. within about ± 0.25 SCB/1000C) to the amount of short chain branching in the first ethylene copolymer (as reported in short chain branches, SCB per thousand carbons in the polymer backbone, lOOOCs).

In an embodiment, the amount of short chain branching in the second ethylene copolymer is less than the amount of short chain branching in the first ethylene copolymer (as reported in short chain branches, SCB per thousand carbons in the polymer backbone, lOOOCs).

The density of the second ethylene copolymer of composition III is higher than the density of the first ethylene copolymer but is less than 0.967 g/cm^3. The density of the second ethylene copolymer in another embodiment is higher than the density of the first ethylene copolymer but is less than 0.966 g/cm^3. In another embodiment, the density of the second ethylene copolymer is higher than the density of the first ethylene copolymer but is less than 0.962 g/cm^3.

In other embodiments, the second ethylene copolymer has a molecular weight distribution M_w/M_n of <3.0, or ≤ 2.7, or < 2.7, or ≤ 2.5, or < 2.5, or ≤ 2.3, or from 1.8 to 2.3.

In an embodiment, the melt index I_2 of the second ethylene copolymer can be from 20 to 10,000 g/lOmin. In another embodiment, the melt index I_2 of the second ethylene copolymer can be from 100 to 10,000 g/10 min. In yet another embodiment, the melt index I_2 of the second ethylene copolymer can be from 1,000 to 7,000 g/10 min. In yet another embodiment, the melt index I_2 of the second ethylene copolymer can be greater than 1,500, but less than 7,000 g/10 min.

The density of the second ethylene copolymer may be measured according to ASTM D792. The melt index, I_2, of the second ethylene copolymer may be measured according to ASTM D1238 (when conducted at 190°C, using a 2.16 kg weight).

The density and the melt index, I_2, of the second ethylene copolymer can optionally be estimated from GPC and GPC-FTIR experiments and deconvolutions carried out on a bimodal polyethylene composition as disclosed in CA Patent 2,752,407.

In an embodiment, the second ethylene copolymer of the polyethylene composition is a homogeneous ethylene copolymer having a weight average molecular weight, Mw, of at most 45000; a molecular weight distribution, M_w/M_n, of less than 2.7 and a density higher than the density of said first ethylene copolymer, but less than 0.967 g/cm^3.

In an embodiment, the second ethylene copolymer is homogeneously branched ethylene copolymer and has a CDBI of greater than about 50%, preferably of greater than about 55%. In further embodiments, the second ethylene copolymer has a CDBI of greater than about 60%, or greater than about 65%, or greater than about 70%.

The second ethylene copolymer can comprise from 90 to 30 wt% of the total weight of the first and second ethylene copolymers. In an embodiment, the second ethylene copolymer comprises from 80 to 40 wt% of the total weight of the first and second ethylene copolymers. In an embodiment, the second ethylene copolymer comprises from 70 to 40 wt% of the total weight of the first and second ethylene copolymers. In an embodiment, the second ethylene copolymer of composition III comprises from 60 to 50 wt% of the total weight of the first and second ethylene copolymers.

The second ethylene copolymer of composition III has a density which is higher than the density of the first ethylene copolymer, but less than about 0.037 g/cm^3 higher than the density of the first ethylene copolymer. In another embodiment, the second ethylene copolymer has a density which is higher than the density of the first ethylene copolymer, but less than about 0.030 g/cm^3 higher than the density of the first ethylene copolymer.

In other embodiments, the I_2 of the second ethylene copolymer is at least 100 times, or at least 1000 times, or at least 10,000 the I_2 of the first ethylene copolymer.

Overall Composition III

Composition III has a broad, bimodal or multimodal molecular weight distribution. Minimally, the polyethylene composition will contain a first ethylene copolymer and a second ethylene copolymer (as defined above).

Composition III will minimally comprise a first ethylene copolymer and a second ethylene copolymer (as defined above) and the ratio (SCB 1/SCB2) of the number of short chain branches per thousand carbon atoms in the first ethylene copolymer (i.e. SCBl) to the number of short chain branches per thousand carbon atoms in the second ethylene copolymer (i.e. SCB2) will be greater than 0.5 (i.e. SCBl / SCB2 > 0.5).

In an embodiment, the ratio of the short chain branching in the first ethylene copolymer (SCBl) to the short chain branching in the second ethylene copolymer (SCB2) is at least 0.60. In another embodiment, the ratio of the short chain branching in the first ethylene copolymer (SCBl) to the short chain branching in the second ethylene copolymer (SCB2) is at least 1.5.

In an embodiment, the ratio of the short chain branching in the first ethylene copolymer (SCBl) to the short chain branching in the second ethylene copolymer (SCB2) will be greater than 0.5, but less than 1.0.

In an embodiment, the ratio of the short chain branching in the first ethylene copolymer (SCB 1) to the short chain branching in the second ethylene copolymer (SCB2) will be approximately 1.0 (e.g. within $\pm$ 10%, or from about 0.9 to about 1.1).

In other embodiments, the ratio (SCB 1/SCB2) of the short chain branching in the first ethylene copolymer (SCBl) to the short chain branching in the second ethylene copolymer (SCB2) will be from 0.75 to 12.0, or from 1.0 to 10, or from 1.0 to 7.0, or from 1.0 to 5.0, or from 1.0 to 3.0.

Composition III has a density of greater than or equal to 0.949 g/cm^3, as measured according to ASTM D792; a melt index, I_2, of from about 0.4 to about 5.0 g/10 min, as measured according to ASTM D1238 (when conducted at 190°C, using a 2.16 kg weight); a molecular weight distribution, M_w/M_n, of from about 3 to about 11, a Z-average molecular weight, M_z of less than 400,000, a stress exponent of less than 1.50 and an ESCR Condition B at 10% of at least 20 hours.

In other embodiments, composition III has a comonomer content of less than 0.75 mol%, or less than 0.70 mol%, or less than 0.65 mol%, or less than 0.60 mol%, or less than 0.55 mol% as measured by FTIR or ^{13}C NMR methods, with ^{13}C NMR being preferred, where the comonomer is one or more suitable alpha olefins such as but not limited to 1-butene, 1-hexene, 1-octene and the like, with 1-octene being preferred.

Composition III has a density of at least 0.949 g/cm^3. In further embodiments, composition III has a density of or > 0.949 g/cm^3, or $\geq$ 0.950 g/cm^3, or > 0.950 g/cm^3.

In an embodiment composition III has a density in the range of from 0.949 to 0.960 g/cm^3.

Composition III has a melt index, I_2, of between 0.4 and 5.0 g/10 min according to ASTM D1238 (when conducted at 190°C, using a 2.16 kg weight) and including narrower ranges within this range.

In an embodiment, composition III has a melt index I_5 of at least 1.0 g/10 min according to ASTM D1238 (when conducted at 190°C, using a 5 kg weight). In another embodiment, composition III has a melt index, I_5, of greater than about 1.1 g/10 min, as measured according to ASTM D1238 (when conducted at 190°C, using a 5 kg weight). In further embodiments, composition III has a melt index I_5 of at least 3.0 g/10 min, especially from about 3.0 to about 6.5 g/10 min.

In an embodiment, composition III has a high load melt index, I_{21} of at least 25 g/10 min according to ASTM D1238 (when conducted at 190°C, using a 21 kg weight). In another embodiment, composition III has a high load melt index, I_{21}, of from about 50 g/10 min to about 100 g/10 min.

In an embodiment, the ratio of the melt index, I_2, of the second ethylene copolymer to the melt index, I_5, of composition III is from 200 to 1,500. In another embodiment, the ratio of the melt index, I_2, of the second ethylene copolymer to the melt index, I_5, of composition III is from 400 to 1,300. In yet another embodiment, the ratio of the melt index, I_2, of the second ethylene copolymer to the melt index, I_5, of the polyethylene composition is from 600 to 1,200.

In an embodiment, composition III has a complex viscosity, η^* at a shear stress (G*) anywhere between from about 1 to about 10 kPa which is between 1,000 to 25,000 Pa.s. In an embodiment, composition III has a complex viscosity, η^* at a shear stress (G*) anywhere from about 1 to about 10 kPa which is between 1,000 to 10,000 Pa.s.

In an embodiment composition III has a number average molecular weight, M_n, of below about 30,000, especially below about 20,000.

Composition III has a molecular weight distribution Mw/Mn of from 3 to 11 or a narrower range within this range.

Composition III may have a ratio of Z-average molecular weight to weight average molecular weight (M_z/Mw) of from 2.25 to 4.5, or from 2.5 to 4.25, or from 2.75 to 4.0, or from 2.75 to 3.75, or between 3.0 and 4.0.

In some embodiments, composition III has a melt flow ratio defined as I_{21}/I_2 of >40, or >45, or >50, or >60, or ≥65. In a further embodiment, the polyethylene composition has a melt flow ratio I_{21}/I_2 of from about 40 to about 100, and including narrower ranges within this range. For example, the polyethylene composition may have a melt flow ratio I_{21}/I_2 of from about 45 to about 90, or from about 45 to 80, or from about 45 to 75, or from about 45

to 70, or from about 50 to 90, or from about 50 to 80, or from about 50 to 75, or from about 50 to 70.

In an embodiment, composition III has a melt flow rate defined as I_{21}/I_5 of less than 25. In another embodiment, composition III has a melt flow rate defined as I_{21}/I_5 of less than 20.

In an embodiment, composition III has a shear viscosity at about $1OV^1$ (240°C) of less than about 10 (Pa.s). In further embodiments composition III has a shear viscosity at about $1OV^1$ (240°C) of less than 7.5 Pa.s, or less than 6.0 Pa.s.

In an embodiment, composition III has a hexane extractables level of below 0.55 wt%.

In an embodiment, composition III has at least one type of alpha-olefin that has at least 4 carbon atoms and its content is less than 0.75 mol% as determined by ^{13}C NMR. In an embodiment composition III has at least one type of alpha-olefin that has at least 4 carbon atoms and its content is less than 0.65 mol% as determined by ^{13}C NMR. In an embodiment, composition III has at least one type of alpha-olefin that has at least 4 carbon atoms and its content is less than 0.55 mol% as determined by ^{13}C NMR.

In an embodiment, the shear viscosity ratio, SVR(io,iooo) at 240°C of composition III can be from about 4.0 to 25, or from 4.0 to 20, or from 4.0 to 17. The shear viscosity ratio SVR(io,iooo) is determined by taking the ratio of shear viscosity at shear rate of $10s^{-1}$ and shear viscosity at shear rate of $1000\ s^{-1}$ as measured with a capillary rheometer at constant temperature (e.g. 240°C), and a die with L/D ratio of 20 and diameter of 0.06".

In an embodiment, the shear thinning index, SHI(i,ioo) of composition III is less than about 10; in another embodiment the SHI(i,ioo) will be less than about 7. The shear thinning index (SHI), was calculated using dynamic mechanical analysis (DMA) frequency sweep methods as disclosed in PCT applications WO 2006/048253 and WO 2006/048254. The SHI value is obtained by calculating the complex viscosities $\eta^*(1)$ and $\eta^*(100)$ at a constant shear stress of 1 kPa (G*) and 100 kPa (G*), respectively.

In an embodiment, the SHI(i,ioo) of the polyethylene composition satisfies the equation: SHI(uoo) < -10.58 (log I_2 of composition III in g/1Omin) / (g/1Omin) + 12.94. In another embodiment, the SHI(i,ioo) of composition III satisfies the equation: SHI(uoo) < -5.5 (log I_2 of composition III in g/1Omin) / (g/1Omin) + 9.66.

In an embodiment composition III or a molded article made from the polyethylene composition, has an environment stress crack resistance ESCR Condition B at 10% of at

least 20 hours, as measured according to ASTM D1693 (at 10% IGEPAL and 50°C under condition B).

In an embodiment, composition III or a molded article made from the polyethylene composition, has an environment stress crack resistance ESCR Condition B at 10% of from 60 to 400 hours, as measured according to ASTM D1693 (at 10% IGEPAL and 50°C under condition B).

In an embodiment composition III or a molded article made from the polyethylene composition has a notched Izod impact strength of at least 60 J/m, as measured according to ASTM D256.

In an embodiment, composition III has a density of from 0.949 to 0.956 g/cm^3; a melt index, h, of from 0.5 to 3.0 g/10 min; a molecular weight distribution of from 4.0 to 10.0; a number average molecular weight, M_n, of below 30,000; a shear viscosity at $10^5 s^{-1}$ (240°C) of less than 10 (Pa.s), a hexane extractables of less than 0.55 %, a notched Izod impact strength of more than 60 J/m, and an ESCR B at 10% of at least 20hrs.

In an embodiment, composition III has a density of from 0.949 to 0.956 g/cm^3; a melt index, h, of from 0.5 to 3.0 g/10 min; a molecular weight distribution of from 4.5 to 9.5; a number average molecular weight, M_n, of below 30,000; a shear viscosity at $10^5 s^{-1}$ (240°C) of less than 7 (Pa.s), a hexane extractables of less than 0.55 %, a notched Izod impact strength of more than 60 J/m and an ESCR B at 10% of at least 80 hours.

In an embodiment, composition III has a stress exponent, defined as Logio[l6/l2]/Logio[6.48/2.16], which is ≤ 1.50. In further embodiments, composition III has a stress exponent, Logio[l6/l2]/Logio[6.48/2.16] of less than 1.50, or less than 1.48, or less than 1.45.

In an embodiment, composition III has a comonomer distribution breadth index (CDBI), as determined by temperature elution fractionation (TREF), of >60%. In further embodiments, composition III will have a CDBI of greater than 65%, or greater than 70%, or greater than 75%, or greater than 80%.

Composition III can be made using any conventional blending method such as but not limited to physical blending and in-situ blending by polymerization in multi reactor systems. For example, it is possible to perform the mixing of the first ethylene copolymer with the second ethylene copolymer by molten mixing of the two preformed polymers. Preferred are processes in which the first and second ethylene copolymers are prepared in at least two sequential polymerization stages, however, both in-series, or an in-parallel dual

reactor process are contemplated for use in the current invention. Gas phase, slurry phase or solution phase reactor systems may be used, with solution phase reactor systems being preferred.

5   Homogeneously branched ethylene copolymers can be prepared using any catalyst capable of producing homogeneous branching. Generally, the catalysts will be based on a group 4 metal having at least one cyclopentadienyl ligand that is well known in the art. Examples of such catalysts which include metallocenes, constrained geometry catalysts and phosphinimine catalysts are typically used in combination with activators selected from methylaluminoxanes, boranes or ionic borate salts and are further described in US Patent

10   Nos. 3,645,992; 5,324,800; 5,064,802; 5,055,438; 6,689,847; 6,114,481 and 6,063,879. Such catalysts may also be referred to as "single site catalysts" to distinguish them from traditional Ziegler-Natta or Phillips catalysts which are also well known in the art. In general single site catalysts produce ethylene copolymers having a molecular weight distribution (Mw/M$_n$) of less than about 3.0 and a composition distribution breadth index

15   (CDBI) of greater than about 50%.

In an embodiment, composition III will contain fewer than 0.01 long chain branches per 1,000 carbon atoms (especially no long chain branching).

NUCLEATING AGENTS

The term nucleating agent, as used herein, is meant to convey its conventional

20   meaning to those skilled in the art of preparing nucleated polyolefin compositions, namely an additive that changes the crystallization behavior of a polymer as the polymer melt is cooled.

A review of nucleating agents is provided in US Patent Nos. 5,981,636; 6,465,551 and 6,599,971.

25   Examples of conventional nucleating agents which are commercially available and in widespread use as polypropylene additives are the dibenzylidene sorbital esters (such as the products sold under the trademark MILLAD® 3988 by Milliken Chemical and IRGACLEAR® by Ciba Specialty Chemicals). Examples of other nucleating agents include the cyclic organic structures disclosed in US Patent 5,981,636 (and salts thereof, such as

30   disodium bicyclo [2.2.1] heptene dicarboxylate); the saturated versions of the structures disclosed in US Patent 5,981,636 (as disclosed in US Patent 6,465,551; Zhao et al., to Milliken); the salts of certain cyclic dicarboxylic acids having a hexahydrophtalic acid structure (or "HHPA" structure) as disclosed in US Patent 6,598,971 (Dotson et al., to Milliken); phosphate esters, such as those disclosed in US Patent 5,342,868 and those sold

under the trade names NA-1 1 and NA-21 by Asahi Denka Kogyo and metal salts of glycerol (especially zinc glycerolate). Further examples of nucleating agents include the metal salts of certain phenylphosphoric acids and the derivatives thereof (as disclosed in US Patent 8,835,542; O'Connor et al., assigned to Milliken); the metal salts of mandelic acid and derivatives thereof (as disclosed in US Patent 8,779,045; Dotson et al., assigned to Milliken), and the metal salts of certain sulfonic acids and derivatives thereof (as disclosed in US Patent 8,198,351; Xu et al., assigned to Milliken).

The accompanying examples illustrate that the calcium salt of 1,2 - cyclohexanedicarboxylic acid, calcium salt (CAS registry number 491589-22-1) provides exceptionally good results. The nucleating agents described above might be described as "organic" (in the sense that they contain carbon and hydrogen atoms) and to distinguish them from inorganic additives such as talc and zinc oxide. Talc and zinc oxide are commonly added to polyethylene (to provide anti-blocking and acid scavenging, respectively) and they do provide some limited nucleation functionality. The "organic" nucleating agents described above are generally better (but more expensive) nucleating agents than inorganic nucleating agents. In an embodiment, the amount of organic nucleating agent is from 200 to 2,000 parts per million.

The nucleating agents should be well dispersed in the HDPE. The amount of nucleating agent used is comparatively small - from 200 to 10,000 parts by million per weight (based on the weight of the polyethylene composition) so it will be appreciated by those skilled in the art that some care must be taken to ensure that the nucleating agent is well dispersed. It is preferred to add the nucleating agent in finely divided form (less than 50 microns, especially less than 10 microns) to the polyethylene to facilitate mixing. The use of a "masterbatch" of the nucleator (where the term "masterbatch" refers to the practice of first melt mixing the additive - the nucleator, in this case - with a small amount of polyethylene - then melt mixing the "masterbatch" with the remaining bulk of the polyethylene composition) can also help to disperse the nucleating agent. In an embodiment, the polyethylene that is used to prepare the masterbatch is the same polyethylene composition that is used for the remaining bulk of the overall polyethylene composition. In another embodiment, the polyethylene that is used to prepare the masterbatch is different. (For example, the masterbatch may be prepared with a polyethylene homopolymer composition such as the one disclosed in US Patent 7,737,220; Swabey et al.).

Further non-limiting details of the present invention are provided in the following examples.

EXAMPLE 1

The polyethylene composition used in this example was prepared in a dual reactor solution polymerization process using a phosphinimine catalyst in a manner described in US Patent 8,022,143 (Wang; assigned to NOVA Chemicals). The polyethylene composition has an overall melt index (I_2) of 1 gram per 10 minutes; a density of 0.953 g/cc; and is representative of Polyethylene Composition I described above.

The nucleating agent used in this example is sold under the trademark HYPERFORM® HPN20E by Milliken and is reported to contain the calcium salt of 1,2-cyclohexanedicarboxylic acid (CAS registry number 491589-22-1) and some zinc stearate (as a dispersing agent).

As shown in Table 1, about 80% of the polyethylene was used in the form of pellets (as received from the manufacturing process) and about 20% of the polyethylene was ground into a powder (to improve dispersion of the nucleating agent).

The following formulations were first tumble blended and subsequently melt compounded under nitrogen purge on the Leistritz twin screw extruder at 65 rpm with a melt temp of 200°C.

TABLE 1

Formulation	Pellets	Powder	Nucleating Agent (ppm)
2	80%	20%	250
3	80%	20%	750
4	80%	20%	1000

The control and the three experimental formulations (described above) were injection molded using a Sumitomo SE75EV injection molder with a carbonated soft drink mold (T1881 finish). Closures were made with an injection speed of 45 mm/s (on a 28 mm screw).

The caps were then tested for CO_2 permeation. Testing was conducted by MOCON Testing Service of Minneapolis, USA. The testing was conducted on a MOCON Permatran-C 4/41 Carbon Dioxide Permeability Instrument. The following test conditions were used:

Test Gas: Carbon dioxide;

Test Gas Concentration: 100% CO_2;

Test Gas Humidity: 0% Relative Humidity;

Test Gas Pressure: 760 mmHg; and

Test Temperature: 23°C

Results are shown in Table 2 and are reported as the rate of CO_2 transmission through cap (in cubic centimeters per day).

EXAMPLE 1

TABLE 2

Experiment	Nucleating Agent	CO_2 transmission (cc/cap-day)	CO_2 % (Reduction)
1	0 (Control)	0.204	
2	250 ppm HPN	0.198	3
3	750 ppm HPN	0.185	9
4	1000 ppm HPN	0.163	20

INDUSTRIAL APPLICABILITY

Caps are provided for bottles that contain carbonated beverages. The caps have improved barrier properties which reduce the permeation of carbon dioxide through the caps.

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CLAIMS

1.   A bottle cap prepared from

(I)   a bimodal polyethylene composition comprising:

(1)   10 to 70 wt% of a first ethylene polymer having a melt index, I_2, of less than 0.4 g/10 min; a molecular weight distribution, M_w/M_n, of less than 3.0; a CBDI >50 and a density of from 0.932 to 0.955 g/cm^3; and

(2)   90 to 30 wt% of a second ethylene polymer having a melt index, I_2, of from 20 to 1000 g/lOmin; a molecular weight distribution, M_w/M_n, of less than 3.0; a CBDI >50 and a density higher than the density of said first ethylene polymer, but less than 0.962 g/cm^3; wherein the density of said second ethylene polymer is less than 0.035 g/cm^3 higher than the density of said first ethylene polymer; and wherein said polyethylene composition has a molecular weight distribution, Mw/M_n, of from 3 to 7; a density of more than 0.949 g/cm^3; a melt index of from 0.4 to 3 g/10 min and a comonomer content of less than 0.5 mol%; and

(II)   from 200 to 2000 parts per million of a nucleating agent comprising the calcium salt of 1,2-cyclohexanedicarboxylic acid;

wherein said bottle cap has a carbon dioxide transmission rate that is at least 10% lower than the carbon dioxide transmission rate of a comparative bottle cap that is made in the absence of said nucleating agent.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L23/06 B65D41/04
ADD.

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)
C08L B65D

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 practicable, search terms used)

EPO-Internal , WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 2 752 407 A1 (NOVA CHEMICALS CORP [CA]) 19 March 2013 (2013-03-19) cited in the application claims 1,17 page 1, line 3 - line 4 page 10, line 9 page 14, line 14 page 17, line 17 page 28, line 18 - page 29, line 5 page 29, line 20 - line 26 -----	1
X	US 8 022 143 B2 (WANG XIAOCHUAN [CA]) 20 September 2011 (2011-09-20) cited in the application claim 1 column 8, line 28 column 8, line 47 - line 52 ----- -/--	1

☒ Further documents are listed in the continuation of Box C. ☒ 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
5 April 2016	12/04/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	van Bergen , Marc

Form PCT/ISA/210 (second sheet) (April 2005)

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/136849 A1 (DOW GLOBAL TECHNOLOGIES INC [US] ; MICHIE WILLIAM [US] ; WHITED STEPHANI) 13 November 2008 (2008-11-13) claims 1,40,48-50 page 30, line 14 - line 18 -----	1
A	WO 2014/089670 A1 (NOVA CHEM INT SA [CH] ; WANG XIAOCHUAN [CA] ; LACOMBE YVES [CA] ; CHECKNI) 19 June 2014 (2014-06-19) abstract claims 1, 19,22 page 7, line 5 page 17, line 19 - line 20 page 25, line 18 - line 19 page 26, line 8 - line 12 page 57, line 15 - line 22 -----	1

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No

PCT/IB2016/05Q859

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
CA 2752407	AI	19-03-2013	CA 2752407	AI	19-03-2013
			CL 2014000670	AI	09-01-2015
			CN 103917592	A	09-07-2014
			EP 2751193	AI	09-07-2014
			JP 2014526577	A	06-10-2014
			US 2013072632	AI	21-03-2013
			US 2015094418	AI	02-04-2015
			WO 2013040676	AI	28-03-2013
US 8022143	B2	20-09-2011	CA 2629576	AI	21-10-2009
			US 2010261848	AI	14-10-2010
			WO 2009129597	AI	29-10-2009
WO 2008136849	AI	13-11-2008	AR 063766	AI	18-02-2009
			AT 450569	T	15-12-2009
			AU 2007352541	AI	13-11-2008
			BR PI0713185	A2	17-04-2012
			CA 2656845	AI	13-11-2008
			CN 101490163	A	22-07-2009
			CN 103396604	A	20-11-2013
			EP 2052026	AI	29-04-2009
			ES 2333828	T3	01-03-2010
			JP 2010526169	A	29-07-2010
			KR 20100014214	A	10-02-2010
			RU 2009106863	A	10-09-2010
			US 2010084363	AI	08-04-2010
			WO 2008136849	AI	13-11-2008
WO 2014089670	AI	19-06-2014	CA 2798854	AI	14-06-2014
			CN 105164197	A	16-12-2015
			EP 2931807	AI	21-10-2015
			JP 2016500380	A	12-01-2016
			KR 20150094663	A	19-08-2015
			US 2014171582	AI	19-06-2014
			WO 2014089670	AI	19-06-2014