

HIGH-DENSITY POLYETHYLENE COMPOSITIONS, METHOD OF MAKING THE SAME, INJECTION MOLDED ARTICLES MADE THEREFROM, AND METHOD OF MAKING SUCH ARTICLES

Field of Invention

The instant invention relates to high-density polyethylene compositions, method of producing the same, and injection molded articles made therefrom, and method of making such articles.

Cross-Reference to Related Applications

This application is a non-provisional application claiming priority from the U.S. Provisional Patent Application Ser. No. 60/927,176, filed on May 2, 2007 entitled “High-Density Polyethylene Compositions, Method of Making the Same, Injection Molded Articles Made Therefrom, and Method of Making Such Articles,” the teachings of which are incorporated herein as if reproduced in full hereinbelow.

Background of the Invention

The use of polymeric materials to manufacture molded articles, such as closure devices, is generally known. Different methods may be employed to manufacture closure devices, e.g. bottle caps. For example, such closure devices may be manufactured via compression molding or injection molding processes.

In compression molding process, a two-piece mold provides a cavity having the shape of a desired molded article. The mold is heated. An appropriate amount of molten molding compound from an extruder is loaded into the lower half of the mold. The two parts of the mold are brought together under pressure. The molding compound, softened by heat, is thereby welded into a continuous mass having the shape of the cavity. If the molding compound is a thermosetting material, the continuous mass may be hardened via further

heating, under pressure, in the mold. If the molding compound is a thermoplastic material, the continuous mass may be hardened via chilling, under pressure, in the mold.

In injection molding process, molding compound is fed into an extruder via a hopper. The extruder conveys, heats, melts, and pressurizes the molding compound to a form a
5 molten stream. The molten stream is forced out of the extruder through a nozzle into a relatively cool mold held closed under pressure thereby filing the mold. The melt cools and hardens until fully set-up. The mold then opens and the molded part is removed.

In general, a closure device, e.g. a soda bottle cap, should be strong enough to withstand the pressure of a carbonated drink, and yet soft enough to provide an excellent seal
10 on the bottle without the need for an inner liner. Additionally, a closure device, e.g. a soda bottle cap, should generally possess good environmental stress crack resistance, good impact strength, good removal torque, and good strip torque. Different techniques have been employed to provide for such closure devices having acceptable properties.

For example, the use of a polypropylene polymer as a bottle cap closure for the needed
15 strength with an inner liner, which may be comprised of soft ethylene/vinyl acetate (EVA), polyvinyl chloride (PVC), butyl rubber, etc., is also generally well known. However, this two-part construction is costly because of the need for an inner liner. Furthermore, it would be easier and more convenient to use a one-piece closure, without a liner. Additionally, customers are always looking for improved shrinkage behavior. All polymers undergo
20 shrinkage from the melt to the solid. Improved shrinkage is defined as consistently the same and having a tight tolerance, especially when various colors are used. In the instant invention, the polymer composition in either natural or colored form provides improved consistency as defined as a lower standard deviation of flow direction shrinkage as a percentage of the mean shrinkage across multiple colored (and natural) parts. This helps
25 customers in that parts having too low or too high shrinkage are not made leading to lower

scrap rates. Furthermore, addition of nucleators, potassium stearate or Milliken HPN-20E, reduce this standard deviation further and are therefore more preferred.

In attempts to eliminate the need for a two-part construction, the use of different blends of polymers has been suggested. However, there is still a need for polymer

- 5 formulations that can be injection molded into closure devices having acceptable properties, such as no need for liners to facilitate a seal, acceptable taste and odor, satisfactory stress crack resistance, and impact strength to prevent cap failure.

Summary of the Invention

- The instant invention is a high-density polyethylene composition, method of
- 10 producing the same, injection molded articles made therefrom, and method of making such articles. The high-density polyethylene composition of the instant invention includes a first component, and a second component. The first component is a high molecular weight ethylene alpha-olefin copolymer having a density in the range of 0.920 to 0.946 g/cm³, and a melt index (I_{21.6}) in the range of 1 to 15 g/10 minutes. The second component is a low
- 15 molecular weight ethylene polymer having a density in the range of 0.965 to 0.980 g/cm³, and a melt index (I₂) in the range of 30 to 1500 g/10 minutes. The high-density polyethylene composition has a melt index (I₂) of at least 1, a density in the range of 0.950 to 0.960 g/cm³. The method of producing a high-density polyethylene composition includes the following steps: (1) introducing ethylene, and one or more alpha-olefin comonomers into a first reactor;
- 20 (2) (co)polymerizing the ethylene in the presence of one or more alpha-olefin comonomers in the first reactor thereby producing a first component, wherein the first component being a high molecular weight ethylene alpha-olefin copolymer having a density in the range of 0.920 to 0.946 g/cm³, and a melt index (I_{21.6}) in the range of 1 to 15 g/10 minutes; (3) introducing the first component and additional ethylene into a second reactor; (4) polymerizing the
- 25 additional ethylene in the second reactor thereby producing a second component, wherein the

second component being a low molecular weight ethylene polymer having a density in the range of 0.965 to 0.980 g/cm³, and a melt index (I₂) in the range of 30 to 1500 g/10 minutes; and (5) thereby producing the high-density polyethylene composition, wherein the high-density polyethylene composition having a melt index (I₂) of at least 1, a density in the range of 0.950 to 0.960 g/cm³. The injection molded articles according to instant invention comprise the above-described inventive high-density polyethylene composition, and such articles are made via injection molding.

In one embodiment, the instant invention provides a high-density polyethylene composition comprising a high molecular weight polyethylene alpha-olefin copolymer having a density in the range of 0.920 to 0.946 g/cm³, and a melt index (I_{21.6}) in the range of 1 to 15 g/10 minutes, and a low molecular weight ethylene polymer having a density in the range of 0.965 to 0.980 g/cm³, and a melt index (I₂) in the range of 30 to 1500 g/10 minutes, wherein the inventive high-density polyethylene composition having a melt index (I₂) of at least 1 g/10 minutes, a density in the range of 0.950 to 0.960 g/cm³.

In an alternative embodiment, the instant invention further provides a method for producing a high-density polyethylene composition comprising the steps of : (1) introducing ethylene, and one or more alpha-olefin comonomers into a first reactor; (2) (co)polymerizing the ethylene in the presence of one or more alpha-olefin comonomers in the first reactor thereby producing a high molecular weight ethylene alpha-olefin copolymer having a density in the range of 0.920 to 0.946 g/cm³, and a melt index (I₂₁) in the range of 1 to 15 g/10 minutes; (3) introducing the high molecular weight ethylene alpha-olefin copolymer and additional ethylene into a second reactor; (4) polymerizing the additional ethylene in the second reactor thereby producing a low molecular weight ethylene polymer having a density in the range of 0.965 to 0.980 g/cm³, and a melt index (I₂) in the range of 30 to 1500 g/10 minutes; and (5) thereby producing the high-density polyethylene composition, wherein the

high-density polyethylene composition having a melt index (I_2) of at least 1, a density in the range of 0.950 to 0.960 g/cm³.

In another alternative embodiment, the instant invention provides an injection molded article comprising a high-density polyethylene composition, wherein the high-density polyethylene composition comprising a high molecular weight polyethylene alpha-olefin copolymer having a density in the range of 0.920 to 0.946 g/cm³, and a melt index ($I_{21.6}$) in the range of 1 to 15 g/10 minutes, and a low molecular weight ethylene polymer having a density in the range of 0.965 to 0.980 g/cm³, and a melt index (I_2) in the range of 30 to 1500 g/10 minutes, wherein the inventive high-density polyethylene composition having a melt index (I_2) of at least 1 g/10 minutes, a density in the range of 0.950 to 0.960 g/cm³.

In another alternative embodiment, the instant invention provides a method of making an article comprising the steps of: (1) providing a high-density polyethylene composition comprising a high molecular weight ethylene alpha-olefin copolymer having a density in the range of 0.920 to 0.946 g/cm³, and a melt index ($I_{21.6}$) in the range of 1 to 15 g/10 minutes; and a low molecular weight ethylene polymer having a density in the range of 0.965 to 0.980 g/cm³, and a melt index (I_2) in the range of 30 to 1500 g/10 minutes; wherein the high-density polyethylene composition having a melt index (I_2) of at least 1 g/10 minutes, a density in the range of 0.950 to 0.960 g/cm³; (2) injection molding the high-density polyethylene composition (3) thereby forming the article.

In an alternative embodiment, the instant invention provides a method for producing a high-density polyethylene composition, in accordance with any of the preceding embodiments except that the second reactor being substantially free of any other alpha-olefin copolymers.

In an alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and

method of making such articles, in accordance with any of the preceding embodiments, except that the high-density polyethylene composition having a standard deviation of flow direction shrinkage of less than 7 percent across different colors.

5 In an alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and method of making such articles, in accordance with any of the preceding embodiments, except that the high-density polyethylene composition having a standard deviation of flow direction shrinkage of less than 6 percent across different colors.

10 In an alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and method of making such articles, in accordance with any of the preceding embodiments, except that the high-density polyethylene composition having a standard deviation of flow direction shrinkage of less than 4.5 percent across different colors.

15 In an alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and method of making such articles, in accordance with any of the preceding embodiments, except that the high-density polyethylene composition further comprising 100 to 10,000 ppm by weight of a nucleator. More preferred ranges include 200 to 5000 parts per million, even more preferred 300 to 3000 parts per million, an most preferred 400 to 2000 parts per million.

20 In an alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and method of making such articles, in accordance with any of the preceding embodiments, except that the high-density polyethylene composition further comprising 100 to 10,000 ppm by weight of potassium stearate or HPN-20E as a nucleator, wherein the inventive high-

density polyethylene composition having a standard deviation of flow direction shrinkage of less than 4 percent across different colors.

In an alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and method of making such articles, in accordance with any of the preceding embodiments, except that the high-density polyethylene composition further comprising 100 to 10,000 ppm by weight of potassium stearate or HPN-20E as a nucleator, wherein the inventive high-density polyethylene composition having a standard deviation of flow direction shrinkage of less than 3 percent across different colors.

In an alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and method of making such articles, in accordance with any of the preceding embodiments, except that the high-density polyethylene composition further comprising 100 to 10,000 ppm by weight of potassium stearate or HPN-20E as a nucleator, wherein the inventive high-density polyethylene composition having a standard deviation of flow direction shrinkage of less than 2 percent across different colors.

In an alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and method of making such articles, in accordance with any of the preceding embodiments, except that the high-density polyethylene composition having a 1% secant modulus in psi of equal or greater to the following relationship: $[(7,492,165 * \text{density}(\text{g}/\text{cm}^3)) - 6,975,000] \text{ psi}/(\text{g}/\text{cm}^3)$.

In an alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and method of making such articles, in accordance with any of the preceding embodiments,

except that the high molecular weight polyethylene alpha-olefin copolymer having a density in the range of 0.925 to 0.945 g/cm³.

In another alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and
5 method of making such articles, in accordance with any of the preceding embodiments, except that the high molecular weight polyethylene alpha-olefin copolymer having a density in the range of 0.928 to 0.944 g/cm³.

In another alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and
10 method of making such articles, in accordance with any of the preceding embodiments, except that the high molecular weight polyethylene alpha-olefin copolymer having a melt index (I_{21.6}) in the range of 2 to 12 g/10 minutes.

In another alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and
15 method of making such articles, in accordance with any of the preceding embodiments, except that the high molecular weight polyethylene alpha-olefin copolymer having a melt index (I_{21.6}) in the range of 2.5 to 11 g/10 minutes.

In another alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and
20 method of making such articles, in accordance with any of the preceding embodiments, except that the low molecular weight ethylene polymer having a density in the range of 0.965 to 0.975 g/cm³.

In another alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and
25 method of making such articles, in accordance with any of the preceding embodiments,

except that the low molecular weight ethylene polymer having a melt index (I_2) in the range of 40 to 1300 g/10 minutes.

In another alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and
5 method of making such articles, in accordance with any of the preceding embodiments, except that the low molecular weight ethylene polymer having a melt index (I_2) in the range of 50 to 1000 g/10 minutes.

In another alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and
10 method of making such articles, in accordance with any of the preceding embodiments, except that the high-density polyethylene composition having a melt index (I_2) in the range of 1 to 2 g/10 minutes; or in the alternative, having a melt index (I_2) of at least 2 g/10 minutes .

In another alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and
15 method of making such articles, in accordance with any of the preceding embodiments, except that the high molecular weight ethylene alpha-olefin copolymer having a molecular weight in the range of 150,000 to 300,000.

In another alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and
20 method of making such articles, in accordance with any of the preceding embodiments, except that the low molecular weight ethylene polymer having a molecular weight in the range of 12,000 to 45,000.

In another alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and
25 method of making such articles, in accordance with any of the preceding embodiments,

except that the high molecular weight polyethylene alpha-olefin copolymer having a density in the range of 0.928 to 0.944 g/cm³, and a melt index (I_{21.6}) in the range of 2.5 to 11 g/10 minutes, and the low molecular weight ethylene polymer having a density in the range of 0.965 to 0.975 g/cm³, and a melt index (I₂) in the range of 50 to 1000 g/10 minutes.

5 In another alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and method of making such articles, in accordance with any of the preceding embodiments, except that both the high molecular weight polyethylene alpha-olefin copolymer and the low molecular weight ethylene polymer being substantially free of any long chain branching.

10 In another alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and method of making such articles, in accordance with any of the preceding embodiments, except that the high-density polyethylene composition being substantially free of any long chain branching.

15 In another alternative embodiment, the instant invention provides a high-density polyethylene composition, method of producing the same, articles made therefrom, and method of making such articles, in accordance with any of the preceding embodiments, except that the high-density polyethylene composition having a single ATREF temperature peak, wherein the ATREF temperature peak having a temperature peak maximum between
20 about 90 °C to about 105 °C; and wherein calculated purge fraction in the range of less than 15.5 percent.

 In another alternative embodiment, the instant invention provides an article and a method of making such an article, in accordance with any of the preceding embodiments, except that the article having an environmental stress crack resistance of at least 10 hours

measured via ASTM D-1693 condition B, 10% Igepal, or at least 100 hours measured via ASTM D-1693 condition B, 100 % Igepal.

In another alternative embodiment, the instant invention provides an article and a method of making such an article, in accordance with any of the preceding embodiments,
5 except that the article being a closure device.

In another alternative embodiment, the instant invention provides an injection molded article and a method of making such an article, in accordance with any of the preceding embodiments, except that the article being a bottle cap.

In another alternative embodiment, the instant invention provides an injection molded
10 article and a method of making such an article, in accordance with any of the preceding embodiments, except that the article being a cap including a skirt that axially extends from the periphery of a base, and having internal threads for securing the cap to a container.

Brief Description of the Drawings

15 For the purpose of illustrating the instant invention, there is shown in the drawings a form that is presently preferred; it being understood, however, that this invention is not limited to the precise arrangements and instrumentalities shown.

Fig. 1 is a graph illustrating how the calculated ATREF high-density fraction and purge fraction of the high molecular weight polyethylene component of the inventive
20 Example 1 was determined.

Fig. 2 is a graph illustrating how the calculated ATREF high-density fraction and purge fraction of the high molecular weight polyethylene component of the inventive Example 2 was determined.

Fig. 3 is a graph illustrating how the calculated ATREF high-density fraction and purge fraction of the high molecular weight polyethylene component of the inventive Example 3 was determined.

Fig. 4 is a graph illustrating how the calculated ATREF high-density fraction and
5 purge fraction of the high molecular weight polyethylene component of the inventive Example 4 was determined.

Fig. 5 is a graph illustrating how the calculated ATREF high-density fraction and purge fraction of the high molecular weight polyethylene component of the inventive Example 5 was determined.

10 **Fig. 6** is a graph illustrating how the calculated ATREF high-density fraction and purge fraction of the high molecular weight polyethylene component of the inventive Example 6 was determined.

Fig. 7 is a graph illustrating the relationship between the density in g/cm^3 and 1% secant modulus in psi, where the inventive high-density polyethylene composition having a
15 1% secant modulus in psi of equal or greater to the following relationship:
$$[(7,492,165 * \text{density}(\text{g/cm}^3)) - 6,975,000] \text{ psi}(\text{g/cm}^3).$$

Detailed Description of the Invention

The high-density polyethylene composition of the instant invention includes a first component, and a second component. The first component is preferably a high molecular
20 weight ethylene alpha-olefin copolymer having a density in the range of 0.920 to 0.946 g/cm^3 , and a melt index (I_{21}) of 1 to 15 g/10 minutes. The second component is preferably a low molecular weight ethylene polymer having a density in the range of 0.965 to 0.980 g/cm^3 , and a melt index (I_2) in the range of 30 to 1500 g/10 minutes. The high-density polyethylene composition has a melt index (I_2) of at least 1 g/10 minutes, a density in the
25 range of 0.950 to 0.960 g/cm^3 . The high-density polyethylene composition may further

include additional components, additives, or adjuvants. The high-density polyethylene composition is a bimodal polymer, or in the alternative, the high-density polyethylene is a multimodal polymer.

The term “bimodal,” as used herein, means that the molecular weight distribution (MWD) in a Gel Permeation Chromatography (GPC) curve exhibits two component polymers, for example, two peaks or wherein one component polymer may even exist as a hump, shoulder, or tail relative to the MWD of the other component polymer; or in the alternative, for example, wherein the two components may have only one single peak with no bumps, shoulders, or tails.

The term “multimodal” as used herein means that the MWD in a GPC curve exhibits more than two component polymers, for example, three or more peaks or wherein one component polymer may even exist as a hump, shoulder, or tail, relative to the MWD of the other component polymers; or in the alternative, wherein three or more components may have only one single pick with no bumps, shoulders, or tails.

The term “polymer” is used herein to indicate a homopolymer, an interpolymer (or copolymer), or a terpolymer. The term “polymer,” as used herein, includes interpolymers, such as, for example, those made by the copolymerization of ethylene with one or more C₃-C₂₀ alpha-olefin(s).

The term “interpolymer,” as used herein, refers to polymers prepared by the polymerization of at least two different types of monomers. The generic term interpolymer thus includes copolymers, usually employed to refer to polymers prepared from two different types of monomers, and polymers prepared from more than two different types of monomers.

The term (co)polymerization, as used herein, refers to polymerization of ethylene in the presence of one or more alpha-olefin comonomers.

The first component is a polymer, for example a polyolefin. The first component is preferably be an ethylene polymer; for example, the first component is preferably a high molecular weight ethylene alpha-olefin copolymer. The first component is substantially free of any long chain branching. Substantially free of any long chain branching, as used herein, refers to an ethylene polymer preferably substituted with less than about 0.1 long chain branch per 1000 total carbons, and more preferably, less than about 0.01 long chain branch per 1000 total carbons. The presence of long chain branches is typically determined according to the methods known in the art, such as gel permeation chromatography coupled with low angle laser light scattering detector (GPC-LALLS) and gel permeation chromatography coupled with a differential viscometer detector (GPC-DV). The first component has a density in the range of 0.920 to 0.946 g/cm³. All individual values and subranges from 0.920 to 0.946 g/cm³ are included herein and disclosed herein; for example, the first component has a density in the range of 0.925 to 0.945 g/cm³, or in the alternative, the first component has a density in the range of 0.928 to 0.944 g/cm³. The first component has a melt index (I_{21.6}); in the range of 1 to 15 g/10 minutes. All individual values and subranges from 1 to 15 g/10 minutes are included herein and disclosed herein; for example, the first component has a melt index (I_{21.6}) in the range of 2 to 12 g/10 minutes, or in the alternative, the first component has a melt index (I_{21.6}) in the range of 2.5 to 11 g/10 minutes. The first component has molecular weight in the range of 150,000 to 300,000. All individual values and subranges from 150,000 to 300,000 are included herein and disclosed herein; for example, the first component has a molecular weight in the range of 150,000 to 270,000; or in the alternative, the first component has a molecular weight in the range of 150,000 to 240,000. The first component may comprise any amount of one or more alpha-olefin copolymers; for example, the first component comprises about less than 10 percent by weight of one or more alpha-olefin comonomers, based on the weight of the first component. All

individual values and subranges less than 10 weight percent are included herein and disclosed herein. The first component may comprise any amount of ethylene; for example, the first component comprises at least about 90 percent by weight of ethylene, based on the weight of the first component. All individual values and subranges above 90 weight percent are
5 included herein and disclosed herein; for example, the first component comprises at least 95 percent by weight of ethylene, based on the weight of the first component.

The alpha-olefin comonomers typically have no more than 20 carbon atoms. For example, the alpha-olefin comonomers may preferably have 3 to 10 carbon atoms, and more preferably 3 to 8 carbon atoms. Exemplary alpha-olefin comonomers include, but are not
10 limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 4-methyl-1-pentene. The alpha-olefin comonomers are preferably selected from the group consisting of propylene, 1-butene, 1-hexene, and 1-octene, and more preferably from the group consisting of 1-hexene and 1-octene.

The second component is a polymer, for example a polyolefin. The second
15 component is preferably an ethylene polymer; for example, the second component is preferably a low molecular weight ethylene homopolymer. The ethylene homopolymer may contain trace amounts of contaminate comonomers, e.g. alpha-olefin comonomers. The term ethylene homopolymer, as used herein, refers to an ethylene polymer containing at least 99 percent by weight of ethylene units. The second component is preferably substantially free of
20 any long chain branching. Substantially free of any long chain branching, as used herein, refers to an ethylene polymer preferably substituted with less than about 0.1 long chain branch per 1000 total carbons, and more preferably, less than about 0.01 long chain branch per 1000 total carbons. The presence of long chain branches is typically determined according to the methods known in the art, as mentioned above. The second component has a
25 density in the range of 0.965 to 0.980 g/cm³. All individual values and subranges from 0.965

to 0.980 g/cm³ are included herein and disclosed herein; for example, the second component has a density in the range of 0.965 to 0.975 g/cm³. The second component has a melt index (I₂) in the range of 30 to 1500 g/10 minutes. All individual values and subranges from 30 to 1500 g/10 minutes are included herein and disclosed herein; for example, the second

5 component has a melt index (I₂) in the range of 40 to 1300 g/10 minutes; or in the alternative, the second component has a melt index (I₂) in the range of 50 to 1000 g/10 minutes. The second component has a molecular weight in the range of 12,000 to 45,000. All individual values and subranges from 12,000 to 45,000 are included herein and disclosed herein; for example, the second component has a molecular weight in the range of 15,000 to 45,000; or

10 in the alternative, the second component has a molecular weight in the range of 20,000 to 45,000. The second component comprises less than 1.00 percent by weight of one or more additional alpha-olefin copolymers, based on the weight of the second component. All individual values and subranges from less than 1.00 weight percent are included herein and disclosed herein; for example, the second component may comprise about 0.0001 to about

15 1.00 percent by weight of one or more additional alpha-olefin copolymers; the second component may comprise about 0.001 to about 1.00 percent by weight of one or more additional alpha-olefin copolymers; or in the alternative, the second component is free of any additional alpha-olefin copolymers. The second component comprises at least about 99 percent by weight of ethylene, based on the weight of the second component. All individual

20 values and subranges from about 99 to about 100 weight percent are included herein and disclosed herein; for example, the second component comprises about 99.5 to about 100 percent by weight of ethylene, based on the weight of the second component.

The high-density polyethylene composition has a density in the range of 0.950 to 0.960 g/cm³. All individual values and subranges from 0.950 to 0.960 g/cm³ are included

25 herein and disclosed herein. The high-density polyethylene composition has a melt index (I₂)

of at least 1 g/10 minutes. All individual values and subranges equal or greater than 1 g/10 minutes are included herein and disclosed herein; for example, the high-density polyethylene composition has a melt index (I_2) in the range of 1 to 2 g/10 minutes; or in the alternative, the high-density polyethylene composition has a melt index (I_2) of at least 2 g/10 minutes. The high-density polyethylene composition is substantially free of any long chain branching.

Substantially free of any long chain branching, as used herein, refers to a polyethylene composition preferably substituted with less than about 0.1 long chain branch per 1000 total carbons, and more preferably, less than about 0.01 long chain branch per 1000 total carbons.

The presence of long chain branches is typically determined according to the methods known

in the art, as mentioned above. The high-density polyethylene composition has a molecular weight distribution in the range of 4 to 15. All individual values and subranges from 4 to 15 are included herein and disclosed herein; for example, the high-density polyethylene

composition has a molecular weight distribution in the range of 5 to 13; or in the alternative, the high-density polyethylene composition has a molecular weight distribution in the range of 5 to 11. The term molecular weight distribution or "MWD," as used herein, refers to the ratio of weight average molecular weight (M_w) to number average molecular weight (M_n), i.e.

(M_w/M_n), described in further details hereinbelow. The high-density polyethylene

composition has an environmental stress crack resistance of at least 10 hours measured via ASTM D-1693, Condition B, 10% Igepal, or preferably at least 20 hours measured via ASTM

D-1693, Condition B, 10% Igepal, or more preferably, at least 40 hours measured via ASTM D-1693, Condition B, 10% Igepal. In the alternative, the high-density polyethylene

composition has an environmental stress crack resistance of at least 100 hours measured via ASTM D-1693, Condition B, 100 % Igepal, or preferably, at least 125 hours measured via

ASTM D-1693, Condition B, 100 % Igepal, or more preferably, at least 150 hours measured

via ASTM D-1693, Condition B, 100 % Igepal. The high-density polyethylene composition

may comprise any amounts of first component, second component, or combinations thereof.

The high-density polyethylene composition comprises about 40 to about 65 percent by weight of the first component, based on the total weight of the first and second components. All

individual values and subranges from about 40 to about 65 weight percent are included herein

5 and disclosed herein; for example, the high-density polyethylene composition comprises

about 42 to about 64 percent by weight of the first component, based on the total weight of

first and second components. The high-density polyethylene composition further comprises

about 35 to about 60 percent by weight of the second component, based on the total weight of the first and second components. All individual values and subranges from about 35 to about

10 60 weight percent are included herein and disclosed herein; for example, the high-density

polyethylene composition further comprises about 36 to about 58 percent by weight of the

second component, based on the total weight of the first and second components. Preferably,

the high-density polyethylene composition has a single ATREF temperature peak, wherein

the ATREF temperature peak having a temperature peak maximum between about 90 °C to

15 about 105 °C. The high-density polyethylene composition further has a calculated purge

fraction in the range of less than 15.5 percent.

The high-density polyethylene composition may further include additional components such as other polymers, adjuvants, and/or additives. Such adjuvants or additives include, but are not limited to, antistatic agents, color enhancers, dyes, lubricants, fillers,

20 pigments, primary antioxidants, secondary antioxidants, processing aids, UV stabilizers,

nucleators, and combinations thereof. The high-density polyethylene composition

comprises about less than 10 percent by the combined weight of one or more additives,

based on the weight of the high-density polyethylene composition. All individual values and

subranges from about less than 10 weight percent are included herein and disclosed herein;

25 for example, the high-density polyethylene composition comprises about less than 5 percent

by the combined weight of one or more additives, based on the weight of the high-density polyethylene composition; or in the alternative, the high-density polyethylene composition comprises about less than 1 percent by the combined weight of one or more additives, based on the weight of the high-density polyethylene composition; or in another alternative, the high-density polyethylene composition may comprise about less than 0.5 percent by the combined weight of one or more additives, based on the weight of the high-density polyethylene composition. Nucleators include, but are not limited to, potassium stearate, HPN-20E, which is commercially available from Milliken. Antioxidants, such as Irgafos[®] 168 and Irganox[®] 1010, are commonly used to protect the polymer from thermal and/or oxidative degradation. Irganox[®] 1010 is tetrakis (methylene (3,5-di-tert-butyl-4hydroxyhydrocinnamate), which is commercially available from Ciba Geigy Inc. Irgafos[®] 168 is tris (2,4 di-tert-butylphenyl) phosphite, which is commercially available from Ciba Geigy Inc.

The inventive high-density polyethylene composition may further be blended with other polymers. Such other polymers are generally known to a person of ordinary skill in the art. Blends comprising the inventive high-density polyethylene composition is formed via any conventional methods. For example, the selected polymers are melt blended via a single or twin screw extruder, or a mixer, e.g. a Banbury mixer, a Haake mixer, a Barbender internal mixer.

In general, blends containing the inventive high-density polyethylene composition comprises at least 40 percent by weight of the inventive high-density polyethylene composition, based on the total weight of the blend. All individual values and subranges in the range of at least 40 weight percent are included herein and disclosed herein; for example, the blend comprises at least 50 percent by weight of the inventive high-density polyethylene composition, based on the total weight of the blend; or in the alternative, the blend comprises

at least 60 percent by weight of the inventive high-density polyethylene composition, based on the total weight of the blend; or in the alternative, the blend comprises at least 70 percent by weight of the inventive high-density polyethylene composition, based on the total weight of the blend; or in the alternative, the blend comprises at least 80 percent by weight of the
5 inventive high-density polyethylene composition, based on the total weight of the blend; or in the alternative, the blend comprises at least 90 percent by weight of the inventive high-density polyethylene composition, based on the total weight of the blend; or in the alternative, the blend comprises at least 95 percent by weight of the inventive high-density polyethylene composition, based on the total weight of the blend; or in the alternative, the blend comprises
10 at least 99.99 percent by weight of the inventive high-density polyethylene composition, based on the total weight of the blend.

Different polymerization reactions and catalyst systems may be employed to produce the inventive high-density polyethylene composition. Typical transition metal catalyst systems used to prepare the high-density polyethylene composition are magnesium/titanium
15 based catalyst systems, exemplified by the catalyst system described in U.S. 4,302,565; vanadium based catalyst systems, such as those described in U.S. 4,508,842; U.S. 5,332,793; U.S. 5,342,907; and U.S. 5,410,003; and a metallocene catalyst system, such as those described in U.S. 4,937,299; U.S. 5,317,036; and U.S. 5,527,752. Catalyst systems that use molybdenum oxides on silica-alumina supports are also useful. Preferred catalyst systems for
20 preparing the components for the inventive high-density polyethylene composition are Ziegler-Natta catalyst systems and metallocene catalyst systems.

In some embodiments, preferred catalysts used in the process to make the high-density polyethylene compositions are of the magnesium/titanium type. In particular, for the gas phase polymerizations, the catalyst is made from a precursor comprising magnesium and
25 titanium chlorides in an electron donor solvent. This solution is often either deposited on a

porous catalyst support, or a filler is added, which, on subsequent spray drying, provides additional mechanical strength to the particles. The solid particles from either support methods are often slurried in a diluent producing a high viscosity mixture, which is then used as catalyst precursor. Exemplary catalyst types are described in U.S. 6,187,866 and U.S.

5 5,290,745, the entire contents of both of which are herein incorporated by reference.

Precipitated/crystallized catalyst systems, such as those described in U.S. 6,511,935 and U.S. 6,248,831, the entire contents of both of which are herein incorporated by reference, may also be used. Such catalysts may further be modified with one precursor activator. Such further modifications are described in US patent publication No.: US2006/0287445 A1.

10 Preferably the catalyst precursor has the formula $Mg_dTi(OR)_e X_f(ED)_g$ wherein R is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms or COR' wherein R' is a aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms; each OR group is the same or different; X is independently chlorine, bromine or iodine; ED is an electron donor; d is 0.5 to 56; e is 0, 1, or 2; f is 2 to 116; and g is >2 and up to $1.5*d + 3$. It is
15 prepared from a titanium compound, a magnesium compound, and an electron donor.

The electron donor is an organic Lewis base, liquid at temperatures in the range of 0 °C to 200 °C, in which the magnesium and titanium compounds are soluble. The electron donor compounds are sometimes also referred to as Lewis bases. The electron donor can be an alkyl ester of an aliphatic or aromatic carboxylic acid, an aliphatic ketone, an aliphatic
20 amine, an aliphatic alcohol, an alkyl or cycloalkyl ether, or mixtures thereof, each electron donor having 2 to 20 carbon atoms. Among these electron donors, the preferred are alkyl and cycloalkyl ethers having 2 to 20 carbon atoms; dialkyl, diaryl, and alkylaryl ketones having 3 to 20 carbon atoms; and alkyl, alkoxy, and alkylalkoxy esters of alkyl and aryl carboxylic acids having 2 to 20 carbon atoms. The most preferred electron donor is tetrahydrofuran.
25 Other examples of suitable electron donors are methyl formate, ethyl acetate, butyl acetate,

ethyl ether, dioxane, di-n-propyl ether, dibutyl ether, ethanol, 1-butanol, ethyl formate, methyl acetate, ethyl anisate, ethylene carbonate, tetrahydropyran, and ethyl propionate.

While a large excess of electron donor may be used initially to provide the reaction product of titanium compound and electron donor, the final catalyst precursor contains

5 approximately 1 to approximately 20 moles of electron donor per mole of titanium compound and preferably approximately 1 to approximately 10 moles of electron donor per mole of titanium compound.

Since the catalyst will act as a template for the growth of the polymer, it is essential that the catalyst precursor be converted into a solid. It is also essential that the resultant solid
10 has the appropriate particle size and shape to produce polymer particles with relatively narrow size distribution, low amounts of fines and good fluidization characteristics.

Although this solution of Lewis Base, magnesium and titanium compounds may be impregnated into a porous support and dried to form a solid catalyst; it is preferred that the solution be converted into a solid catalyst via spray drying. Each of these methods thus

15 forms a "supported catalyst precursor."

The spray dried catalyst product is then preferentially placed into a mineral oil slurry. The viscosity of the hydrocarbon slurry diluent is sufficiently low, so that the slurry can be conveniently pumped through the pre-activation apparatus, and eventually into the polymerization reactor. The catalyst is fed using a slurry catalyst feeder. A progressive
20 cavity pump, such as a Moyno pump is typically used in commercial reaction systems, while a dual piston syringe pump is typically used in pilot scale reaction systems, where the catalyst flows are less than, or equal to, $10 \text{ cm}^3/\text{hour}$ ($2.78 \times 10^{-9} \text{ m}^3/\text{s}$) of slurry.

A cocatalyst, or activator, is also fed to the reactor to effect the polymerization. Complete activation by additional cocatalyst is required to achieve full activity. The

complete activation normally occurs in the polymerization reactor, although the techniques taught in EP 1,200,483 may also be used.

The cocatalysts, which are reducing agents, conventionally used, are comprised of aluminum compounds, but compounds of lithium, sodium and potassium, alkaline earth metals, as well as compounds of other earth metals than aluminum are possible. The compounds are usually hydrides, organometal or halide compounds. Butyl lithium and dibutyl magnesium are examples of useful compounds of other than aluminum.

An activator compound, which is generally used with any of the titanium based catalyst precursors, can have the formula $AlR_aX_bH_c$, wherein each X is independently chlorine, bromine, iodine, or OR'; each R and R' is independently a saturated aliphatic hydrocarbon radical having 1 to 14 carbon atoms; b is 0 to 1.5; c is 0 or 1; and $a+b+c=3$.

Preferred activators include alkylaluminum mono- and dichlorides, wherein each alkyl radical has 1 to 6 carbon atoms and the trialkylaluminums. Examples are diethylaluminum chloride and tri-n-hexylaluminum. About 0.10 to 10 moles, and preferably 0.15 to 2.5 moles, of activator are used per mole of electron donor. The molar ratio of activator to titanium is in the range from 1:1 to 10:1, and is preferably in the range from 2:1 to 5:1.

The hydrocarbyl aluminum cocatalyst can be represented by the formula R_3Al or R_2AlX , wherein each R is independently alkyl, cycloalkyl, aryl, or hydrogen; at least one R is hydrocarbyl; and two or three R radicals can be joined to form a heterocyclic structure. Each R, which is a hydrocarbyl radical, can have 1 to 20 carbon atoms, and preferably has 1 to 10 carbon atoms. X is a halogen, preferably chlorine, bromine, or iodine. Examples of hydrocarbyl aluminum compounds are as follows: triisobutylaluminum, tri-n-hexylaluminum, di-isobutyl-aluminum hydride, dihexylaluminum hydride, di-isobutylhexylaluminum, isobutyl dihexylaluminum, trimethylaluminum, triethylaluminum, tripropylaluminum, triisopropylaluminum, tri-n-butylaluminum, trioctylaluminum, tridecylaluminum,

tridodecylaluminum, tribenzylaluminum, triphenylaluminum, trinaphthylaluminum, tritolylaluminum, dibutylaluminum chloride, diethylaluminum chloride, and ethylaluminum sesquichloride. The cocatalyst compounds can also serve as activators and modifiers.

Activators can be added to the precursor either before and/or during polymerization.

5 In one procedure, the precursor is fully activated before polymerization. In another procedure, the precursor is partially activated before polymerization, and activation is completed in the reactor. Where a modifier is used instead of an activator, the modifiers are usually dissolved in an organic solvent such as isopentane and, where a support is used, impregnated into the support following impregnation of the titanium compound or complex,
10 after which the supported catalyst precursor is dried. Otherwise, the modifier solution is added by itself directly to the reactor. Modifiers are similar in chemical structure and function to the activators as are cocatalysts. For variations, see for example, U.S. 5,106,926, incorporated herein by reference in its entirety. The cocatalyst is preferably added separately neat or as a solution in an inert solvent, such as isopentane, to the polymerization reactor at
15 the same time as the flow of ethylene is initiated.

In those embodiments that use a support, the precursor is supported on an inorganic oxide support such as silica, aluminum phosphate, alumina, silica/alumina mixtures, silica that has been modified with an organoaluminum compound such as triethyl aluminum, and silica modified with diethyl zinc. In some embodiments silica is a preferred support. A
20 typical support is a solid, particulate, porous material essentially inert to the polymerization. It is used as a dry powder having an average particle size of 10 to 250 μm and preferably 30 to 100 μm ; a surface area of at least 200 m^2/g and preferably at least 250 m^2/g ; and a pore size of at least $100 \times 10^{-10} \text{ m}$ and preferably at least $200 \times 10^{-10} \text{ m}$. Generally, the amount of support used is that which will provide 0.1 to 1.0 millimole of titanium per gram of support
25 and preferably 0.4 to 0.9 millimole of titanium per gram of support. Impregnation of the

above mentioned catalyst precursor into a silica support can be accomplished by mixing the precursor and silica gel in the electron donor solvent or other solvent followed by solvent removal under reduced pressure. When a support is not desired, the catalyst precursor can be used in liquid form.

5 In another embodiment, metallocene catalysts, single-site catalysts and constrained geometry catalysts may be used in the practice of the invention. Generally, metallocene catalyst compounds include half and full sandwich compounds having one or more π -bonded ligands including cyclopentadienyl-type structures or other similar functioning structure such as pentadiene, cyclooctatetraendiyl and imides. Typical compounds are generally described
10 as containing one or more ligands capable of π -bonding to a transition metal atom, usually, cyclopentadienyl derived ligands or moieties, in combination with a transition metal selected from Group 3 to 8, preferably 4, 5 or 6 or from the lanthanide and actinide series of the Periodic Table of Elements.

Exemplary of metallocene-type catalyst compounds are described in, for example,
15 U.S. Patents: 4,530,914; 4,871,705; 4,937,299; 5,017,714; 5,055,438; 5,096,867; 5,120,867; 5,124,418; 5,198,401; 5,210,352; 5,229,478; 5,264,405; 5,278,264; 5,278,119; 5,304,614; 5,324,800; 5,347,025; 5,350,723; 5,384,299; 5,391,790; 5,391,789; 5,399,636; 5,408,017; 5,491,207; 5,455,366; 5,534,473; 5,539,124; 5,554,775; 5,621,126; 5,684,098; 5,693,730; 5,698,634; 5,710,297; 5,712,354; 5,714,427; 5,714,555; 5,728,641; 5,728,839; 5,753,577;
20 5,767,209; 5,770,753 and 5,770,664; European publications: EP-A-0 591 756; EP-A-0 520 732; EP-A-0 420 436; EP-A-0 485 822; EP-A-0 485 823; EP-A-0 743 324; EP-A-0 518 092; and PCT publications: WO 91/04257; WO 92/00333; WO 93/08221; WO 93/08199; WO 94/01471; WO 96/20233; WO 97/15582; WO 97/19959; WO 97/46567; WO 98/01455; WO 98/06759 and WO 98/011144. All of these references are incorporated herein, in their
25 entirety, by reference.

Suitable catalysts for use herein, preferably include constrained geometry catalysts as disclosed in U.S. Patent Nos. 5,272,236 and 5,278,272, which are both incorporated, in their entirety, by reference.

5 The monocyclopentadienyl transition metal olefin polymerization catalysts taught in U.S. Patent No. 5,026,798, the teachings of which are incorporated herein by reference, are also suitable as catalysts of the invention.

The foregoing catalysts may be further described as comprising a metal coordination complex comprising a metal of groups 3-10 or the Lanthanide series of the Periodic Table of the Elements, and a delocalized π -bonded moiety, substituted with a constrain-inducing
10 moiety. Such a complex has a constrained geometry about the metal atom. The catalyst further comprises an activating cocatalyst.

Any conventional ethylene homopolymerization or (co)polymerization reactions may be employed to produce the inventive high-density polyethylene composition. Such conventional ethylene homopolymerization or (co)polymerization reactions include, but are
15 not limited to, gas phase polymerization, slurry phase polymerization, liquid phase polymerization, and combinations thereof using conventional reactors, e.g. gas phase reactors, loop reactors, stirred tank reactors, and batch reactors in series, or in series and parallel. The polymerization system of the instant invention is a dual sequential polymerization system or a multi-sequential polymerization system. Examples of dual
20 sequential polymerization system include, but are not limited to, gas phase polymerization/gas phase polymerization; gas phase polymerization/liquid phase polymerization; liquid phase polymerization/gas phase polymerization; liquid phase polymerization/liquid phase polymerization; slurry phase polymerization/slurry phase polymerization; liquid phase polymerization/slurry phase polymerization; slurry phase
25 polymerization/liquid phase polymerization; slurry phase polymerization/gas phase

polymerization; and gas phase polymerization/slurry phase polymerization. The multi-sequential polymerization systems includes at least three polymerization reactions. The catalyst system, described above, may also be a conventional catalyst system. The inventive high-density polyethylene composition is preferably produced via a dual gas phase polymerization process, e.g. gas phase polymerization/gas phase polymerization; however, the instant invention is not so limited, and any of the above combinations may be employed.

In production, a dual sequential polymerization system connected in series, as described above, may be used. The first component, i.e. the high molecular weight ethylene polymer, can be produced in the first stage of the dual sequential polymerization system, and the second component, i.e. the low molecular weight ethylene polymer, can be prepared in the second stage of the dual sequential polymerization system. Alternatively, the second component, i.e. the low molecular weight ethylene polymer, can be made in the first stage of the dual sequential polymerization system, and the first component, i.e. the high molecular weight ethylene polymer, can be made in the second stage of the dual sequential polymerization system.

For purposes of the present disclosure, the reactor, in which the conditions are conducive to making the first component is known as the first reactor. Alternatively, the reactor in which the conditions are conducive to making the second component is known as the second reactor.

In production, a catalyst system including a cocatalyst, ethylene, one or more alpha-olefin comonomers, hydrogen, and optionally inert gases and/or liquids, e.g. N₂, isopentane, and hexane, are continuously fed into a first reactor, which is connected to a second reactor in series; the first component/active catalyst mixture is then continuously transferred, for example, in batches from the first reactor to the second reactor. Ethylene, hydrogen, cocatalyst, and optionally inert gases and/or liquids, e.g. N₂, isopentane, hexane, are

continuously fed to the second reactor, and the final product, i.e. the inventive high-density polyethylene composition, is continuously removed, for example, in batches from the second reactor. A preferred mode is to take batch quantities of first component from the first reactor, and transfer these to the second reactor using the differential pressure generated by a recycled
5 gas compression system. The inventive high-density polyethylene composition is then transferred to a purge bin under inert atmosphere conditions. Subsequently, the residual hydrocarbons are removed, and moisture is introduced to reduce any residual aluminum alkyls and any residual catalysts before the inventive high-density polyethylene composition is exposed to oxygen. The inventive high-density polyethylene composition is then
10 transferred to an extruder to be pelletized. Such pelletization techniques are generally known. The inventive high-density polyethylene composition may further be melt screened. Subsequent to the melting process in the extruder, the molten composition is passed through one or more active screens (positioned in series of more than one) with each active screen having a micron retention size of from about 2 to about 400 ($2 \text{ to } 4 \times 10^{-5} \text{ m}$), and preferably
15 about 2 to about 300 ($2 \text{ to } 3 \times 10^{-5} \text{ m}$), and most preferably about 2 to about 70 ($2 \text{ to } 7 \times 10^{-6} \text{ m}$), at a mass flux of about 5 to about 100 lb/hr/in² (1.0 to about 20 kg/s/m²). Such further melt screening is disclosed in U.S. Patent No. 6,485,662, which is incorporated herein by reference to the extent that it discloses melt screening.

In an alternative production, a multi-sequential polymerization system connected in
20 series and parallel, as described above, may be used. In one embodiment of the instant invention, a catalyst system including a cocatalyst, ethylene, one or more alpha-olefin comonomers, hydrogen, and optionally inert gases and/or liquids, e.g. N₂, isopentane, and hexane, are continuously fed into a first reactor, which is connected to a second reactor, wherein the second reactor is connected to a third reactor in series; the first component/active
25 catalyst mixture is then continuously transferred, for example, in batches from the first

reactor to the second reactor, and then to the third reactor. Ethylene, hydrogen, cocatalyst, and optionally inert gases and/or liquids, e.g. N₂, isopentane, and hexane, are continuously fed to the second and third reactors, and the final product, i.e. high-density polyethylene composition, is continuously removed, for example, in batches from the third reactor. A

5 preferred mode is to take batch quantities of first component from the first reactor, and transfer these to the second reactor, and then take batches from the second reactor and transfer these to the third reactor in series using the differential pressure generated by a recycled gas compression system. Alternatively, the first reactor may feed to both a second reactor and a third reactor in parallel, and the product from first reactor may be transferred to
10 either second or third reactor. The high-density polyethylene composition is then transferred to a purge bin under inert atmosphere conditions. Subsequently, the residual hydrocarbons are removed, and moisture may be introduced to reduce any residual aluminum alkyls and any residual catalysts before the polymer, i.e. the inventive high-density polyethylene composition, is exposed to oxygen. The inventive high-density polyethylene composition is
15 then transferred to an extruder to be pelletized. Such pelletization techniques are generally known. The inventive high-density polyethylene composition may further be melt screened. Subsequent to the melting process in the extruder, the molten composition is passed through one or more active screens (positioned in series of more than one) with each active screen having a micron retention size of from about 2 to about 400 ($2 \text{ to } 4 \times 10^{-5} \text{ m}$), and preferably
20 about 2 to about 300 ($2 \text{ to } 3 \times 10^{-5} \text{ m}$), and most preferably about 2 to about 70 ($2 \text{ to } 7 \times 10^{-6} \text{ m}$), at a mass flux of about 5 to about 100 lb/hr/in² (1.0 to about 20 kg/s/m²). Such further melt screening is disclosed in U.S. Patent No. 6,485,662, which is incorporated herein by reference to the extent that it discloses melt screening.

In another alternative production, the inventive high-density polyethylene
25 composition may be produced from polymers made in two or more independent reactors

(each using the same or different catalyst) with post reaction blending.

In application, the inventive high-density polyethylene composition may be used to manufacture shaped articles. Such articles may include, but are not limited to, closure devices, e.g. bottle caps. Different methods may be employed to manufacture articles such as bottle caps. Suitable conversion techniques include, but are not limited to, injection molding.

In injection molding process, the inventive high-density polyethylene composition is fed into an extruder via a hopper. The extruder conveys, heats, melts, and pressurizes the inventive high-density polyethylene composition to a form a molten stream. The molten stream is forced out of the extruder through a nozzle into a relatively cool mold held closed under pressure thereby filling the mold. The melt cools and hardens until fully set-up. The mold then opens and the molded article, e.g. bottle cap, is removed. The injection molded cap may include a skirt that axially extends from the periphery of a base, and may further include internal threads for securing the cap to a container.

Closure devices, e.g. bottle caps, including the inventive high-density polyethylene composition exhibit improved environmental crack resistance. Such bottle caps are adapted to withstand the pressure of carbonated drinks. Such bottle caps further facilitate closure, and sealing of a bottle, i.e. optimum torque provided by a machine to screw the cap on the bottle, or unsealing a bottle, i.e. optimum torque provide by a person to unscrew the cap.

Examples

It is understood that the present invention is operable in the absence of any component, which has not been specifically disclosed. The following examples are provided in order to further illustrate the invention and are not to be construed as limiting.

Inventive Examples 1-6

Inventive Examples 1-6 were prepared according to the following procedures: a dual-sequential polymerization system, e.g. a first gas phase reactor and a second gas phase reactor

operating in series, was provided. Ethylene, one or more alpha-olefin comonomers, hydrogen, catalyst, e.g. Ziegler-Natta catalyst, slurried in mineral oil, N₂, and isopentane were fed continuously into the first reactor. Subsequently, a cocatalyst, e.g. triethylaluminum (TEAL), was fed continuously into the first reactor to activate the catalyst. The first

5 polymerization reaction of the ethylene in the presence of 1-hexene was carried out in the first reactor under the conditions shown below in Table I thereby producing first component-catalyst complex. The first component-catalyst complex was continuously transferred to the second reactor. Additional, ethylene, hydrogen, cocatalyst, e.g. TEAL, N₂, and isopentane were fed continuously into the second reactor. No additional catalyst was added to the

10 second reactor. The second polymerization reaction of ethylene was carried out in the second reactor under the conditions shown below in Table I thereby producing the first component-catalyst-second component complex. The first component-catalyst-second component complex was continuously removed from the second reactor in batches into the product chamber, where it was purged to remove residual hydrocarbons, and then transferred to a

15 fiberpak drum. The fiberpak drum was continuously purged with humidified nitrogen. The polymer, i.e. the inventive high-density polyethylene composition, was further processed in a mixer/pelletizer. The polymer, i.e. the inventive high-density polyethylene composition, was melted in the mixer, and additives were dispersed therein the polymer, inventive high-density polyethylene composition, matrix. The inventive high-density polyethylene composition was

20 extruded through a die plate, pelletized, and cooled. The resin samples of the Inventive Examples 1-6 were tested for their properties from pellets, or were formed into testing plaques according to ASTM D-4703-00 and then were tested for their properties. Such properties are shown in Tables I and II, and Figs. 1-6. The resin samples of the Inventive Examples 1-6 were also tested for shrinkage properties according to ASTM D-955 utilizing a

25 60 mm x 60 mm x 2 mm plaques, and the results are shown in Table IV.

Comparative Examples A

Comparative example A is a high-density polyethylene copolymer, which is commercially available under the tradename B4020N1331 from INEOS Olefins & Polymers, USA. The resin samples of the comparative examples A were tested for their properties from pellets, or were formed into testing plaques according to ASTM D-4703-00 and then tested for their properties. Such properties are shown in Tables III.

Test Methods

Unless otherwise noted, the values reported herein were determined according to the following test methods.

Density (g/cm^3) was measured according to ASTM-D 792-03, Method B, in isopropanol. Specimens were measured within 1 hour of molding after conditioning in the isopropanol bath at 23 °C for 8 min to achieve thermal equilibrium prior to measurement. The specimens were compression molded according to ASTM D-4703-00 Annex A with a 5 min initial heating period at about 190 °C and a 15 °C/min cooling rate per Procedure C. The specimen was cooled to 45 °C in the press with continued cooling until “cool to the touch.”

Melt index (I_2) was measured at 190 °C under a load of 2.16 kg according to ASTM D-1238-03.

Melt index (I_5) was measured at 190 °C under a load of 5.0 kg according to ASTM D-1238-03.

Melt index (I_{10}) was measured at 190 °C under a load of 10.0 kg according to ASTM D-1238-03.

Melt index ($I_{21.6}$) was measured at 190 °C under a load of 21.6 kg according to ASTM D-1238-03.

Shrinkage was measured according to ASTM D-955 utilizing a 60 mm x 60 mm x 2 mm plaques.

Weight average molecular weight (M_w) and number average molecular weight (M_n) were determined according to methods known in the art using conventional GPC, as described herein below.

The molecular weight distributions of ethylene polymers were determined by gel permeation chromatography (GPC). The chromatographic system consisted of a Waters (Millford, MA) 150 °C high temperature gel permeation chromatograph, equipped with a Precision Detectors (Amherst, MA) 2-angle laser light scattering detector Model 2040. The 15° angle of the light scattering detector was used for calculation purposes. Data collection was performed using Viscotek TriSEC software version 3 and a 4-channel Viscotek Data Manager DM400. The system was equipped with an on-line solvent degas device from Polymer Laboratories. The carousel compartment was operated at 140 °C and the column compartment was operated at 150 °C. The columns used were four Shodex HT 806M 300 mm, 13 µm columns and one Shodex HT803M 150 mm, 12 µm column. The solvent used was 1,2,4 trichlorobenzene. The samples were prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent. The chromatographic solvent and the sample preparation solvent contained 200 µg/g of butylated hydroxytoluene (BHT). Both solvent sources were nitrogen sparged. Polyethylene samples were stirred gently at 160 °C for 4 hours. The injection volume used was 200 microliters, and the flow rate was 0.67 milliliters/min. Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards, with molecular weights ranging from 580 to 8,400,000 g/mol, which were arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards were purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards were prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to, or greater than, 1,000,000 g/mol, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000 g/mol. The

polystyrene standards were dissolved at 80 °C with gentle agitation for 30 minutes. The narrow standards mixtures were run first, and in order of decreasing highest molecular weight component, to minimize degradation. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using the following equation (as described in Williams and Ward, *J. Polym. Sci., Polym. Let.*, 6, 621 (1968)):

$$M_{\text{polyethylene}} = A \times (M_{\text{polystyrene}})^B,$$

where M is the molecular weight, A has a value of 0.41 and B is equal to 1.0. The Systematic Approach for the determination of multi-detector offsets was done in a manner consistent with that published by Balke, Mourey, et al. (Mourey and Balke, *Chromatography Polym.* Chpt 12, (1992) and Balke, Thitiratsakul, Lew, Cheung, Mourey, *Chromatography Polym.* Chpt 13, (1992)), optimizing dual detector log results from Dow broad polystyrene 1683 to the narrow standard column calibration results from the narrow standards calibration curve using in-house software. The molecular weight data for off-set determination was obtained in a manner consistent with that published by Zimm (Zimm, B.H., *J. Chem. Phys.*, 16, 1099 (1948)) and Kratochvil (Kratochvil, P., *Classical Light Scattering from Polymer Solutions*, Elsevier, Oxford, NY (1987)). The overall injected concentration used for the determination of the molecular weight was obtained from the sample refractive index area and the refractive index detector calibration from a linear polyethylene homopolymer of 115,000 g/mol molecular weight, which was measured in reference to NIST polyethylene homopolymer standard 1475. The chromatographic concentrations were assumed low enough to eliminate addressing 2nd Virial coefficient effects (concentration effects on molecular weight). Molecular weight calculations were performed using in-house software. The calculation of the number-average molecular weight, weight-average molecular weight, and z-average molecular weight were made according to the following equations, assuming that the refractometer signal is directly proportional to weight fraction. The baseline-

subtracted refractometer signal can be directly substituted for weight fraction in the equations below. Note that the molecular weight can be from the conventional calibration curve or the absolute molecular weight from the light scattering to refractometer ratio. An improved estimation of z-average molecular weight, the baseline-subtracted light scattering signal can be substituted for the product of weight average molecular weight and weight fraction in equation (2) below:

$$\begin{aligned} \text{a) } \overline{Mn} &= \frac{\sum_i w f_i}{\sum_i \left(\frac{w f_i}{M_i} \right)} & \text{b) } \overline{Mw} &= \frac{\sum_i (w f_i * M_i)}{\sum_i w f_i} \\ \text{c) } \overline{Mz} &= \frac{\sum_i (w f_i * M_i^2)}{\sum_i (w f_i * M_i)} \quad (2) \end{aligned}$$

Bimodality of distributions was characterized according to the weight fraction of the highest temperature peak in temperature rising elution fractionation (typically abbreviated as "TREF") data as described, for example, in Wild et al., *Journal of Polymer Science, Poly. Phys. Ed.*, Vol. 20, p. 441 (1982), in U.S. 4,798,081 (Hazlitt et al.), or in U.S. 5,089,321 (Chum et al.), the disclosures of all of which are incorporated herein by reference. In analytical temperature rising elution fractionation analysis (as described in U.S. 4,798,081 and abbreviated herein as "ATREF"), the composition to be analyzed is dissolved in a suitable hot solvent (for example, 1,2,4 trichlorobenzene), and allowed to crystallized in a column containing an inert support (for example, stainless steel shot) by slowly reducing the temperature. The column was equipped with both an infra-red detector and a differential viscometer (DV) detector. An ATREF-DV chromatogram curve was then generated by eluting the crystallized polymer sample from the column by slowly increasing the temperature of the eluting solvent (1,2,4 trichlorobenzene). The ATREF-DV method is

described in further detail in WO 99/14271, the disclosure of which is incorporated herein by reference.

High Density Fraction (percent) was measured via analytical temperature rising elution fractionation analysis (as described in U.S. 4,798,081 and abbreviated herein as

5 “ATREF”), which is described in further details hereinafter. Analytical temperature rising elution fractionation (ATREF) analysis was conducted according to the method described in U.S. Patent No. 4,798,081 and Wilde, L.; Ryle, T.R.; Knobloch, D.C.; Peat, I.R.;

Determination of Branching Distributions in Polyethylene and Ethylene Copolymers, J. Polym. Sci., 20, 441-455 (1982), which are incorporated by reference herein in their entirety.

10 The composition to be analyzed was dissolved in trichlorobenzene and allowed to crystallize in a column containing an inert support (stainless steel shot) by slowly reducing the temperature to 20 °C at a cooling rate of 0.1 °C/min. The column was equipped with an infrared detector. An ATREF chromatogram curve was then generated by eluting the crystallized polymer sample from the column by slowly increasing the temperature of the
15 eluting solvent (trichlorobenzene) from 20 to 120 °C at a rate of 1.5 °C/min.

Branching distributions were determined via crystallization analysis fractionation (CRYSTAF); described herein below. Crystallization analysis fractionation (CRYSTAF) was conducted via a CRYSTAF 200 unit commercially available from PolymerChar, Valencia, Spain. The samples were dissolved in 1,2,4 trichlorobenzene at 160 °C (0.66 mg/mL) for 1 hr
20 and stabilized at 95 °C for 45 minutes. The sampling temperatures ranged from 95 to 30 °C at a cooling rate of 0.2 °C/min. An infrared detector was used to measure the polymer solution concentrations. The cumulative soluble concentration was measured as the polymer crystallizes while the temperature was decreased. The analytical derivative of the cumulative profile reflects the short chain branching distribution of the polymer.

The CRYSTAF temperature peak and area are identified by the peak analysis module included in the CRYSTAF Software (Version 2001.b, PolymerChar, Valencia, Spain). The CRYSTAF peak finding routine identifies a temperature peak as a maximum in the dW/dT curve and the area between the largest positive inflections on either side of the identified peak

5 in the derivative curve. To calculate the CRYSTAF curve, the preferred processing parameters are with a temperature limit of 70 °C and with smoothing parameters above the temperature limit of 0.1, and below the temperature limit of 0.3.

Solubility Distribution Breadth Index (SDBI) is the statistical value for the breadth of the CRYSTAF method which is calculated based on the following formula:

$$10 \quad SDBI = \int \sqrt[4]{(T - T_w)^4 \cdot w(T)} dT$$

$$T_w = \int T \cdot w(T) dT$$

$$\int w(T) dT = 1$$

wherein T is temperature, W is weight fraction, and T_w weight average temperature.

Long Chain Branching was determined according to the methods known in the art,

15 such as gel permeation chromatography coupled with low angle laser light scattering detector (GPC-LALLS) and gel permeation chromatography coupled with a differential viscometer detector (GPC-DV).

Resin stiffness was characterized by measuring the Flexural Modulus at 5 percent strain and Secant Moduli at 1 percent and 2 percent strain, and a test speed of 0.5 inch/min

20 (13 mm/min) according to ASTM D 790-99 Method B.

Tensile strength at yield and elongation at break were measured according to ASTM D-638-03 employing Type IV Specimen at 2 inch/minute (50 mm/minute).

The environmental stress crack resistance (ESCR) was measured according to ASTM-D 1693-01, Condition B. The susceptibility of the resin to mechanical failure by cracking was measured under constant strain conditions, and in the presence of a crack accelerating agent such as soaps, wetting agents, etc.. Measurements were carried out on notched
5 specimens, in a 10 percent, by volume, Igepal CO-630 (vendor Rhone-Poulec, NJ) aqueous solution, maintained at 50 °C, and a 100 percent, by volume, Igepal CO-630 (vendor Rhone-Poulec, NJ) aqueous solution, maintained at 50 °C . The ESCR value was reported as F_{50} , the calculated 50 percent failure time from the probability graph, and F_0 , where there are no failures in the trial.

10 Short chain branching distribution and comonomer content was measured using C_{13} NMR, as discussed in Randall, *Rev. Macromol. Chem. Chys.*, C29 (2&3), pp. 285-297, and in U.S. 5,292,845, the disclosures of which are incorporated herein by reference to the extent related to such measurement. The samples were prepared by adding approximately 3g of a 50/50 mixture of tetrachloroethane- d_2 /orthodichlorobenzene that was 0.025M in chromium
15 acetylacetonate (relaxation agent) to 0.4g sample in a 10mm NMR tube. The samples were dissolved and homogenized by heating the tube and its contents to 150°C. The data was collected using a JEOL Eclipse 400 MHz NMR spectrometer, corresponding to a ^{13}C resonance frequency of 100.6 MHz. Acquisition parameters were selected to ensure quantitative ^{13}C data acquisition in the presence of the relaxation agent. The data was
20 acquired using gated 1H decoupling, 4000 transients per data file, a 4.7sec relaxation delay and 1.3 second acquisition time, a spectral width of 24,200 Hz and a file size of 64K data points, with the probe head heated to 130 °C. The spectra were referenced to the methylene peak at 30 ppm. The results were calculated according to ASTM method D5017-91.

The resin rheology was measured on the ARES I (Advanced Rheometric Expansion
25 System) Rheometer. The ARES I was a strain controlled rheometer. A rotary actuator

(servomotor) applied shear deformation in the form of strain to a sample. In response, the sample generated torque, which was measured by the transducer. Strain and torque were used to calculate dynamic mechanical properties, such as modulus and viscosity. The viscoelastic properties of the sample were measured in the melt using a 25 mm in diameter parallel plate set up, at constant strain (5 percent) and temperature (190 °C) and N₂ purge, and as a function of varying frequency (0.01 to 500 s⁻¹). The storage modulus, loss modulus, tan delta, and complex viscosity of the resin were determined using Rheometrics Orchestrator software (v. 6.5.8). The viscosity ratio (0.1 rad*s⁻¹/100 rad*s⁻¹) was determined to be the ratio of the viscosity measured at a shear rate of 0.1 rad/s to the viscosity measured at a shear rate of 100 rad/s.

Vinyl unsaturations were measured according to ASTM D-6248-98.

Low shear rheological characterization is performed on a Rheometrics SR5000 in stress controlled mode, using a 25mm parallel plates fixture. This type of geometry is preferred to cone and plate because it requires only minimal squeezing flow during sample loading, thus reducing residual stresses.

g' average was determined according to the following procedure. The chromatographic system consisted of a Waters (Millford, MA) 150 °C high temperature chromatograph equipped with a Precision Detectors (Amherst, MA) 2-angle laser light scattering detector Model 2040, an IR4 infra-red detector from Polymer Char (Valencia, Spain), and a Viscotek (Houston, TX) 150R 4-capillary viscometer. The 15-degree angle of the light scattering detector was used for calculation purposes. Data collection was performed using Viscotek TriSEC software version 3 and a 4-channel Viscotek Data Manager DM400. The system was equipped with an on-line solvent degas device from Polymer Laboratories. The carousel compartment was operated at 140 °C and the column compartment was operated at 150 °C. The columns used were 4 20-micron mixed-bed light

scattering “Mixed A-LS” columns from Polymer Laboratories. The solvent used was 1,2,4 trichlorobenzene. The samples were prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent. The chromatographic solvent and the sample preparation solvent contained 200 ppm of butylated hydroxytoluene (BHT). Both solvent sources were nitrogen sparged. Polyethylene samples were stirred gently at 160 degrees Celsius for 4 hours. The injection volume used was 200 microliters and the flow rate was 1 milliliters/minute.

Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000, and were arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards were purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards were prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards were dissolved at 80 °C with gentle agitation for 30 minutes. The narrow standards mixtures were run first and in order of decreasing highest molecular weight component to minimize degradation. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using the following equation (as described in Williams and Ward, *J. Polym. Sci., Polym. Let.*, 6, 621 (1968)).:

$$M_{\text{polyethylene}} = A \times (M_{\text{polystyrene}})^B$$

Where M is the molecular weight, A has a value of 0.43 and B is equal to 1.0.

The Systematic Approach for the determination of multi-detector offsets was done in a manner consistent with that published by Balke, Mourey, et. al. (Mourey and Balke, *Chromatography Polym.* Chpt 12, (1992)) (Balke, Thitiratsakul, Lew, Cheung, Mourey, *Chromatography Polym.* Chpt 13, (1992)), optimizing triple detector log (MW and IV) results from Dow Broad Polystyrene 1683 to the narrow standard column calibration results

from the narrow standards calibration curve using a software. The molecular weight data for off-set determination was obtained in a manner consistent with that published by Zimm (Zimm, B.H., J.Chem. Phys., 16, 1099 (1948)) and Kratochvil (Kratochvil, P., *Classical Light Scattering from Polymer Solutions*, Elsevier, Oxford, NY (1987)). The overall injected concentration used for the determination of the molecular weight was obtained from the sample refractive index area and the refractive index detector calibration from a linear polyethylene homopolymer of 115,000 molecular weight. The chromatographic concentrations were assumed low enough to eliminate addressing 2nd Virial coefficient effects (concentration effects on molecular weight).

g' average was calculated for the samples as follow:

1. The light scattering, viscosity, and concentration detectors were calibrated with NBS 1475 homopolymer polyethylene (or equivalent reference);

2. The light scattering and viscometer detector offsets relative to the concentration detector was corrected as described in the calibration section;

3. Baselines were subtracted from the light scattering, viscometer, and concentration chromatograms and set integration windows making certain to integrate all of the low molecular weight retention volume range in the light scattering chromatogram that were observable from the refractometer chromatogram;

4. A linear homopolymer polyethylene Mark-Houwink reference line was established by injecting a standard with a polydispersity of at least 3.0, and the data file (from above calibration method), was calculated and the intrinsic viscosity and molecular weight from the mass constant corrected data for each chromatographic slice was recorded;

5. The HDPE sample of interest was injected and the data file (from above calibration method), was calculated and the intrinsic viscosity and molecular weight from the mass constant corrected data for each chromatographic slice was recorded;

6. The homopolymer linear reference intrinsic viscosity was shifted by the following factor: $IV = IV + 1 / (1 + 2 * SCB / 1,000C * \text{branch point length})$ where IV is the intrinsic viscosity of the HDPE sample of interest, SCB/1,000C was determined from C13 NMR, and the branch point length is 2 for butene, 4 for hexene, or 6 for octene);

5 7. g' average was calculated according to the following equation.

$$g' = \frac{\sum_{j=\text{Where } M > 40,000}^{\text{Highest } M} \left[c_j \times \left(\frac{IV_j}{IV_{Lj}} \right)_M \right] + \sum_{j=\text{Lowest } M}^{\text{Where } M > 40,000} c_j}{\sum_{j=\text{Lowest } M}^{\text{Highest } M} c_j}$$

Where c is the concentration of the slice, IV is the intrinsic viscosity of the HDPE, and IV_L is the intrinsic viscosity of the linear homopolymer polyethylene reference (corrected for SCB of the HDPE sample of interest) at the same molecular weight (M). The IV ratio was assumed to be one at molecular weights less than 40,000 to account for natural scatter in the light scattering data.

The present invention may be embodied in other forms without departing from the spirit and the essential attributes thereof, and, accordingly, reference should be made to the appended claims, rather than to the foregoing specification, as indicating the scope of the invention.

Table I

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Co-Monomer Type	1-hexene	1-hexene	1-hexene	1-hexene	1-hexene	1-hexene
Catalyst	Ziegler-Natta	Ziegler-Natta	Ziegler-Natta	Ziegler-Natta	Ziegler-Natta	Ziegler-Natta
Co-Catalyst	2.5 % TEAL	2.5 % TEAL	2.5 % TEAL	2.5 % TEAL	2.5 % TEAL	2.5 % TEAL
1st Reactor Type	Gas Phase	Gas Phase	Gas Phase	Gas Phase	Gas Phase	Gas Phase
2nd Reactor Type	Gas Phase	Gas Phase	Gas Phase	Gas Phase	Gas Phase	Gas Phase
1st Reaction Temperature (°C)	85	85	85	85	85	85
2nd Reaction Temperature (°C)	95	110	95	95	95	95
1st Reaction Pressure (psi)	348	350	349	348	350	350
2nd Reaction Pressure (psi)	384	399	398	394	397	398
1st Reactor C₂ Partial Pressure (psi)	22.9	32.3	33.9	29.1	45.2	48.1
2nd Reactor C₂ Partial Pressure (psi)	112.1	92.1	88.8	103.0	87.4	86.2
1st Reactor H₂/C₂ Molar Ratio	0.090	0.145	0.146	0.145	0.207	0.203
2nd Reactor H₂/C₂ Molar Ratio	1.40	1.80	1.40	0.80	0.80	1.40
1st Reactor C₆/C₂ Molar Ratio	0.060	0.036	0.031	0.032	0.020	0.021
2nd Reactor C₆/C₂ Molar Ratio	0.002	0.002	0.002	0.002	0.003	0.003
1st Reactor Isopentane (Mole %)	10.586	9.714	4.893	10.185	9.728	9.454
2nd Reactor Isopentane (Mole %)	1.117	0.971	0.976	1.046	1.055	1.005

Table II

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Split (1st reactor/2nd reactor)	0.425/0.575	0.551/0.449	0.520/0.480	0.450/0.550	0.581/0.419	0.640/0.360
Cocatalyst Feed Rate (cc/hr) (1st reactor/2nd reactor)	150/167	146/170	144/169	146/169	143/172	147/169
Production Rate (lb/hr) (1st reactor/2nd reactor)	23.0/30.8	29.9/24.4	30.1/27.6	25.1/30.4	30.0/21.6	29.9/16.7
Bed Weight (lbs) (1st reactor/2nd reactor)	80.7/120.8	79.6/125.2	85/122.2	81.7/111.8	79.1/114.2	79.9/122.2
FBD (lb/ft³) (1st reactor/2nd reactor)	12.0/15.4	12.0/15.9	12.4/14.7	12.2/13.9	12.0/14.0	12.2/14.9
Bed Volume (ft³) (1st reactor/2nd reactor)	6.7/7.9	6.7/7.9	6.8/8.3	6.7/8.0	6.6/8.2	6.6/8.2
Residence Time (hr) (1st reactor/2nd reactor)	3.5/2.2	2.7/2.3	2.8/2.1	3.3/2.0	2.6/2.2	2.7/2.6
STY (lb/hr/ft³) (1st reactor/2nd reactor)	3.4/3.9	4.5/3.1	4.4/3.3	3.8/3.8	4.6/2.6	4.5/2.0
Melt index (I₂₁) (1st Component) (~) (g/10 minutes)	2.46	4.84	4.79	4.63	10.79	11.04
Density (First Component) (~) (g/cm³)	0.9288	0.9358	0.9369	0.9366	0.9433	0.9430
Residual Ti (ppm) (1st component /2nd component)	3.93/1.75	3.57/2.15	3.87/1.96	3.6/1.78	2.57/1.65	2.35/1.54
Residual Al (ppm) (1st component /2nd component)	108/66.8	86.4/61.5	88.4/60.2	100.2/72.7	82.0/68.4	77.7/67.7
Al/Ti Molar Residual Ti (ppm) (1st component /2nd component)	49.2/68.6	43.3/52.3	41.0/55.0	49.7/71.0	56.6/73.7	59.1/78.4
Bulk Density (lb/ft³) Residual Ti (ppm) (1st component /2nd component)	18.3/24.0	18.6/24.8	18.3/22.9	19.0/23.0	19.5/22.7	19.2/22.7

Table II Continued

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
H-D Polyethylene Composition Melt Index (I ₂) (2.16 g/10 minutes)	1.6	1.5	1.4	1.5	1.6	1.6
H-D Polyethylene Composition Melt Index (I ₅) (5.0 g/10 minutes)	5.9	5.3	4.8	4.8	5.0	5.1
H-D Polyethylene Composition Melt Index (I _{21.6}) (21.6 g/10 minutes)	89.1	86.4	63.0	53.2	50.9	57.7
H-D Polyethylene Composition Melt Flow Ratio (MI ₂ /MI ₅)	57	58	44	36	32	36
H-D Polyethylene Composition Melt Flow Ratio (MI ₂ /MI ₅)	15	16	13	11	10	11
H-D Polyethylene Composition (M _n)	12730	10030	11700	14670	19600	13400
H-D Polyethylene Composition (M _w)	115750	105460	106790	106710	106580	104680
H-D Polyethylene Composition (M _w /M _n)	791400	579000	482600	473000	423800	463300

Table II Continued

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Atref HD Fraction (%)	83.0	83.2	79.3	82.0	83.2	86.7
Atref Purge fraction (%)	10.5	13.3	10.6	14.2	8.3	10.5
Atref MV average	70412	77439	65518	75618	68449	70887
Atref Purge Mv	78227	81700	72441	82924	73951	70948
Viscosity at 10-2 sec-1 Shear Rate (Pa.s)	10265	9110	8764	8294	6973	7460
Viscosity at 10+2 sec-1 Shear Rate (Pa.s)	910	932	1059	1123	1184	1102
Ratio 10-2/10+2	11.3	9.8	8.3	7.4	5.9	6.8
Flexural Modulus (0.5 in/min) (psi)	227051	240071	235814	239265	233248	240173
2% Secant Modulus (psi)	151884	162889	155572	160280	153836	161766
1% Secant Modulus (psi)	184733	198177	189700	195254	187175	196579
Tensile Strength (psi)	1716	1423	2786	3340	3707	4095
Elongation at Break (%)	931.1	698.9	583.5	754.1	917.9	1139.5
Yield Strength (psi)	3500	3500	3519	3305	3694	3943
Elongation at Yield (%)	4.66	5.84	5.10	90.49	7.58	9.06
ESCR Test Data						
50 °C; 10 % Igepal; 75 mil plaque, 12 mil slit (F50 hours)	282.5	101.2	64.2	44.2	24.8	45
50 °C; 100 % Igepal; 75 mil plaque, 12 mil slit (F50 hours)	F0>2000	>1470	>740	242.4	146.9	151.2

Table III

	Comparative A
Melt Index (I₂) (2.16 g/10 minutes)	2.2
Melt Index (I₅) (5.0 g/10 minutes)	7.0
Melt Index (I_{21.6}) (21.6 g/10 minutes)	90.2
Melt Flow Ratio (MI₂₁/MI₂)	42
Melt Flow Ratio (MI₂₁/MI₅)	12.9
Density (g/cm³)	0.9533
M_n	17910
M_w	111930
M_w/M_n	6.25
Atref HD Fraction (%)	74.4
Atref Purge fraction (%)	15.8
Atref MV average	68498
Atref Purge MV	76271
Viscosity at 10-2 sec-1 Shear Rate (Pa.s)	5100
Viscosity at 10+2 sec-1 Shear Rate (Pa.s)	960
Ratio 10-2/10+2	5.3
Flexural Modulus (0.5 in/min) (psi)	203238
2% Secant Modulus (psi)	131837

Table III Continued

Comparative Example No.	Comparative A
1% Secant Modulus (psi)	159092
Tensile Strength (psi)	2765
Elongation at Break (%)	990.6
Yield Strength (psi)	3870
Elongation at Yield (%)	-
ESCR Test Data	
50 C 10 % Igepal 75 mil plaque, 12 mil slit (F50 hours)	35.2
50 C 100 % Igepal 75 mil plaque, 12 mil slit (F50 hours)	26.1

Example No.	Color	Nucleator	Shrinkage in flow direction after 48 hours (%)	Shrinkage in cross-flow direction after 48 hours (%)
Inventive 1	Natural	None	3.51	1.01
Inventive 1	Green	None	3.65	0.96
Inventive 1	Blue	None	3.68	1.05
Inventive 2	Natural	None	3.77	0.99
Inventive 2	Green	None	3.78	1.25
Inventive 2	Blue	None	3.93	0.93
Inventive 3	Natural	None	3.48	1.02
Inventive 3	Green	None	3.59	0.83
Inventive 3	Blue	None	3.65	1.05
Inventive 4	Natural	None	3.47	1.25
Inventive 4	Green	None	3.53	0.78
Inventive 4	Blue	None	3.77	1.35
Inventive 5	Natural	None	3.44	1.20
Inventive 5	Natural	HPN-20E	3.52	0.53
Inventive 5	Natural	KSt	3.59	0.91
Inventive 5	White	None	3.77	1.17
Inventive 5	Green	None	3.53	1.10
Inventive 5	Red	None	3.62	0.76
Inventive 5	White-2	None	3.69	1.18
Inventive 5	Blue	None	3.45	1.11
Inventive 5	Orange	None	3.70	0.65
Inventive 5	White	HPN-20E	3.52	0.53
Inventive 5	Green	HPN-20E	3.53	0.73
Inventive 5	Red	HPN-20E	3.59	0.59
Inventive 5	White-2	HPN-20E	3.63	0.39
Inventive 5	Blue	HPN-20E	3.50	0.56
Inventive 5	Orange	HPN-20E	3.63	0.48
Inventive 5	Green	KSt	3.53	0.97
Inventive 5	Blue	KSt	3.56	0.91
Inventive 6	Natural	None	3.48	1.10
Inventive 6	Green	None	3.54	1.08
Inventive 6	Blue	None	3.65	1.09
Comparative A	Natural	None	3.57	1.39
Comparative A	White	None	3.38	1.22
Comparative A	Blue	None	3.39	1.24
Comparative A	Orange	None	3.93	0.91

We Claim:

1. A high-density polyethylene composition comprising:
a first component, said first component being a high molecular weight ethylene alpha-olefin copolymer having a density in the range of 0.920 to 0.946 g/cm³, and a melt index (I_{21.6}) in the range of 1 to 15 g/10 minutes; and
a second component, said second component being a low molecular weight ethylene polymer having a density in the range of 0.965 to 0.980 g/cm³, and a melt index (I₂) in the range of 30 to 1500 g/10 minutes;
wherein said high-density polyethylene composition having a melt index (I₂) of at least 1 g/10 minutes, a density in the range of 0.950 to 0.960 g/cm³.
2. The high-density polyethylene composition according to Claim 1, wherein said first component having a density in the range of 0.925 to 0.945 g/cm³.
3. The high-density polyethylene composition according to Claim 1, wherein said first component having a density in the range of 0.928 to 0.944 g/cm³.
4. The high-density polyethylene composition according to Claim 1, wherein said first component having a melt index (I_{21.6}) in the range of 2 to 12 g/10 minutes.
5. The high-density polyethylene composition according to Claim 1, wherein said first component having a melt index (I_{21.6}) in the range of 2.5 to 11 g/10 minutes.

6. The high-density polyethylene composition according to Claim 1, wherein said second component having a density in the range of 0.965 to 0.975 g/cm³.
7. The high-density polyethylene composition according to Claim 1, wherein said second component having a melt index (I₂) in the range of 40 to 1300 g/10 minutes.
8. The high-density polyethylene composition according to Claim 1, wherein said second component having a melt index (I₂) in the range of 50 to 1000 g/10 minutes.
9. The high-density polyethylene composition according to Claim 1, wherein said high-density polyethylene composition having a melt index (I₂) in the range of 1 to 2 g/10 minutes.
10. The high-density polyethylene composition according to Claim 1, wherein said high-density polyethylene composition having a melt index (I₂) of at least 2 g/10 minutes.
11. The high-density polyethylene composition according to Claim 1, wherein said first component having a molecular weight in the range of 150,000 to 300,000.
12. The high-density polyethylene composition according to Claim 1, wherein said second component having a molecular weight in the range of 12,000 to 45,000.
13. The high-density polyethylene composition according to Claim 1, wherein said first component having a density in the range of 0.928 to 0.944 g/cm³, and a melt index

($I_{21.6}$) in the range of 2.5 to 11 g/10 minutes; wherein said second component having a density in the range of 0.965 to 0.975 g/cm³, and a melt index (I_2) in the range of 50 to 1000 g/10 minutes.

14. The high-density polyethylene composition according to Claim 1, wherein said first component being substantially free of any long chain branching, and said second component being substantially free of any long chain branching.

15. The high-density polyethylene composition according to Claim 14, wherein said high-density polyethylene composition being substantially free of any long chain branching.

16. The high-density polyethylene composition according to Claim 1, wherein said high-density polyethylene composition having a single ATREF temperature peak, wherein said ATREF temperature peak having a temperature peak maximum between about 90 °C to about 105 °C;

wherein said high-density polyethylene composition having a calculated purge fraction of less than 15.5 percent.

19. A method of producing a high-density polyethylene composition comprising the steps of:

introducing ethylene, and an alpha-olefin comonomer into a first reactor;

polymerizing said ethylene in the presence of said alpha-olefin comonomer in said first reactor thereby producing a first component, wherein said first component being a

high molecular weight ethylene alpha-olefin copolymer having a density in the range of 0.920 to 0.946 g/cm³, and a melt index (I₂₁) in the range of 1 to 15 g/10 minutes;

introducing said first component and additional ethylene into a second reactor;

polymerizing said additional ethylene in said second reactor thereby producing a second component, wherein said second component being a low molecular weight ethylene polymer having a density in the range of 0.965 to 0.980 g/cm³, and a melt index (I₂) in the range of 30 to 1500 g/10 minutes; and

thereby producing said high-density polyethylene composition, wherein high-density polyethylene composition having a melt index (I₂) of at least 1 g/10 minutes, a density in the range of 0.950 to 0.960 g/cm³.

20. The method of producing a high-density polyethylene composition according to Claim 19, wherein said first component having a density in the range of 0.925 to 0.945 g/cm³.

21. The method of producing a high-density polyethylene composition according to Claim 19, wherein said first component having a density in the range of 0.928 to 0.944 g/cm³.

22. The method of producing a high-density polyethylene composition according to Claim 19, wherein said first component having a melt index (I_{21.6}) in the range of 2 to 12 g/10 minutes.

23. The method of producing a high-density polyethylene composition according to Claim 19, wherein said first component having a melt index ($I_{21.6}$) in the range of 2.5 to 11 g/10 minutes.

24. The method of producing a high-density polyethylene composition according to Claim 19, wherein said second component having a density in the range of 0.965 to 0.975 g/cm³.

25. The method of producing a high-density polyethylene composition according to Claim 17, wherein said second component having a melt index (I_2) in the range of 40 to 1300 g/10 minutes.

26. The method of producing a high-density polyethylene composition according to Claim 19, wherein said second component having a melt index (I_2) in the range of 50 to 1000 g/10 minutes.

27. The method of producing a high-density polyethylene composition according to Claim 19, wherein said high-density polyethylene composition having a melt index (I_2) in the range of 1 to 2 g/10 minutes.

28. The method of producing a high-density polyethylene composition according to Claim 19, wherein said high-density polyethylene composition having a melt index (I_2) of at least 2 g/10 minutes.

29. The method of producing a high-density polyethylene composition according to Claim 19, wherein said first component having a molecular weight in the range of 150,000 to 300,000.

30. The method of producing a high-density polyethylene composition according to Claim 19, wherein said second component having a molecular weight in the range of 12,000 to 45,000.

31. The method of producing a high-density polyethylene composition according to Claim 19, wherein said first component having a density in the range of 0.928 to 0.944 g/cm³, and a melt index (I_{21.6}) in the range of 2.5 to 11 g/10 minutes; wherein said second component having a density in the range of 0.965 to 0.975 g/cm³, and a melt index (I₂) in the range of 50 to 1000 g/10 minutes.

32. The method of producing a high-density polyethylene composition according to Claim 19, wherein said first component being substantially free of any long chain branching, and said second component being substantially free of any long chain branching.

33. The method of producing a high-density polyethylene composition according to Claim 32, wherein said high-density polyethylene composition being substantially free of any long chain branching.

34. The method of producing a high-density polyethylene composition according to Claim 19, wherein said high-density polyethylene composition having a single ATREF

temperature peak, wherein said ATREF temperature peak having a temperature peak maximum between about 90 °C to about 105 °C;

wherein said high-density polyethylene composition having a calculated purge fraction of less than 15.5 percent.

37. An article comprising:

a high-density polyethylene composition comprising:

a first component, said first component being a high molecular weight ethylene alpha-olefin copolymer having a density in the range of 0.920 to 0.946 g/cm³, and a melt index (I_{21.6}) in the range of 1 to 15 g/10 minutes; and

a second component, said second component being a low molecular weight ethylene polymer having a density in the range of 0.965 to 0.980 g/cm³, and a melt index (I₂) in the range of 30 to 1500 g/10 minutes;

wherein said high-density polyethylene composition having a melt index (I₂) of at least 1 g/10 minutes, a density in the range of 0.950 to 0.960 g/cm³.

38. The article according to Claim 37, wherein said high-density composition having an environmental stress crack resistance of at least 10 hours measured via ASTM D-1693 condition B, 10% Igepal, or at least 100 hours measured via ASTM D-1693 condition B, 100 % Igepal.

39. The article according to Claim 37, wherein said article being a wire cable jacketing, a conduit pipe, or an injection blow molded bottle.

40. A bottle cap closure comprising:

a high-density polyethylene composition comprising:

a first component, said first component being a high molecular weight ethylene alpha-olefin copolymer having a density in the range of 0.920 to 0.946 g/cm³, and a melt index (I_{21.6}) in the range of 1 to 15 g/10 minutes; and

a second component, said second component being a low molecular weight ethylene polymer having a density in the range of 0.965 to 0.980 g/cm³, and a melt index (I₂) in the range of 30 to 1500 g/10 minutes;

wherein said high-density polyethylene composition having a melt index (I₂) of at least 1 g/10 minutes, a density in the range of 0.950 to 0.960 g/cm³.

41. The bottle cap closure of according to Claim 40, wherein said high-density polyethylene composition having an environmental stress crack resistance of at least 10 hours measured via ASTM D-1693 condition B, 10% Igepal, or at least 100 hours measured via ASTM D-1693 condition B, 100 % Igepal.

42. A method of improving bottle cap closures comprising the steps of:

providing a high-density polyethylene composition comprising;

a first component, said first component being a high molecular weight ethylene alpha-olefin copolymer having a density in the range of 0.920 to 0.946 g/cm³, and a melt index (I_{21.6}) in the range of 1 to 15 g/10 minutes; and

a second component, said second component being a low molecular weight ethylene polymer having a density in the range of 0.965 to 0.980 g/cm³, and a melt index (I₂) in the range of 30 to 1500 g/10 minutes;

wherein said high-density polyethylene composition having a melt index (I₂) of at least 1 g/10 minutes, a density in the range of 0.950 to 0.960 g/cm³;

compression molding, blow molding, or injection molding said high-density polyethylene composition thereby forming said improved bottle cap closures.

43. A method of producing an article comprising the steps of:

providing a high-density polyethylene composition comprising;

a first component, said first component being a high molecular weight ethylene alpha-olefin copolymer having a density in the range of 0.920 to 0.946 g/cm³, and a melt index (I_{21.6}) in the range of 1 to 15 g/10 minutes; and

a second component, said second component being a low molecular weight ethylene polymer having a density in the range of 0.965 to 0.980 g/cm³, and a melt index (I₂) in the range of 30 to 1500 g/10 minutes;

wherein said high-density polyethylene composition having a melt index (I₂) of at least 1 g/10 minutes, a density in the range of 0.950 to 0.960 g/cm³;

compression molding, blow molding, or injection molding said high-density polyethylene composition thereby forming said article.

44. The high-density polyethylene composition according to Claim 1, wherein said high-density polyethylene composition having a standard deviation of flow direction shrinkage of less than 7 percent across different colors.

45. The high-density polyethylene composition according to Claim 1, wherein said high-density polyethylene composition having a standard deviation of flow direction shrinkage of less than 6 percent across different colors.

46. The high-density polyethylene composition according to Claim 1, wherein said high-density polyethylene composition having a standard deviation of flow direction shrinkage of less than 4.5 percent across different colors.

47. The high-density polyethylene composition according to Claim 1, wherein said high-density polyethylene composition further comprising 100 to 10,000 ppm by weight of a nucleator.

48. The high-density polyethylene composition according to Claim 1, wherein said high-density polyethylene composition further comprising 100 to 10,000 ppm by weight of potassium stearate or HPN-20E as a nucleator, wherein the inventive high-density polyethylene composition having a standard deviation of flow direction shrinkage of less than 4 percent across different colors.

49. The high-density polyethylene composition according to Claim 1, wherein said high-density polyethylene composition further comprising 100 to 10,000 ppm by weight of potassium stearate or HPN-20E as a nucleator, wherein the inventive high-density polyethylene composition having a standard deviation of flow direction shrinkage of less than 3 percent across different colors.

50. The high-density polyethylene composition according to Claim 1, wherein said high-density polyethylene composition further comprising 100 to 10,000 ppm by weight of potassium stearate or HPN-20E as a nucleator, wherein the inventive high-density polyethylene composition having a standard deviation of flow direction shrinkage of less than 2 percent across different colors.

51. The high-density polyethylene composition according to Claim 1, wherein said high-density polyethylene composition having a 1% secant modulus in psi of equal or greater to the following relationship: $[(7,492,165 * \text{density (g/cm}^3\text{)}) - 6,975,000]$ psi/(g/cm³)).