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(54) Title: POLYMER COMPOSITIONS, METHODS OF MAKING THE SAME, AND ARTICLES PREPARED FROM THE SAME

(57) Abstract: The invention provides a composition comprising at least the following: A) an ethylene-based polymer having at least the following characteristics: (i) a melting temperature of greater than, or equal to, 100°C, as determined by DSC, and (ii) a molecular weight ratio, $M_z(\text{abs})/M_z(\text{conv})$ greater than 2.2; and B) an oil.



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**POLYMER COMPOSITIONS, METHODS OF MAKING THE SAME,
AND ARTICLES PREPARED FROM THE SAME**

REFERENCE TO RELATED APPLICATIONS

5 This application claims the benefit of U.S. Provisional Patent Application No. 61/348,873, filed on May 27, 2010, and fully incorporated herein by reference.

BACKGROUND OF THE INVENTION

10 Oil-extended or oil-containing thermoplastic elastomers (TPE) compositions are widely used for applications, such as automotive, consumer durables, sporting goods, health & hygiene, toys, and construction materials. Such compositions require oil to provide the desired soft feel, to improve processing, and to reduce the composition cost. However, it is often encountered that oil exudes, or bleeds out, of the fabricated articles, which may negatively affect the physical properties of the composition, such as causing surface
15 stickiness and material brittleness. The oil exudation may even render the parts unacceptable in performance. The ability of a composition to retain oil is an even greater challenge when such compositions are used to form articles for use over long periods of time and/or articles subject to temperature fluctuations.

20 Attempts have been made to develop polyolefin-based compositions involving the use of conventional elastomers and rubbers. Polymers with high modulus or high temperature resistance, such as polypropylene, HDPE, and inorganic fillers, such as calcium carbonate, were also often added to “oil containing” compositions to enhance thermal resistance or mechanical strength. It is generally believed that amorphous elastomers may exhibit higher capacity to retain oil and to reduce oil bleeding compared to semi-crystalline
25 polymers. Styrene-based thermoplastic elastomers have been added to elastomer compositions in order to increase the ability of the composition to retain oil. Similarly, elastomers with lower crystallinity have been used for the same purpose. However, the composition is often limited by the physical property (such as tensile strength) and processing requirements of the elastomer. Furthermore, at moderate oil levels, the use of
30 polyolefin elastomer compositions with low crystallinity, the use of styrenic block copolymers, or the use of EPDM hydrocarbon rubbers, may exhibit moderate improvement in, or delay, the oil exudation. With increase levels of oil, severe oil exudation (bleed-out) still occurs with these compositions over time or through temperature fluctuation cycles, which adversely affects the performance properties of the formed articles.

There is a strong demand for soft and flexible thermoplastics, especially polyolefin-based compositions that can be used to form parts with significantly reduced, or without any, oil exudation for extended periods of time.

U.S. Patent 5,505,773 discloses a thioxotropic gel compositions comprising
5 polybutene, polyethylene wax, hydrophobic fumed silica, and optionally, an antioxidant. These compositions do not contain substantial amounts of elastomers.

U.S. Patent 5,741,843 discloses sealant compositions comprising elastomeric thermoplastic polymers comprising diblock and triblock copolymers, a primary extender such as polybutene oil, a secondary extender, such as mineral oil, and/or fumed silica. The
10 composition is believed to form an interpenetrating polymer network to reduce or eliminate exudation of the extender.

Additional compositions are disclosed in the following: U.S. Patent Nos. 5,082,348; 7,101,247; 6,905,431; 5,994,450; 6,026,527; 6,835,015 and US 6,413,458, and U.S. Publication Nos. 2003/0236313 and 2004/0048018.

15 As discussed, there is a need to develop new compositions with significantly reduced oil bleed (rate), and which can be used to form articles with no, or no detectable, oil exudation. These needs and others have been met by the following invention.

SUMMARY OF THE INVENTION

20 The invention provides a composition comprising at least the following:

- A) an ethylene-based polymer having at least the following characteristics: (i) a melting temperature of greater than, or equal to, 100°C, as determined by DSC, and (ii) a molecular weight ratio, $M_z(\text{abs})/M_z(\text{conv})$ greater than 2.2; and
- B) an oil.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 represents optical images of three interfaces, each formed from an “oil-containing elastomeric polymer composition” and the inner surface of a plastic bag.

30 Figure 2 is a bar graph depicting Gloss at 60° (%) for an inventive example and several comparative examples.

Figure 3 depicts melt strength profiles for an inventive example and several comparative examples.

Figure 4 is a bar graph depicting Gloss at 60° (%) for some inventive and comparative examples.

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DETAILED DESCRIPTION OF THE INVENTION

Overview

As discussed above, the invention provides a composition comprising at least the following:

- 5 A) an ethylene-based polymer having at least the following characteristics: (i) a melting temperature of greater than, or equal to, 100°C, as determined by DSC, and (ii) a molecular weight ratio, $M_z(\text{abs})/M_z(\text{conv})$ greater than 2.2; and
- B) an oil.

10 An inventive composition may comprise a combination of two or more embodiments as described herein.

 In one embodiment, the ethylene-based polymer has a percent crystallinity greater than 28%, as determined by DSC.

 In one embodiment, the ethylene-based polymer has a number average molecular weight ($M_n(\text{conv})$) greater than 2800 g/mole.

15 In one embodiment, the ethylene-based polymer, Component A, has a MR value less than 200 g/10 min, where $MR = I_2 \times RR$.

 In one embodiment, the ethylene-based polymer, Component A, has a molecular weight ratio ($M_z(\text{abs})/M_z(\text{conv})$) greater than, or equal to, 2.5, preferably greater than, or equal to, 2.9. An $M_z(\text{abs})/M_z(\text{conv})$ ratio of 2.2 or higher indicates a highly branched

20 polymer.

 In one embodiment, the ethylene-based polymer, Component A, is a low density polyethylene (LDPE), an ethylene vinylacetate (EVA), or an ethylene acrylic acid (EAA), and preferably a low density polyethylene (LDPE).

 In one embodiment, the ethylene-based polymer, Component A, has a density from

25 0.900 to 0.940 g/cc, preferably from 0.905 to 0.935, more preferably from 0.910 to 0.930 g/cc ($1 \text{ cc} = 1 \text{ cm}^3$).

 In one embodiment, the ethylene-based polymer, Component A, has melt index (I_2) from 0.1 to 50 g/10 min, preferably from 0.2 to 30 g/10 min, more preferably from 0.3 to 25

30 g/10 min.

 In one embodiment, the ethylene-based polymer, Component A, is present in an amount from 2 to 50 weight percent, based on the weight of the composition.

 In one embodiment, the oil is present in an amount from 10 to 70 weight percent, based on the weight of the composition.

 In one embodiment, the oil is present in an amount from 35 to 90 weight percent,

35 based on the sum weight of the ethylene-based polymer and the oil.

In one embodiment, the oil is present in an amount from 35 to 70 weight percent, based on the sum weight of the ethylene-based polymer and the oil.

In one embodiment, the oil is present in an amount from 35 to 50 weight percent, based on the sum weight of the ethylene-based polymer and the oil.

5 In one embodiment, the composition further comprises an olefin-based polymer.

In one embodiment, the olefin-based polymer is present in an amount from 40 to 90 weight percent, based on the weight of the composition.

In one embodiment, the olefin-based polymer is a second ethylene-based polymer. In a further embodiment, the second ethylene-based polymer is selected from the group
10 consisting of ethylene/ α -olefin multiblock interpolymers, and preferably copolymers; homogeneously branched substantially linear ethylene/ α -olefin interpolymers, and preferably copolymers; homogeneously branched linear ethylene/ α -olefin interpolymers, and preferably copolymers; and polyethylene homopolymers.

It has been discovered that, in comparison to compositions of the prior art, the
15 compositions of this invention unexpectedly exhibit superior oil retaining ability, with significantly reduced oil bleed, or completely eliminated oil bleed, while exhibiting desirable thermal and mechanical properties suitable for the targeted applications. The inventive compositions also show improved surface-staining resistance and improved resistance to imprint. Furthermore, fabricated articles formed from the inventive
20 compositions retain desirable, low-gloss surface for extended period of time.

The compositions of this invention provide superior mechanical strength compared with compositions using oil-reducing additives of prior art. Fabricated flexible or soft articles made of compositions of this invention allows the articles to be used for applications which require higher mechanical strength, including tensile strength, tear
25 strength, as well as good mechanical integrity. The ethylene-based polymer component contributes to the overall mechanical strength of the fabricated articles, unlike other low molecular weight additives of prior arts.

Inventive Composition

30 As discussed above, an inventive composition comprises:

- A) an ethylene-based polymer having at least the following characteristics: (i) a melting temperature of greater than, or equal to, 100°C, as determined by DSC, and (ii) a molecular weight ratio, $M_z(\text{abs})/M_z(\text{conv})$ greater than 2.2;
- and B) an oil.

In one embodiment, the ethylene-based polymer has a molecular weight ratio ($M_z(\text{abs})/M_z(\text{conv})$), greater than, or equal to, 2.3, preferably greater than, or equal to, 2.5, and more preferably greater than, or equal to, 2.9, as determined by GPC.

In one embodiment, the ethylene-based polymer has a molecular weight ratio ($M_z(\text{abs})/M_z(\text{conv})$) less than, or equal to, 15, preferably less than, or equal to, 12, and more preferably less than, or equal to, 7.0, as determined by GPC.

In one embodiment, the ethylene-based polymer has a density from 0.900 to 0.940 g/cc, preferably from 0.905 to 0.935 g/cc, and more preferably from 0.910 to 0.930 g/cc (1 cc = 1 cm³).

In one embodiment, the ethylene-based polymer has a melt index (I₂) from 0.1 to 50 g/10 min, preferably from 0.2 to 30 g/10 min, and more preferably from 0.3 to 25 g/10 min.

In one embodiment, the ethylene-based polymer has a melt index (I₂) from 0.1 to 12 g/10 min, preferably from 0.2 to 10 g/10 min, and more preferably from 0.3 to 7 g/10 min.

In one embodiment, the ethylene-base polymer is formed from a high pressure, free radical process. In a further embodiment, the ethylene-based polymer is formed by high pressure autoclave or tubular process.

In one embodiment, the ethylene-based polymer is selected from a low density polyethylene (LDPE), an ethylene vinyl acetate (EVA), or an ethylene acrylic acid (EAA). In a further embodiment, the ethylene-based polymer is selected from a low density polyethylene (LDPE), or an ethylene vinylacetate (EVA). In a further embodiment, the ethylene-based polymer is a LDPE. Suitable LDPE resins are available from The Dow Chemical Company.

In one embodiment, the ethylene-based polymer has a percent crystallinity greater than, or equal to, 28 percent, preferably greater than, or equal to, 30 percent, and more preferably greater than, or equal to, 35 percent, as determined by DSC.

In one embodiment, the ethylene-based polymer has a percent crystallinity less than, or equal to, 50 percent, preferably less than, or equal to, 48 percent, and more preferably less than, or equal to, 46 percent, as determined by DSC.

In one embodiment, the ethylene-based polymer has a melting point, T_m, greater than, or equal to, 104°C, preferably greater than, or equal to, 106°C, and more preferably greater than, or equal to, 108°C, as determined by DSC.

In one embodiment, the ethylene-based polymer has a melting point, T_m, less than, or equal to, 128°C, preferably less than, or equal to, 125°C, and more preferably less than, or equal to, 122°C, as determined by DSC.

In one embodiment, the ethylene-based polymer has a molecular weight distribution ($M_w(\text{conv})/M_n(\text{conv})$), greater than, or equal to, 3, preferably greater than, or equal to, 5, and more preferably greater than, or equal to, 7, and even more preferably greater than, or equal to, 9, as determined by GPC.

5 In one embodiment, the ethylene-based polymer has a molecular weight distribution ($M_w(\text{conv})/M_n(\text{conv})$), less than, or equal to, 50, preferably less than, or equal to, 45, more preferably less than, or equal to, 30, and even more preferably less than, or equal to, 20, as determined by GPC.

10 In one embodiment, the ethylene-based polymer has a molecular weight ($M_n(\text{conv})$), greater than, or equal to, 2800 g/mole preferably greater than, or equal to, 4000, and more preferably greater than, or equal to, 8,000, as determined by GPC.

In one embodiment, the ethylene-based polymer has a molecular weight ($M_n(\text{conv})$), less than, or equal to, 30,000 g/mole preferably less than, or equal to, 25,000, and more preferably less than, or equal to, 22,000, as determined by GPC.

15 In one embodiment, the ethylene-based polymer has a "MR" less than, or equal to, 200 g/10 min, preferably less than, or equal to, 150 g/10 min, and more preferably less than, or equal to, 125 g/10 min, and even more preferably less than, or equal to, 100 g/10 min. Here M is the melt index (I2, 2.16 kg, 190°C) in g/10 min, and R is the rheology ratio (RR) or $V_{0.1}/V_{100}$, where $V_{0.1}$ is the melt viscosity of polymer at 190°C, measured at a shear rate of 0.1 rad/sec, and V_{100} is the melt viscosity of polymer at 190°C, measured at a shear rate of 100 rad/sec. Melt viscosities are measured under a nitrogen atmosphere, using a dynamic mechanical spectrometer (such as a RMS-800 or ARES from Rheometrics), under a dynamic sweep made from 0.1 to 100 rad/sec.

25 In one embodiment, the ethylene-based polymer has a "MR" greater than, or equal to, 10, preferably greater than, or equal to, 12, and more preferably greater than, or equal to, 14.

30 In one embodiment, the ethylene-based polymer has $M_w(\text{conv})$ greater than 20,000 g/mol, preferably greater than 40,000 g/mol, more preferably greater than 60,000 g/mol; a rheology ratio (RR) greater than 15, preferably greater than 30; and a percent crystallinity of greater 30, preferably greater than 32, and more preferably greater than 35, as determined by DSC.

In one embodiment, the ethylene-based polymer is present in an amount from 2 to 50 weight percent, preferably from 5 to 45 weight percent, and more preferably from 7 to 40 weight percent, based on the weight of the composition.

35 An ethylene-based polymer may comprise a combination of two or more

embodiments as described herein.

Examples of oils include, but are not limited to, mineral oils or processing oils (may include paraffinic, naphthenic, aromatic or mixed types), or other processing or softening additives such as plasticizers and polybutene. Oils include, but are not limited to, petroleum
5 oils, such as aromatic and naphthenic oils; polyalkylbenzene oils; synthetic oils, mineral oils, organic acid monoesters, such as alkyl and alkoxyalkyl oleates and stearates; organic acid diesters, such as dialkyl, dialkoxyalkyl, and alkyl aryl phthalates, terephthalates, sebacates, adipates, and glutarates; glycol diesters, such as tri-, tetra-, and polyethylene glycol dialkanoates; trialkyl trimellitates; trialkyl, trialkoxyalkyl, alkyl diaryl, and triaryl
10 phosphates; chlorinated paraffin oils; coumarone-indene resins; pine tars; vegetable oils, such as castor, tall, rapeseed, and soybean oils and esters and epoxidized derivatives thereof; and the like.

In one embodiment, the oil is selected from petroleum oils, synthetic oils, chlorinated paraffin oils, paraffinic mineral oil, white mineral oil or vegetable oils, and
15 preferably selected from paraffinic mineral oil, or white mineral oil.

In one embodiment, the oil is present in an amount from 10 to 70 weight percent, preferably from 15 to 65 weight percent, and more preferably from 20 to 60 weight percent, based on the weight of the composition.

In one embodiment, the oil is present in an amount from 15 to 50 weight percent, preferably from 15 to 65 weight percent, and more preferably from 20 to 45 weight percent, based on the weight of the composition.

In one embodiment, the oil is present in an amount from 35 to 90 weight percent, preferably from 40 to 90 weight percent, and more preferably from 45 to 90 weight percent, based on the sum weight of the ethylene-based polymer and the oil.

25 In one embodiment, the oil is present in an amount from 45 to 90 weight percent, preferably from 50 to 85 weight percent, and more preferably from 55 to 80 weight percent, based on the sum weight of the ethylene-based polymer and the oil.

In one embodiment, the composition further comprises an olefin-based polymer as described below.

30 In one embodiment, the inventive composition further comprises a styrenic block copolymer.

In one embodiment, the inventive composition further comprises a halogenated ethylene/ α -olefin (C3-C8 or higher) copolymer.

In one embodiment, the inventive composition further comprises one or more
35 additives. Suitable additives include, but are not limited to, antioxidants, UV stabilizers,

vulcanizing agents, foaming agents, flame retardants, plasticizers, pigments, curing agents and combinations thereof, and preferably antioxidants, UV stabilizers, flame retardants, pigments and combinations thereof, and more preferably antioxidants, UV stabilizers and combinations thereof.

5 In one embodiment, the composition further comprises one or more inorganic filler(s). In a further embodiment, the filler is selected from calcium carbonate, fumed silica, alumina, TiO₂, kaolin, or combinations thereof.

 In one embodiment, the composition comprises from 0.1 to 50 weight percent of an inorganic filler, based on the weight of the composition.

10 In one embodiment, the inventive composition further comprises one or more antioxidants and/or stabilizers.

 In one embodiment, the composition comprises a second ethylene-based polymer as described herein, and a propylene-based polymer, as described herein. In a further embodiment, the composition further comprises a polyethylene homopolymer as described
15 herein.

 In one embodiment, the composition comprises two second ethylene-based polymers, each independently described herein. In a further embodiment, the composition further comprises a polyethylene homopolymer as described herein.

 In one embodiment, the composition comprises a second ethylene-based polymer as
20 described herein, and a polyethylene homopolymer as described herein.

 In one embodiment, the composition is prepared using batch compounding processes such as Banbury mixers; continuous melt mixing/compounding processes, such as single screw extruders, twin screw extruders; roll mills; HAAKE-type mixers, and other processes known in the art.

25 An inventive composition may comprise a combination of two or more embodiments as described herein.

Olefin-based Polymers

 In one embodiment, the inventive composition further comprises an olefin-based
30 polymer, as discussed above. Olefin-based polymers include, for example, ethylene-based polymers and propylene-based polymers.

 In one embodiment, the composition comprises 10 to 80 weight percent, preferably from 15 to 60 weight percent, and more preferably from 20 to 50 weight percent of an olefin-based polymer, based on the weight of the composition.

In one embodiment, the olefin-based polymer is selected from polypropylene homopolymer, propylene/ α -olefin copolymer, propylene/ethylene copolymer, or high density polyethylene (HDPE).

In one embodiment, the olefin-based polymer has a melt index (I2, 2.16 kg, 190°C) or a melt flow rate (MFR, 2.16 kg, 230°C) less than 25 g/10 min, preferably less than 10 g/10 min, more preferably less than 5 g/10min, most preferably less than 2 dg/min or lower.

In one embodiment, the olefin-based polymer has a melt index (I2, 2.16 kg, 190°C) or a melt flow rate (MFR, 2.16 kg, 230°C) greater than, or equal to, 0.05 g/10 min, preferably greater than, or equal to, 0.1 g/10 min, more preferably greater than, or equal to, 0.5 g/10 min.

In one embodiment, the olefin-based polymer has a RR less than 12, preferably less than 10; and a percent crystallinity greater than 40 percent, as determined by DSC. In a further embodiment, the olefin-based polymer is selected from polypropylene homopolymer, propylene/ α -olefin copolymer, propylene/ethylene copolymer, or polyethylene homopolymer.

In one embodiment, the olefin-based polymer has a melt index (I2, 2.16 kg, 190°C) less than, or equal to, 0.9 dg/min, preferably less than, or equal to, 0.8 dg/min; and has a MWD (measured by GPC) of less than, or equal to, 3.5, preferably less than, or equal to, 3.0.

An olefin-based polymer may comprise a combination of two or more embodiments as described herein.

In one embodiment, the olefin-based polymer is a propylene-based polymer.

In one embodiment, the propylene-based polymer has a density from 0.840 to 0.920 g/cc, preferably from 0.845 to 0.910 g/cc (1 cc = 1 cm³).

In one embodiment, the propylene-based polymer has a melt flow rate (MFR) from 0.05 to 20 g/10 min, preferably from 0.1 to 10 g/10 min, more preferably from 0.2 to 5 g/10 min.

In one embodiment, the propylene-based polymer is present in an amount from 1 to 30 weight percent, preferably from 2 to 25 weight percent, and more preferably from 5 to 20 weight percent, based on the weight of the composition.

In one embodiment, the propylene-based polymer, is present in an amount from 40 to 60 weight percent, preferably from 45 to 55 weight percent, and more preferably from 48 to 52 weight percent, based on the sum weight of the ethylene-based polymer and the propylene-based polymer.

An propylene-based polymer may comprise a combination of two or more embodiments as described herein.

In one embodiment, the olefin-base polymer is a second ethylene-based polymer.

In one embodiment, the second ethylene-based polymer has a density from 0.850 to 0.960 g/cc, preferably from 0.855 to 0.955 g/cc, more preferably from 0.860 to 0.950 g/cc (1 cc = 1 cm³).

In one embodiment, the second ethylene-based polymer has a melt index (I2) from 0.05 to 20 g/10 min, preferably from 0.1 to 10 g/10 min, more preferably from 0.2 to 5 g/10 min.

In one embodiment, the second ethylene-based polymer has molecular weight distribution (Mw(conv)/Mn(conv)) from 1.1 to 5, preferably from 1.1 to 4, more preferably from 1.1 to 3, as determined by GPC.

In one embodiment, the second ethylene-based polymer is a polyethylene homopolymer, for example HDPE.

In one embodiment, the polyethylene homopolymer has a density from 0.940 to 0.970 g/cc, preferably from 0.945 to 0.960 g/cc.

In one embodiment, the polyethylene homopolymer has a melt index (I2) from 0.01 to 70 g/10 min, preferably from 0.02 to 35 g/10 min, more preferably from 0.04 to 20 g/10 min, and even more preferably from 0.05 to 10 g/10 min.

In one embodiment, the polyethylene homopolymer has a melt index (I2) from 0.01 to 10 g/10 min, preferably from 0.02 to 5 g/10 min, more preferably from 0.04 to 2 g/10 min, and even more preferably from 0.05 to 1 g/10 min.

In one embodiment, the polyethylene homopolymer, is present in an amount from 5 to 40 weight percent, preferably from 6 to 35 weight percent, and more preferably from 7 to 30 weight percent, based on the weight of the composition.

In one embodiment, the polyethylene homopolymer is present in an amount from 50 to 85 weight percent, preferably from 55 to 80 weight percent, and more preferably from 60 to 75 weight percent, based on the sum weight of the ethylene-based polymer and the polyethylene homopolymer.

In one embodiment, the second ethylene-based polymer is selected from an ethylene/ α -olefin interpolymers, and preferably an ethylene/ α -olefin copolymer; an ethylene/ α -olefin/diene interpolymers, and preferably an ethylene/ α -olefin/diene terpolymer; or an ethylene/ α -olefin multiblock interpolymers, and preferably an ethylene/ α -olefin multiblock copolymer.

Typically and preferably, the ethylene is copolymerized with one C3-C20 α -olefin, and preferably one C3-C10 α -olefin. Preferred comonomers include propene, 1-butene, 1-pentene, 1-hexene, 1-heptene and 1-octene, and more preferably include propene, 1-butene, 1-hexene and 1-octene.

5 In one embodiment, the second ethylene-based polymer is present in an amount from 10 to 55 weight percent, preferably from 15 to 50 weight percent, and more preferably from 18 to 47 weight percent, based on the weight of the composition.

In one embodiment, the second ethylene-based polymer, is present in an amount from 40 to 90 weight percent, preferably from 45 to 85 weight percent, and more preferably
10 from 50 to 80 weight percent, based on the sum weight of the ethylene-based polymer and the second ethylene-based polymer.

Commercial examples of second ethylene-base interpolymers include ENGAGE Polyolefin Elastomers, ATTANE Polyethylene Resins, AFFINITY Polyolefin Plastomers, DOWLEX Polyethylene Resins, ELITE Polyethylene Resins, and INFUSE Olefin Block
15 Copolymers, each available from The Dow Chemical Company; EXCEED and EXACT polymers available from ExxonMobil Chemical Company; and TAFMER polymers available from the Mitsui Chemical Company.

A second ethylene-based polymer may comprise a combination of two or more embodiments as described herein.

20 In one embodiment, the second ethylene-based polymer is an ethylene/ α -olefin interpolymer, and preferably an ethylene/ α -olefin copolymer.

Illustrative α -olefins include propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene and 1-decene. The α -olefin is desirably a C3-C10 α -olefin. Preferably, the α -olefin is propylene, 1-butene, 1-hexene or 1-octene. Illustrative
25 copolymers include ethylene/propylene (EP) copolymers, ethylene/butene (EB) copolymers, ethylene/hexene (EH) copolymers, ethylene/octene (EO) copolymers. Preferred copolymers include EP, EB, EH and EO polymers.

In one embodiment, the ethylene/ α -olefin interpolymer has a melting point (T_m) greater than, or equal to, 25°C, preferably greater than, or equal to, 30°C, more preferably
30 greater than, or equal to, 34°C. In a further embodiment, the ethylene/ α -olefin interpolymer is an ethylene/ α -olefin copolymer.

In one embodiment, the ethylene/ α -olefin interpolymer has a melting point (T_m) less than, or equal to, 95°C, preferably less than, or equal to, 90°C, more preferably less than, or
35 equal to, 85°C. In a further embodiment, the ethylene/ α -olefin interpolymer is an ethylene/ α -olefin copolymer.

In one embodiment, the ethylene/ α -olefin interpolymer has a melting point (T_m) less than, or equal to, 70°C, preferably less than, or equal to, 65°C, more preferably less than, or equal to, 62°C. In a further embodiment, the ethylene/ α -olefin interpolymer is an ethylene/ α -olefin copolymer.

5 In one embodiment, the ethylene/ α -olefin interpolymer has a density from 0.850 to 0.890 g/cc, preferably from 0.855 to 0.880 g/cc. In a further embodiment, the ethylene/ α -olefin interpolymer is an ethylene/ α -olefin copolymer.

In one embodiment, the ethylene/ α -olefin interpolymer has a melt index (I2) from 0.02 g/10 min to 30 g/10 min, preferably from 0.05 g/10 min to 15 g/10 min, more
10 preferably from 0.1 g/10 min to 10 g/10 min. In a further embodiment, the ethylene/ α -olefin interpolymer is an ethylene/ α -olefin copolymer.

In one embodiment, the ethylene/ α -olefin interpolymer has a melt index (I2) from 0.02 g/10 min to 10 g/10 min, preferably from 0.05 g/10 min to 5 g/10 min, more preferably
15 from 0.1 g/10 min to 2 g/10 min. In a further embodiment, the ethylene/ α -olefin interpolymer is an ethylene/ α -olefin copolymer.

In one embodiment, the ethylene/ α -olefin interpolymer has molecular weight distribution ($M_w(\text{conv})/M_n(\text{conv})$) from 1.1 to 4, preferably from 1.1 to 3.5, more preferably from 1.1 to 3, as determined by GPC. In a further embodiment, the ethylene/ α -olefin interpolymer is an ethylene/ α -olefin copolymer.

20 In one embodiment, the ethylene/ α -olefin interpolymer is a homogeneously branched linear interpolymer, and preferably a copolymer; or a homogeneous branched substantially linear interpolymer, and preferably a copolymer.

In one embodiment, the ethylene/ α -olefin interpolymer is a homogeneously branched linear interpolymer, and preferably a copolymer.

25 In one embodiment, the ethylene/ α -olefin interpolymer is homogeneous branched substantially linear interpolymer, and preferably a copolymer.

The terms "homogeneous" and "homogeneously-branched" are used in reference to an ethylene/ α -olefin interpolymer, in which the α -olefin comonomer is randomly distributed within a given polymer molecule, and all of the polymer molecules have the same or
30 substantially the same comonomer-to-ethylene ratio.

The homogeneously branched linear ethylene interpolymers are ethylene polymers, which lack long chain branching, but do have short chain branches, derived from the comonomer polymerized into the interpolymer, and which are homogeneously distributed, both within the same polymer chain, and between different polymer chains. These
35 ethylene/ α -olefin interpolymers have a linear polymer backbone, no measurable long chain

branching, and a narrow molecular weight distribution. This class of polymers is disclosed for example, by Elston in US Patent No. 3,645,992, and subsequent processes to produce such polymers, using bis-metallocene catalysts, have been developed, as shown, for example, in EP 0 129 368; EP 0 260 999; US Patent No. 4,701,432; US Patent No. 5 4,937,301; US Patent No. 4,935,397; US Patent No. 5,055,438; and WO 90/07526; each incorporated herein by reference. Commercial examples of homogeneously branched linear ethylene/ α -olefin interpolymers include TAFMER polymers supplied by the Mitsui Chemical Company, and EXACT and EXCEED polymers supplied by ExxonMobil Chemical Company.

10 The homogeneously branched substantially linear ethylene/ α -olefin interpolymers are described in US Patent Nos. 5,272,236; 5,278,272; 6,054,544; 6,335,410 and 6,723,810; each incorporated herein by reference. The substantially linear ethylene/ α -olefin interpolymers have long chain branching. The long chain branches have the same comonomer distribution as the polymer backbone, and can have about the same length as 15 the length of the polymer backbone. "Substantially linear," typically, is in reference to a polymer that is substituted, on average, with "0.01 long chain branches per 1000 carbons" to "3 long chain branches per 1000 carbons." The length of a long chain branch is longer than the carbon length of a short chain branch, formed from the incorporation of one comonomer into the polymer backbone.

20 The homogeneously branched substantially linear ethylene/ α -olefin interpolymers form a unique class of homogeneously branched ethylene polymers. They differ substantially from the well-known class of conventional, homogeneously branched linear ethylene/ α -olefin interpolymers, as discussed above, and, moreover, they are not in the same class as conventional heterogeneous "Ziegler-Natta catalyst polymerized" linear ethylene 25 polymers (for example, ultra low density polyethylene (ULDPE), linear low density polyethylene (LLDPE) or high density polyethylene (HDPE) made, for example, using the technique disclosed by Anderson et al., in U.S. Patent 4,076,698); nor are they in the same class as high pressure, free-radical initiated, highly branched polyethylenes, such as, for example, low density polyethylene (LDPE), ethylene-acrylic acid (EAA) copolymers and 30 ethylene vinyl acetate (EVA) copolymers.

 The homogeneously branched, substantially linear ethylene/ α -olefin interpolymers have excellent processability, even though they have a relatively narrow molecular weight distribution. Surprisingly, the melt flow ratio (I_{10}/I_2), according to ASTM D 1238, of the substantially linear ethylene interpolymers can be varied widely, and essentially 35 independently of the molecular weight distribution (M_w/M_n or MWD). This surprising

behavior is contrary to conventional homogeneously branched linear ethylene interpolymers, such as those described, for example, by Elston in U.S. 3,645,992, and heterogeneously branched conventional "Ziegler-Natta polymerized" linear polyethylene interpolymers, such as those described, for example, by Anderson et al., in U.S. 4,076,698.

5 Unlike substantially linear ethylene interpolymers, linear ethylene interpolymers (whether homogeneously or heterogeneously branched) have rheological properties, such that, as the molecular weight distribution increases, the I_{10}/I_2 value also increases.

Long chain branching can be determined by using ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy, and can be quantified using the method of Randall (Rev. Macromol. Chem. Phys., C29 (2 &3), 1989, p. 285-297), the disclosure of which is incorporated herein

10 by reference. Two other methods are Gel Permeation Chromatography, couple with a Low Angle Laser Light Scattering detector (GPC/LALLS), and Gel Permeation Chromatography, coupled with a Differential Viscometer detector (GPC-DV). The use of these techniques for long chain branch detection, and the underlying theories, have been well documented in the

15 literature. See, for example, Zimm, B.H. and Stockmayer, W.H., J. Chem. Phys., 17,1301(1949) and Rudin, A., Modern Methods of Polymer Characterization, John Wiley & Sons, New York (1991) pp. 103-112.

In contrast to "substantially linear ethylene polymer," "linear ethylene polymer" means that the polymer lacks measurable or demonstrable long chain branches, that is, the

20 polymer is substituted with an average of less than 0.01 long chain branches per 1000 carbons.

The homogeneous branched ethylene polymers will preferably have a single melting peak, as measured using Differential Scanning Calorimetry (DSC), in contrast to heterogeneously branched linear ethylene polymers, which have two or more melting peaks,

25 due to the heterogeneously branched polymer's broad branching distribution.

In one embodiment, the ethylene/ α -olefin interpolymer has a PRR (Processing Rheology Ratio) greater than, or equal to 4, preferably greater than, or equal to, 8, more preferably greater than, or equal to, 12, even more preferably greater than, or equal to, 15. In a further embodiment, the ethylene/ α -olefin interpolymer is an ethylene/ α -olefin

30 copolymer.

In one embodiment, the ethylene/ α -olefin interpolymer has a PRR from 4 to 70, or from 8 to 70. In a further embodiment, the ethylene/ α -olefin interpolymer is an ethylene/ α -olefin copolymer.

In one embodiment, the ethylene/ α -olefin interpolmer has a PRR from 12 to 60, preferably from 15 to 55, and more preferably from 18 to 50. In a further embodiment, the ethylene/ α -olefin interpolmer is an ethylene/ α -olefin copolymer.

Interpolymer viscosity is conveniently measured in poise (dyne-second/square centimeter (d-sec/cm²)) at shear rates within a range of 0.1-100 radian per second (rad/sec), at 190°C, under a nitrogen atmosphere, using a dynamic mechanical spectrometer (such as a RMS-800 or ARES from Rheometrics), under a dynamic sweep made from 0.1 to 100 rad/sec. The viscosities at 0.1 rad/sec and 100 rad/sec may be represented, respectively, as “V0.1” and “V100,” with a ratio of the two referred to as “RR,” and expressed as “V0.1/V100.”

The PRR value is calculated by the formula:

$$\text{PRR} = \text{RR} + [3.82 - \text{interpolymer Mooney Viscosity (ML1+4 at 125°C)}] \times 0.3.$$
 The PRR determination is described in U.S. Patent 6,680,361 (see also equivalent WO 00/26268), fully incorporated herein by reference.

In one embodiment, the ethylene/ α -olefin interpolmer, and preferably copolymer, is present in an amount from 15 to 40 weight percent, preferably from 20 to 35 weight percent, and more preferably from 25 to 30 weight percent, based on the weight of the composition.

In one embodiment, the ethylene/ α -olefin interpolmer, is present in an amount from 40 to 90 weight percent, preferably from 50 to 85 weight percent, and more preferably from 60 to 80 weight percent, based on the sum weight of the ethylene-based polymer and the ethylene/ α -olefin interpolmer.

An ethylene/ α -olefin interpolmer may comprise a combination of two or more embodiments as described herein.

An ethylene/ α -olefin copolymer may comprise a combination of two or more embodiments as described herein.

In one embodiment, the second ethylene-based polymer is an ethylene/ α -olefin/diene interpolmer, and preferably an ethylene/ α -olefin/diene terpolymer.

The ethylene/ α -olefin/diene interpolymers have polymerized therein C₂ (ethylene), at least one α -olefin and a diene. Suitable examples of α -olefins include the C₃-C₂₀ α -olefins. Suitable examples of suitable dienes include the C₄-C₄₀ nonconjugated dienes.

Illustrative nonconjugated dienes are straight chain acyclic dienes, such as 1,4-hexadiene and 1,5-heptadiene; branched chain acyclic dienes, such as 5-methyl-1,4-hexadiene, 2-methyl-1,5-hexadiene, 6-methyl-1,5-heptadiene, 7-methyl-1,6-octadiene, 3,7-dimethyl-1,6-octadiene, 3,7-dimethyl-1,7-octadiene, 5,7-dimethyl-1,7-octadiene, 1,9-

decadiene, and mixed isomers of dihydromyrcene; single ring alicyclic dienes such as 1,4-cyclohexadiene, 1,5-cyclooctadiene and 1,5-cyclododecadiene; multi-ring alicyclic fused and bridged ring dienes, such as tetrahydroindene, methyl tetrahydroindene; alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes such as 5-methylene-2-norbornene (MNB), 5-ethylidene-2-norbornene (ENB), 5-vinyl-2-norbornene, 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, and 5-cyclohexylidene-2-norbornene. The diene is preferably a nonconjugated diene selected from the group consisting of ENB, dicyclopentadiene, 1,4-hexadiene, 7-methyl-1,6-octadiene, and preferably, ENB, dicyclopentadiene and 1,4-hexadiene, more preferably ENB and dicyclopentadiene, and even more preferably ENB.

The α -olefin is preferably a C3-C20 aliphatic compound, preferably a C3-C16 aliphatic compound, and more preferably a C3-C10 aliphatic compound. Preferred C3-C10 aliphatic α -olefins are selected from the group consisting of propylene, 1-butene, 1-hexene and 1-octene, and more preferably propylene. In a preferred embodiment, the interpolymer is an EPDM interpolymer. In a further embodiment, the diene is 5-ethylidene-2-norbornene (ENB).

Some examples of ethylene/ α -olefin/diene interpolymers include the NORDEL IP Hydrocarbon Rubbers from The Dow Chemical Company.

In a preferred embodiment, the ethylene/ α -olefin/diene interpolymer comprises a majority amount of polymerized ethylene, based on the weight of the interpolymer.

In one embodiment of the invention, the ethylene/ α -olefin/diene interpolymer has a molecular weight distribution ($M_w(\text{conv})/M_n(\text{conv})$) from 2.0 to 3.0, preferably from 2.0 to 2.8 and more preferably from 2.0 to 2.5. In a further embodiment, the interpolymer is an ethylene/propylene/diene interpolymer, and further an EPDM terpolymer. In a further embodiment, the diene is ENB.

In one embodiment, the ethylene/ α -olefin interpolymer has a density from 0.850 to 0.880 g/cc, preferably from 0.855 to 0.875 g/cc. In a further embodiment, the interpolymer is an ethylene/propylene/diene interpolymer, and further an EPDM terpolymer. In a further embodiment, the diene is ENB.

In one embodiment, the ethylene/ α -olefin interpolymer has a melt index (I2) from 0.01 g/10 min to 1 g/10 min, preferably from 0.02 g/10 min to 0.5 g/10 min. In a further embodiment, the interpolymer is an ethylene/propylene/diene interpolymer, and further an EPDM terpolymer. In a further embodiment, the diene is ENB.

In one embodiment, the ethylene/ α -olefin/diene interpolymers has a Mooney viscosity, ML(1+4) at 125°C, from 20 to 200, preferably from 40 to 150. In a further embodiment, the interpolymers is an ethylene/propylene/diene interpolymers, and further an EPDM terpolymers. In a further embodiment, the diene is ENB.

5 Mooney viscosity is that of the neat interpolymers (or-calculated viscosity of neat polymer for polymers that contain a filler, such as carbon black, and/or an oil). The neat polymer refers to the polymer without filler and without oil.

An ethylene/ α -olefin/diene interpolymers may comprise a combination of two or more embodiments as described herein.

10 In one embodiment, the second ethylene-based polymer is an ethylene/ α -olefin multi-block interpolymers, and preferably an ethylene/ α -olefin multi-block copolymers.

Ethylene/ α -olefin multi-block interpolymers, and preferably copolymers, may be made with two catalysts, incorporating differing quantities of comonomers, and a chain shuttling agent. Preferred α -olefins include propylene, 1-butene, 1-pentene, 1-hexene, 4-
15 methyl-1-pentene, 1-heptene, 1-octene, 1-nonene and 1-decene. The α -olefin is desirably a C3-C10 α -olefin. Preferably, the α -olefin is propylene, 1-butene, 1-hexene or 1-octene.

An ethylene/ α -olefin multi-block copolymers has one or more of the following characteristics:

(1) an average block index greater than zero and up to about 1.0 and a molecular weight distribution, Mw/Mn, greater than about 1.3; or

(2) at least one molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a block index of at least 0.5 and up to about 1; or

(3) an Mw/Mn from about 1.7 to about 3.5, at least one melting point, Tm, in
25 degrees Celsius, and a density, d, in grams/cubic centimeter, wherein the numerical values of Tm and d correspond to the relationship:

$$T_m > -6553.3 + 13735(d) - 7051.7(d)^2; \text{ or}$$

(4) an Mw/Mn from about 1.7 to about 3.5, and is characterized by a heat of fusion, ΔH in J/g, and a delta quantity, ΔT , in degrees Celsius defined as the temperature
30 difference between the tallest DSC peak and the tallest CRYSTAF peak, wherein the numerical values of ΔT and ΔH have the following relationships:

$$\Delta T > -0.1299(\Delta H) + 62.81 \text{ for } \Delta H \text{ greater than zero and up to } 130 \text{ J/g,}$$

$$\Delta T \geq 48^\circ\text{C for } \Delta H \text{ greater than } 130 \text{ J/g,}$$

wherein the CRYSTAF peak is determined using at least 5 percent of the cumulative polymer, and if less than 5 percent of the polymer has an identifiable CRYSTAF peak, then the CRYSTAF temperature is 30°C; or

5 (5) an elastic recovery, Re , in percent at 300 percent strain and 1 cycle measured with a compression-molded coated substrate of the ethylene/ α -olefin interpolymer, and has a density, d , in grams/cubic centimeter, wherein the numerical values of Re and d satisfy the following relationship when ethylene/ α -olefin interpolymer is substantially free of a cross-linked phase: $Re > 1481 - 1629(d)$; or

10 (6) a molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a molar comonomer content of at least 5 percent higher than that of a comparable random ethylene interpolymer fraction eluting between the same temperatures, wherein said comparable random ethylene interpolymer has the same comonomer(s) and has a melt index, density, and molar comonomer content (based on the whole polymer) within 10 percent of that of the ethylene/ α -olefin
15 interpolymer; or

(7) a storage modulus at 25°C, $G'(25^\circ\text{C})$, and a storage modulus at 100°C, $G'(100^\circ\text{C})$, wherein the ratio of $G'(25^\circ\text{C})$ to $G'(100^\circ\text{C})$ is in the range of about 1:1 to about 9:1.

The term “multi-block copolymer” or “segmented copolymer” refers to a polymer
20 comprising two or more chemically distinct regions or segments (referred to as “blocks”) preferably joined in a linear manner, that is, a polymer comprising chemically differentiated units, which are joined end-to-end with respect to polymerized ethylenic functionality, rather than in pendent or grafted fashion. In a preferred embodiment, the blocks differ in the amount or type of comonomer incorporated therein, the density, the amount of
25 crystallinity, the crystallite size attributable to a polymer of such composition, the type or degree of tacticity (isotactic or syndiotactic), regio-regularity or regio-irregularity, the amount of branching, including long chain branching or hyper-branching, the homogeneity, or any other chemical or physical property. The multi-block copolymers are characterized by unique distributions of both polydispersity index (PDI or M_w/M_n), block length
30 distribution, and/or block number distribution due to the unique process making of the copolymers. More specifically, when produced in a continuous process, the polymers desirably possess PDI from 1.7 to 2.9, preferably from 1.8 to 2.5, more preferably from 1.8 to 2.2, and most preferably from 1.8 to 2.1. When produced in a batch or semi-batch process, the polymers possess PDI from 1.0 to 2.9, preferably from 1.3 to 2.5, more
35 preferably from 1.4 to 2.0, and most preferably from 1.4 to 1.8.

In one embodiment, the ethylene/ α -olefin multi-block copolymer has a density of from 0.850 g/cc to 0.900 g/cc, preferably from 0.855 to 0.890 g/cc, more preferably from 0.860 to 0.885 g/cc. Density is measured by the procedure of ASTM D-792-08.

In one embodiment, the ethylene/ α -olefin multi-block copolymer has a melting point
5 of greater than 90°C, preferably greater than 100°C, more preferably greater than 110°C. The melting point is measured by Differential Scanning Calorimetry (DSC) method described in U.S. Patent 7608668 (WO 2005/090427), incorporated herein by reference.

In another embodiment, the ethylene/ α -olefin multi-block copolymer has a melt
10 index (I2) from 0.05 g/10 min to 10 g/10 min, preferably from 0.1 g/10 min to 5 g/10 min, and more preferably from 0.2 g/10 min to 2 g/10 min, as determined using ASTM D-1238-04 (190°C, 2.16 kg load).

In one embodiment, the ethylene/ α -olefin multiblock interpolymer, and preferably
15 copolymer, is present in an amount from 10 to 55 weight percent, preferably from 15 to 50 weight percent, and more preferably from 20 to 45 weight percent, based on the weight of the composition.

In one embodiment, the ethylene/ α -olefin multiblock interpolymer, and preferably
copolymer, is present in an amount from 40 to 90 weight percent, preferably from 45 to 85
weight percent, and more preferably from 50 to 80 weight percent, based on the sum weight
of the ethylene-based polymer and the ethylene/ α -olefin multiblock interpolymer.

20 The ethylene multi-block copolymers and their preparation and use, are more fully described in WO 2005/090427, US2006/0199931, US7608668, US2006/0199914, US2006/0199912, US7671106, US7579408, US2006/0199908, US7355089, US7622529, US7671131, US7524911, US7662881, US2006/0199887, US7514517, US7666918, US7687442, US7582716, US7504347 and US2006/0199983; each is incorporated herein by
25 reference.

An ethylene/ α -olefin multi-block interpolymer may comprise a combination of two or more embodiments as described herein.

An ethylene/ α -olefin multi-block copolymer may comprise a combination of two or more embodiments as described herein.

30

Articles

The invention also provides an article comprising at least one component formed from an inventive composition. The inventive composition can be used for articles that require flexibility, wear resistance, and desirable appearance. Articles include, but not

limited to, appliance gaskets and other consumer durables, automotive door seals and instrument panels, window profile seals, sporting goods, health & hygiene, and toys.

The thermoplastic elastomer compositions of this invention are suitable for application in, but not limited to, appliance gaskets and other consumer durables, automotive door seals
5 and instrument panels, window profile seals, sporting goods, health & hygiene, toys, and other applications that require flexibility, wear resistance, and desirable appearance.

In one embodiment, the article is a foamed profile extruded article. In a further preferred embodiment, the article is a weather-strip.

In one embodiment, the article is an automotive part.

10 In one embodiment, the article is a hose.

In one embodiment, the article is a flooring material.

In one embodiment, the article is a thermoplastic vulcanizates (TPV).

In one embodiment, the article is a footwear component, such a shoe inner sole or shoe outer sole.

15 Articles suited for these applications may be fabricated through injection molding, over-molding, blow-bolding, compression molding, extrusion, profile extrusion, casting, calendaring, and other processes.

An inventive article may comprise a combination of two or more embodiments as described herein.

20

DEFINITIONS

The term "polymer," as used herein, refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term homopolymer (employed to refer to polymers prepared from only
25 one type of monomer), and the term interpolymer as defined hereinafter.

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 (employed to refer to polymers prepared from two different types of monomers), and polymers prepared from more than two different types of monomers.

30 The term "olefin-based polymer," as used herein, refers to a polymer that comprises, in polymerized form, a majority weight percent of an olefin, for example ethylene or propylene (based on the weight of the polymer), and optionally one or more other comonomers.

The term “ethylene-based polymer,” as used herein, refers to a polymer that comprises, in polymerized form, a majority weight percent of ethylene (based on the weight of the polymer), and optionally one or more other comonomers.

5 The term, “ethylene/ α -olefin interpolmer,” as used herein, refers to an interpolmer that comprises a majority amount of polymerized ethylene monomer (based on the weight of the interpolmer), and at least one α -olefin. As used in the context of this disclosure, ethylene/ α -olefin interpolmer excludes ethylene/ α -olefin multi-block interpolmers.

10 The term, “ethylene/ α -olefin copolymer,” as used herein, refers to a copolymer that comprises a majority amount of polymerized ethylene monomer (based on the weight of the copolymer), and an α -olefin, as the only two monomer types. As used in the context of this disclosure, ethylene/ α -olefin copolymer excludes ethylene/ α -olefin multi-block copolymers.

The term, “propylene-based polymer,” as used herein, refers to a polymer that comprises a majority amount of polymerized propylene monomer (based on the weight of the polymer), and optionally may comprise one or more comonomers.

15 The term “composition,” as used herein, includes a mixture of materials, which comprise the composition, as well as reaction products and decomposition products formed from the materials of the composition.

The terms “comprising,” “including,” “having,” and their derivatives, are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is specifically disclosed. In order to avoid any doubt, all compositions claimed through use of the term “comprising” may include any additional additive, adjuvant, or compound, whether polymeric or otherwise, unless stated to the contrary. In contrast, the term, “consisting essentially of” excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability.

25 The term “consisting of” excludes any component, step or procedure not specifically delineated or listed.

TEST METHODS

Melt index (I2) of an ethylene-based polymer is measured in accordance with ASTM D-1238-04, condition 190°C/2.16 kg. Melt index (I5) of an ethylene-based polymer is measured in accordance with ASTM D-1238-04, condition 190°C/5.0 kg. Melt index (I10) of an ethylene-based polymer is measured in accordance with ASTM D-1238-04, condition 190°C/10.0 kg. High load melt index (I21) of an ethylene-based polymer is measured in accordance with ASTM D-1238-04, condition 190°C/21.0 kg. For propylene-based

polymers, the melt flow rate (MFR) is measured in accordance with ASTM D-1238-04, condition 230°C/2.16 kg.

Polymer density is measured in accordance with ASTM D-792-08.

5

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) can be used to measure crystallinity in ethylene-based polymer (PE) and a propylene-based polymer (PP). About 5 to 8 mg of the polymer sample is weighed and placed in a DSC pan. The lid is crimped on the pan to
10 ensure a closed atmosphere. The sample pan is placed in a DSC cell, and then heated, at a rate of approximately 10°C/min, to a temperature of 180°C for PE (230°C for PP). The sample is kept at this temperature for three minutes. Then the sample is cooled at a rate of 10°C/min to -60°C for PE (-40°C for PP), and kept isothermally at that temperature for three minutes. The sample is next heated at a rate of 10°C/min, until complete melting (second
15 heat). The percent crystallinity is calculated by dividing the heat of fusion (H_f), determined from the second heat curve, by a theoretical heat of fusion of 292 J/g for PE (165 J/g, for PP), and multiplying this quantity by 100 (for example, % cryst. = $(H_f / 292 \text{ J/g}) \times 100$ (for PE)). The melting point(s) (T_m) of each polymer sample is determined from the second heat curve obtained from DSC, as described above. The crystallization temperature (T_c) is
20 measured from the first cooling curve.

Oil Exudation - Plastic Bag Test

Oil exudation ranking were obtained using a plastic zipper storage bag. An injection-molded plaque (4 inches x 6 inches) was placed into the plastic bag
25 (approximately 7 inches x 8 inches in dimension), with the plaque surface in contact with the inner surface of the plastic bag, at room temperature. Most of the air was squeezed out of the bag, by pressing the bag with the sample on a flat surface, and the zipper was pressed to lock the bag, with the plaque sample inside the bag. The oil exudation/bleeding was evaluated by examining the plaque/plastic bag interface. The rank value of "0" meant no
30 sign of any oil wetting, "10" meant complete wetting of surface due to oil bleed; other ranking values represented approximate degrees of oil bleed, with lower numbers indicating less oil bleed. The degree of wetting, a measure of the oil bleed, is a function of diffusion time and temperature.

Figure 1 shows the optical images of the three plaque/bag interfaces. The oil-wet
35 contact areas between the plaque and the bag were manually masked (in black) and rated.

Figure 1A was given an oil-bleed rating of 0-1, Figure 1B was given an oil-bleed rating of 3-4, and Figure 1C was given an oil-bleed rating of 7-8.

The images shown in Figure 1 were also examined using an image processing software SPIP (Image Metrology, Denmark) that distinguishes and quantifies the color/shade of each pixel on the micrograph. An intensity (brightness) distribution histogram was generated by the software. The black pixels formed a separated histogram peak, which was integrated to give the area of the black pixels. Figure 1A had a black pixel percentage of less than 1%, Figure 1B had a black pixel percentage of about 16%, and Figure 1C has a black pixel percentage of about 38%.

10 *B) Cigarette-Paper for Measurement of Oil Exudation (Oil Bleeding) – Percent Shade Change*

This test was designed to measure relative rate of oil bleed from injection or compression molded samples. The test is described below. Injection or compression molded samples were cut to into bars of approximately “3 inch x 6-1/8 inch x 0.125 inch” bars, within two hours after molding. For each polymer composition, the number of bars tested was three, and an average rating was reported.

Each test bar was overlaid with three pieces of zigzag cigarette paper (1 inch in width), laid side-to-side, with the length direction of the paper aligned perpendicular to the length direction of the test bar. A sheet of MYLAR film was placed on exposed side of the paper, to create a “MYLAR – paper – test bar” test configuration. The test configuration was placed in an oven (air convection oven) maintained at specified temperature, with the MYLAR film in contact with a flat metal support placed inside the oven. There was no mass on top of the test bar, and thus, the force on the paper was due to the mass of the bar and gravity.

The bar was then aged for specified durations (for example, 24 hours, 1 week, 2 weeks or 3 or 4 weeks). After a determined period of time, one of the three papers was removed from the bar, and the bar was returned to the oven. After another determined time period, a second paper was removed from the bar, and the bar was returned to the oven. The third paper was removed from the bar at the end of the aging period. After each paper was removed, the paper was examined for oil bleed.

The removed paper from a given specimen was adhered (using double-sided tape) to a standard (approx. 9 x 12 in.) sheet of black paper. Each paper was scanned using a XEROX WORKCENTRE M118i copier/fax/scanner. All samples were scanned as quickly

as possible, one after another, to minimize potential for scanner drift. A control sample was also scanned (a fresh sheet of cigarette paper).

The scanned image was then converted to an “8-bit grayscale image,” so that a grayscale histogram could be created. The grayscale image was then analyzed, using Adobe
5 PHOTOSHOP®CS2 (version 9.0.2) software, to create a histogram showing the percentage of pixels in each of four quadrants of grayscale (ranging from 0 (black – indicated oil) to 255 (white)), and a weighted grayscale value for the imaged area.

The derived grayscale value was used to calculate the Normalized Percent Shade Change according to the following equation:

10
$$\text{Normalized Percent Shade Change} = 100 \times (\% \text{ grey scale sample} - \% \text{ grey scale reference}) / (100 - \% \text{ grey scale reference}).$$

In the above equation, the “% grey scale sample” refers to the percent grey scale measured on the aged sample, and the “% grey scale reference” refers the percent grey scale measured on an un-aged, untreated sheet of cigarette paper used as the reference.

15

Gel Permeation Chromatography (GPC)

Polymer molecular weight was characterized by high temperature, triple detector, Gel Permeation Chromatography (3D-GPC). The chromatographic system consisted of a Polymer Laboratories (Amherst, MA, now part of Varian, Inc, Shropshire, UK) “PL-GPC
20 210” high temperature chromatograph, equipped with a concentration detector (RI), a PRECISION DETECTORS (Amherst, MA) 2-angle laser light scattering detector, Model 2040, and a 4-capillary differential viscometer detector, Model 220, from VISCOTEK (Houston, TX). The 15° angle of the light scattering detector was used for calculation purposes.

25 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 ERC-3415α four channel degasser system from ERC Inc (Tokyo, JP). The carousel compartment was operated at 150°C for polyethylene, and the column compartment was operated at 150°C. The columns were four Polymer Lab Mix-A 30 cm, 20 micron columns.
30 The polymer solutions were prepared in 1,2,4-trichlorobenzene (TCB). The samples were prepared at a concentration of “0.1 grams of polymer” in “50 ml of TCB.” The chromatographic solvent and the sample preparation solvent contained 200 ppm of butylated hydroxytoluene (BHT). Both solvent sources were nitrogen purged. The ethylene-based polymer samples were stirred gently at 160°C for four hours. The injection
35 volume was 200 μl, and the flow rate was 1.0 ml/minute.

Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards. The molecular weights of the standards ranged from 580 to 8,400,000, and were arranged in six “cocktail” mixtures, with at least a decade of separation between individual molecular weights. 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)):

$$M_{\text{polyethylene}} = A \times (M_{\text{polystyrene}})^B \quad (1A),$$

where M is the molecular weight, A has a value of 0.39 and B has a value of 1.0. A fourth order polynomial was used to fit the respective polyethylene-equivalent calibration points.

The total plate count of the GPC column set was performed with EICOSANE (prepared at 0.04 g in 50 milliliters of TCB, and dissolved for 20 minutes with gentle agitation. The plate count and symmetry were measured on a 200 microliter injection according to the following equations:

$$\text{PlateCount} = 5.54 * (\text{RV at Peak Maximum} / (\text{Peak width at } \frac{1}{2} \text{ height}))^2 \quad (2A),$$

where RV is the retention volume in milliliters, and the peak width is in milliliters.

$$\text{Symmetry} = (\text{Rear peak width at one tenth height} - \text{RV at Peak maximum}) / (\text{RV at Peak Maximum} - \text{Front peak width at one tenth height}) \quad (3A),$$

where RV is the retention volume in milliliters, and the peak width is in milliliters.

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 dual detector, log molecular weight results, from a broad polyethylene of 115,000, 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, increment area, and the RI detector calibration from a linear polyethylene homopolymer of 115,000 Dalton molecular weight. The refractive index increment (dn/dc) for polyethylene is -0.104 mL/g. The chromatographic concentrations were assumed low enough to eliminate addressing 2nd Virial coefficient effects (concentration effects on molecular weight).

The calculations of Mn, Mw, and Mz based on GPC (conventional GPC for Mn, Mw and Mz) results, using the RI detector were determined from the following equations:

$$\overline{Mn} = \frac{\sum_i RI_i}{\sum_i \left(\frac{RI_i}{M_{calibration_i}} \right)} \quad (4A),$$

$$\overline{Mw} = \frac{\sum_i (RI_i * M_{cal_i})}{\sum_i RI_i} \quad (5A),$$

$$\overline{Mz} = \frac{\sum_i (RI_i * M_{cal_i}^2)}{\sum_i (RI_i * M_{cal_i})} \quad (6A).$$

- 5 Another form of molecular weight average is the viscosity average (average Mv) which can be calculated using Equation 7A:

$$\overline{Mz} = \left(\frac{\sum_i (RI_i * M_{cal_i}^{\alpha+1})}{\sum_i (RI_i)} \right)^{1/\alpha} \quad (7A),$$

where α is a material dependent parameter which relates the intrinsic viscosity ($[\eta]$) to the molecular weight of the polymer.

- 10 In addition to the above calculations, a set of alternative values [Mw(abs), Mz(abs), Mz (BB) and Mz+1 (BB)] values were also calculated with the method proposed by Yau and Gillespie, Polymer, 42, 8947-8958 (2001), and determined from the following equations:

$$\overline{Mw}(abs) = K_{LS} * \frac{\sum_i (LS_i)}{\sum_i (RI_i)} \quad (8A), \text{ where, } K_{LS} = LS - MW \text{ calibration constant,}$$

$$\overline{Mz}(abs) = \frac{\sum_i RI_i * (LS_i / RI_i)^2}{\sum_i RI_i * (LS_i / RI_i)} \quad (9A),$$

15

$$\overline{Mz}(BB) = \frac{\sum_i (LS_i * M_{calibration_i})}{\sum_i (LS_i)} \quad (10A),$$

$$\overline{M_{z+1}}(BB) = \frac{\sum_i (LS_i * M_{calibration_i}^2)}{\sum_i (LS_i * M_{calibration_i})} \quad (11A),$$

where LS_i is the 15 degree LS signal, and the $M_{calibration}$ uses equation 1A, and the LS detector alignment is as described previously.

20

Durometer Hardness

Durometer A (or Shore A) hardness was measured on molded plaques per ASTM D2240-00. This test method permits hardness measurements based on either initial indentation or indentation after a specified period of time, or both. In this case a specified
5 time period of “5 seconds” was used. An average of five measurements were recorded.

Gloss

Gloss was measured on molded plaques according to ASTM D523, using a BYK GARDNER MICRO-TRI-gloss meter at a 60 degree angle. An average of four readings or
10 more were recorded.

Compression Set

Compression set was measured according to ASTM D 395-01. The diameter of the round testing discs was 29 mm, and the total thickness of the disc stack was 12.9 mm. The
15 sample’s thickness was squeezed 25% between two steel plates, and the sample was placed in a 70°C oven. After 22 hours of thermal treatment, the sample was removed from the oven, and the compression set was taken as the percentage of the original deflection after the material is allowed to recover at standard conditions for 30 minutes. The %
compression set was calculated using the following equation:

$$20 \quad C_B = [(t_o - t_i) / (t_o - t_n)] * 100,$$

where t_o is the original specimen thickness, t_i is the specimen thickness after testing, and t_n is the spacer thickness. Results are reported from an average of 3 values. In cases of limited samples, an average of 2 values was recorded.

25 *Tensile Properties ASTM 638-03*

The tensile properties of the formulated samples were measured by using ASTM D638-03 standard test. Samples were “die cut,” compression molded samples. The samples were tested using an INSTRU-MET/SINTECH Computer Controlled Tester. At least three samples were tested for each formulation at ambient conditions. Samples were
30 strained to failure at a rate of 5-inch/min. From each stress-strain curve, the Strain at Break, the Ultimate Stress (Stress at Break), and the Tensile Toughness were determined.

Melt Strength

A charge of sample was loaded into a GÖTTFERT RHEO-TESTER 2000 at 190°C,
35 and extruded with a piston, with a diameter of 12 mm, at a piston speed of 0.265 mm/sec, and a shear rate of 38.2 1/s. The resulting strand was drawn through rotating take up

wheels, which were then accelerated at a rate of 2.4 mm/sec/sec, until a steady state reading (in cN, from a calibrated transducer) was achieved, prior to strand break. The reported melt strength, in cN, was the average melt strength from all the recorded values for the steady state, until strand break.

5

Tear Strength

The tear strength was measured according to ASTM D624. The samples were compression molded or injection molded, and cut using the ASTM die C. Each sample was loaded to an INSTRON machine. The grip separation was two inches, and the testing speed was 20 in/min. A minimum of three samples were tested for each formulation.

10

EXPERIMENTAL

The following polymers were studied, as shown in Table 1 below. Each polymer was blended with one or more stabilizers, present in low (ppm) amounts, and is available from The Dow Chemical Company.

15

Table 1: Polymers

Polymer*	Type	Density (g/cc)	MI** or MFR**	Tm (°C)
EAO 387	Ethylene/Butene-1 Copolymer	0.870	< 0.5 (MI)	51
EAO 487	Ethylene/Butene-1 Copolymer	0.860	< 0.5 (MI)	37
EAO100	Ethylene/Octene-1 Copolymer	0.870	1.0 (MI)	60
EAO180	Ethylene/Octene-1 Copolymer	0.863	0.5 (MI)	47
EAO386	Ethylene/Propylene Copolymer	0.875	< 0.5 (MI)	55
EPDM 745	Ethylene/Propylene/ENB Terpolymer	0.864	< 0.5 (MI)	
EPDM 722	Ethylene/Propylene/ENB Terpolymer	0.867	< 0.5 (MI)	
OBC 07	Ethylene/Octene-1 Multiblock Copolymer	0.866	0.5 (MI)	119
LDPE 2I	LDPE	0.919	0.47 (MI)	108
LDPE 3I	LDPE	0.923	25 (MI)	110
LDPE 5I	LDPE	0.925	1.9 (MI)	114
LDPE 0I	LDPE	0.922	2 (MI)	112
LDPE 05	LDPE	0.918	5.5 (MI)	108
LDPE 94	LDPE	0.922	0.8	112
HDPE 92	HDPE	0.949	0.06 (MI)	
PP 14	Polypropylene Homopolymer	0.900	0.5 (MFR)	164
PP 02	Polypropylene Homopolymer	0.90	2.0 (MFR)	161

* EAO polymers are homogeneously branched substantially linear copolymers.

**MI is measured at 190°C, 2.16 kg and MFR is measured at 230°C, 2.16 kg.

HYDROBRITE 550 is a white mineral oil with about 70 wt% paraffinic and 30 wt% naphthenic content, and a density of 0.870 g/cc (available from Sonneborn Inc.).

20

PARALUX 6001 is a process oil with about 70 wt% paraffinic and 30 wt% naphthenic content, and a density of 0.872 g/cc (available from Chevron Phillips Chemical Company LLC.).

DAPLOY WB130HMS is a high melt strength grade of polypropylene from

Borealis.

MB50-002 is a siloxane masterbatch containing 50% of an ultra-high molecular weight siloxane polymer dispersed in polyethylene (LDPE) homopolymer (available from Dow Corning Corporation.)

- 5 Molecular weight data for the LDPE polymers in Table 1 are shown below in Table 2. An $M_z(\text{abs})/M_z(\text{conv})$ ratio of 2.2 or higher indicates a highly branched polymer.

Table 2: GPC Molecular Weight (g/mole) Data of Low Density Polyethylenes

	Mn (conv)	Mw (conv)	Mz (conv)	Mw/Mn (conv)	Mn (abs)	Mw (abs)	Mz(BB)	Mz(abs)	Mz(abs)/Mz(conv)
LDPE 94	10120	89960	388200	8.89	5358	135310	177100	984900	2.54
LDPE 5I	3380	79600	321500	23.5	1251	127330	167800	1006000	3.13
LDPE 0I	10190	79280	250900	7.78	7001	126100	144200	732100	2.92
LDPE 05	3620	154480	757100	42.7	1339	416570	371500	3536600	4.67
LDPE 3I	4200	81700	510000	19.4	2260	220820	163000	6084900	11.9
LDPE 2I	19970	236960	865900	11.9	23,606	610520	628600	3095700	3.6

Formulations and Properties

- 10 Inventive and comparative formulations containing 20 weight percent oil are shown in Table 3.

Table 3: Inventive Formulations (IE) and Comparative Formulations (CE) Containing 20% by Weight Mineral Oil

	22-2 (CE)	22-4 (CE)	22-5 (IE)	22-6 (CE)
EAO 386	14.4			
EAO 387				28.7
EAO 100	28.7	28.7	28.7	
EPDM 722		14.4		14.4
LDPE 2I			14.4	
DAPLOY Wb130HMS	14.4	14.4	14.4	14.4
CaCO3	20	20	20	20
PARALUX 6001R oil	20	20	20	20
MB50-002	0.5	0.5	0.5	0.5
TiO2	2	2	2	2
Total Wt	100.0	100.0	100.0	100.0

- 15 The formulations in Table 3 were compounded using a WP ZSK-25 Twin Screw Extruder. The extruder conditions are shown below in Table 4. The resin pellets were dry-blended first, and then fed using a “loss-in-weight” feeder. The oil was fed via oil-injection ports, using a gear pump. The extruded formulation was pelletized with an underwater pelletizer.

20

Table 4: Extruder Conditions

	Setting /Range
Zone #1 Temp (C)	137 - 142
Zone #2 Temp (C)	190 - 192
Zone #3 Temp (C)	190
Zone #4 Temp (C)	197 - 210
Zone #5 Temp (C)	190 - 192
Zone #6 Temp (C)	189 - 191
Zone #7 Temp (C)	189 - 191
Die Temp (C)	179 - 181
Melt Temp (C)	198 - 209
Extruder RPM's	505 - 507
Extruder Torque %	44 - 55
Output (#/hr)	50

Each formulation (pellets) was injection molded into a plaque (4 in x 6 in x 0.125 in). The injection molding (IM) conditions are shown below in Table 5.

5

Table 5: Injection Molding Conditions

	Setting /Range
Zone 1 Temp. (°F)	250-400
Zone 2 Temp. (°F)	350-400
Zone 3 Temp. (°F)	400
Zone 4 Temp. (°F)	400
Nozzle Temp. (°F)	400
Mold Temperature (°F)	65
Extruder RPM (m/min)	20-30
Backpressure (Bar)	15
Dosage (ccm)	70
Injection Speed #1 (ccm/s)	25
Pressure at transfer (bar)	370 - 510
Fill Time (s)	2.1 – 2.4
Pressure #1 (Bar)	370 - 500
Hold Time #1 (s)	30
Cool Time (s)	20
Dosage Time (s)	6.7 - 13
Cycle Time (s)	59 – 60

Gloss was measured on the formulations (injection molded plaques) listed in Table 3. The results are shown in Table 6, and depicted in Figure 2.

Table 6: Gloss (%) of Injection Molded Plaques (Ave.(SD))

	22-2 (CE)	22-4 (CE)	22-5 (IE)	22-6 (CE)
2 days	29.1 (5.6)	36.1 (6.2)	11.8 (1.1)	21.6 (5.8)
168 days	37.3 (2.1)	43.2 (5.0)	12.7 (3.0)	24.7 (6.3)
357 days	41.8 (7.4)	51.8 (5.9)	13.5 (1.2)	23.3 (4.1)

10

As shown in Table 6, Inventive Example of 22-5 unexpectedly exhibited the lowest surface gloss, and this low gloss remained fairly stable over time.

Oil exudation ratings of the formulations listed in Table 3 are shown in Table 7 below. The results were obtained using the “plastic bag” test method as described above.

Table 7: Visual Ratings of Surface Oil Exudation

	22-2 (CE)	22-4 (CE)	22-5 (IE)	22-6 (CE)
121 Day	5	4	1	3
161 Day	9	9	0	6
254 Day	9	9	0	6
357 Day	9	10	0	6

As shown in Table 8, Inventive Example 22-5 unexpectedly exhibited the best (lowest) level of oil exudation, compared to the comparative examples. Even after 357 days, no sign of oil-related wetting at the interface of the contacting plastic bag was observed in the inventive example. Some mechanical properties are shown in Table 8.

Table 8: Mechanical Properties and Melt Strength Data (Ave, (SD))

		22-2 (CE)	22-4 (CE)	22-5 (IE)	22-6 (CE)
Shore A Hardness		78.9 (1.24)	75.7 (1.10)	85.3 (0.60)	75.2 (1.62)
Tear Strength	lbf/in	245 (3.1)	227 (4.8)	287 (2.3)	231 (2.7)
Strain @ Break	%	401 (28.8)	459 (21.5)	321 (62.8)	384 (40.8)
Stress @ Break	psi	872 (25.1)	830 (18.8)	1087 (36.5)	853 (28.7)
Toughness	in*lbf	92.7 (8.1)	100.5 (6.9)	91.3 (16.4)	87.8 (12.7)
Melt strength	cN	3.13 (0.14)	2.85 (0.09)	6.94 (0.19)	5.04 (0.17)

At comparable compositions, Inventive Example 22-5 exhibited higher tear strength and higher tensile strength. The Inventive Example 22-5 also exhibited higher melt strength (see Figure 3), which is desirable to retain dimensional stability without, or with minimal, sagging during over-molding and/or profile extrusion processes.

Additional formulations containing 25 weight percent oil are shown below in Table 9. The formulations in Table 9 were compounded using a WP ZSK-25 Twin Screw Extruder, and injection molded into plaques. Similar compounding and injection molding conditions were employed, as shown in Tables 4 and 5.

Table 9: Inventive (IE) and Comparative (CE) Formulations Containing 25% by Oil

Example	25-1 (CE)	25-2 (IE)	25-3 (CE)	25-4 (IE)	25-6 (IE)	25-7 (IE)
HDPE 92	17.50	17.50	17.50	17.50	17.50	11.67
PP 14						7.29
OBC 07*	35.00	27.71				
EAO 180*			35.00	27.71		26.25
EAO 487*					27.71	
LDPE 2I		7.29		7.29	7.29	7.29
PARALUX 6001R oil	25	25	25	25	25	25
CaCO ₃	20	20	20	20	20	20
MB50-002	0.5	0.5	0.5	0.5	0.5	0.5
TiO ₂	2	2	2	2	2	2
Total Wt	100	100	100	100	100	100

*Elastomer

Gloss values of injection molded plaques of the inventive and comparative examples of Table 9 were measured and tabulated in Table 10 below.

Table 10: Gloss (%) of Injection Molded Plaques (Ave. (SD))

Gloss (%)	25-1 (CE)	25-2 (IE)	25-3 (CE)	25-4 (IE)	25-6 (IE)	25-7 (IE)
1 hr	22.2 (4.0)	11.2 (4.4)	30.3 (4.2)	12.6 (2.8)	5.8 (0.5)	12.1 (4.6)
6 days	25.6 (3.4)	11.4 (4.6)	26.1 (2.2)	11.2 (1.3)	6.2 (0.9)	12.9 (8.3)
13 days	25.2 (4.7)	10.3 (2.8)	24.7 (2.7)	9.6 (2.1)	5.7 (0.3)	9.0 (2.0)
27 days	25.7 (5.0)	12.3 (5.6)	27.0 (7.5)	13.0 (4.1)	5.9 (0.4)	10.4 (2.1)

5 As compared with CE 25-1 at similar composition, IE 25-2 showed lower measured surface gloss, which is desirable for many applications. Similarly, IE 25-4 (vs. CE 25-3) showed lower measured surface gloss. These results are shown in Figure 4.

Oil exudation ratings of the formulations listed in Table 9 are shown in Table 11 below. The results were obtained using the “plastic bag” test method as described above.

10 Table 11: Visual Rating of Surface Oil Exudation

Rank after	25-1 (CE)	25-2 (IE)	25-3 (CE)	25-4 (IE)	25-6 (IE)	25-7 (IE)
3 weeks	0	0	0	0	0	0
7 weeks	2	1	3	0	0	0

15 Compared with Comparative Example 25-1, Inventive Example 25-2, with a lower elastomer/oil weight ratio, unexpectedly exhibited low gloss and reduced oil exudation. Similarly, compared with Comparative Example 25-3, Inventive Example 25-4, with a lower elastomer/oil weight ratio, unexpectedly exhibited low gloss and reduced oil exudation. Inventive Examples of 25-6 and 25-7 exhibited low gloss for extended time, and no sign of oil exudation after seven weeks. Some mechanical properties are shown in Table 12.

Table 12: Mechanical Properties (Ave. (SD))

		25-1 (CE)	25-2 (IE)	25-3 (CE)	25-4 (IE)	25-6 (IE)	25-7 (IE)
Shore A Hardness		71.2 (0.13)	76.1 (0.41)	72.8 (0.55)	80.1 (0.31)	78.4 (0.40)	76.8 (0.43)
Tear Strength	lbf/in	194 (1.6)	255 (4.4)	220 (3.0)	271 (4.7)	284 (4.4)	253 (3.6)
Strain @ Break	%	587 (26.8)	493 (27.1)	586 (25.2)	519 (16.9)	511 (72.1)	529 (30.2)
Stress @ Brk	psi	661 (35.8)	851 (29.1)	720 (36.6)	836 (52.5)	850 (28.9)	860 (26.1)
Toughness	in*lbf	101 (5.0)	114 (9.4)	111 (9.4)	121 (7.5)	129 (23.6)	124 (10.1)

20 At comparable compositions, Inventive Examples 25-2 (vs. 25-1) and 25-4 (vs. 25-3) exhibited higher tear strength, higher tensile strength, and higher tensile toughness.

25 Additional formulations containing 30-60 weight percent oil are shown below in Table 13. The formulations in Table 13 were compounded using a WP ZSK-25 Twin Screw Extruder, and injection molded into plaques. Similar compounding and injection molding conditions were employed as shown in Tables 4 and 5.

Table 13: Inventive (IE) and Comparative (CE) Formulations Containing 30-60 wt% Oil

	6 (CE)	6A (CE)	6B (CE)	6C (CE)	7 (IE)
OBC 07	100	70	50	40	30
Mineral oil*	0	30	50	60	60
LDPE 2I					10

*Mineral oil for the comparative examples was PARALUX 6001R. The mineral oil for Inventive Example 7 was HYDROBRITE 550.

5 Shore A Hardness data and compression set data of oil-extended formulations of Table 13 are shown in Table 14.

Table 14: Shore A Hardness and Compression Set* (Ave. (SD))

	6 (CE)	6A (CE)	6B (CE)	6C (CE)	7 (IE)
Shore A Hardness	64 (0.2)	39 (0.2)	19 (0.1)	9 (0.1)	24 (0.3)
Compression Set @70°C (%)	53 (5.8)	62 (0.1)	73 (5.0)	61 (0.8)	44 (0.8)

*Each Compression Set value in Table 14 was average of two readings.

10 Mineral oil is often added to polymeric compositions to modify the hardness, to provide a soft-touch feel, and to alter the processing characteristics or cost of the compositions for targeted applications. It is generally desired to have polymer compositions which have a low compression set at a comparable hardness, specified for a targeted application. The Inventive Example 7 unexpectedly exhibited significantly lower compression set values (conditioned at 70°C for 22 hrs) as compared to the comparative
15 examples.

Additional formulations containing 30-60 weight percent oil are shown in Table 15. Polymer formulations were prepared in a HAAKE RHEOMIX 3000E mixer, at 190°C, with roller style blades, at 40-60 rpm rotor speed. The mixing bowl was charged with polymer and other components. The oil was slowly added to the molten polymer formulation to
20 avoid slippage. Once polymer and all components were loaded, and good kneading was established, the mixing was continued for five additional minutes. The rotors were then stopped, the mixer disassembled, and the final polymer formulation was collected on MYLAR sheets, cold pressed into a “pancake” shape for further molding later, and cooled to room temperature.

25 The formulations were compression molded on a CARVER press, with a thickness of about 1/8 inch. The above mixed formulation was sandwiched between two sheets of MYLAR or TEFLON, which were placed between two metal plates resting on a tray holder. Samples were molded at 190°C, for four minutes, at 40,000 psi. Sheet samples were removed, and placed between cold platens (cooled by circulating tap water) for four
30 minutes, at 40,000 psi.

Table 15: Inventive (IE) and Comparative (CE) Formulations Containing 30-60 wt% Oil

	26-2 (CE)	26-3 (CE)	26-5 (CE)	26-7 (CE)	26-8 (IE)
OBC 07 (wt%)	70	35.0	41.3	70	35.0
EAO 487 (wt%)		35.0	13.7		
LDPE 2I (wt%)					35.0
HYDROBRITE 550	30	30	45.0	30	30
Total Wt	100	100	100	100	100

The surface oil exudations of the above formulations were measured, after specified
 5 times, by shade changes (%) using cigarette paper. The results are shown in below.

Table 16: Surface Oil Exudation – Percent Shade Changes

	26-2 (CE)	26-3 (CE)	26-5 (CE)	26-7 (CE)	26-8 (IE)
23°C, 24 hr	13.8	5.6	0.2	0.7	0.8
60°C, 24 hr	13.1	19.0	18.5	1.4	4.8
23°C, 1 week	4.9	0.0	0.0	0.0	2.9
60°C, 1 week	7.3	34.7	73.3	7.6	0.0
Oil/Elastomer(s)* weight ratio	0.43	0.43	0.82	0.43	0.86

*Elastomer(s) = amount of OBC + amount of EAO

Compared with Comparative Examples 26-2 (and 26-7), Inventive Example 26-8,
 with a significantly higher oil/elastomer weight ratio, showed a lower degree of oil
 10 exudation, as indicated by lower increase in the “percentage shade change” of each oil-
 absorbing cigarette paper.

A very high oil levels, for example an “oil to elastomer” ratio of three or higher, an
 excessive amount of oil bleed occurs, even in formulations containing LDPE, since such
 formulations contains an overwhelmingly high oil level.

15 Although the invention has been described in considerable detail in the preceding
 examples, this detail is for the purpose of illustration, and is not to be construed as a
 limitation on the invention as described in the following claims.

CLAIMS

1. A composition comprising at least the following:
 - A) an ethylene-based polymer having at least the following characteristics: (i) a melting temperature of greater than, or equal to, 100°C, as determined by DSC,
5 and (ii) a molecular weight ratio, $M_z(\text{abs})/M_z(\text{conv})$ greater than 2.2; and
 - B) an oil.
2. The composition of Claim 1, wherein the ethylene-based polymer has a percent crystallinity greater than 28%, as determined by DSC.
3. The composition of any of the previous claims, wherein the ethylene-based polymer
10 has a number average molecular weight ($M_n(\text{conv})$) greater than 2800 g/mole.
4. The composition of any of the previous claims, wherein the ethylene-based polymer, Component A, has a MR value less than 200 g/10 min, where $MR = I_2 \times RR$.
5. The composition of any of the previous claims, wherein the ethylene-based polymer, Component A, has a molecular weight ratio ($M_z(\text{abs})/M_z(\text{conv})$) greater than, or equal to,
15 2.5, preferably greater than, or equal to, 2.9.
6. The composition of any of the previous claims, wherein the ethylene-based polymer, Component A, is a low density polyethylene (LDPE).
7. The composition of any of the previous claims, wherein the ethylene-based polymer, Component A, has a density from 0.900 to 0.940 g/cc.
- 20 8. The composition of any of the previous claims, wherein the ethylene-based polymer, Component A, has melt index (I_2) from 0.2 to 50 g/10 min.
9. The composition of any of the previous claims, wherein the ethylene-based polymer, Component A, is present in an amount from 2 to 50 weight percent, based on the weight of the composition.
- 25 10. The composition of any of the previous claims, wherein the oil is present in an amount from 10 to 70 weight percent, based on the weight of the composition.
11. The composition of any of the previous claims, wherein the oil is present in an amount from 35 to 90 weight percent, based on the sum weight of the ethylene-based polymer and the oil.
- 30 12. The composition of any of the previous claims, further comprising an olefin-based polymer.
13. The composition of Claim 12, wherein the olefin-based polymer is a second ethylene-based polymer.

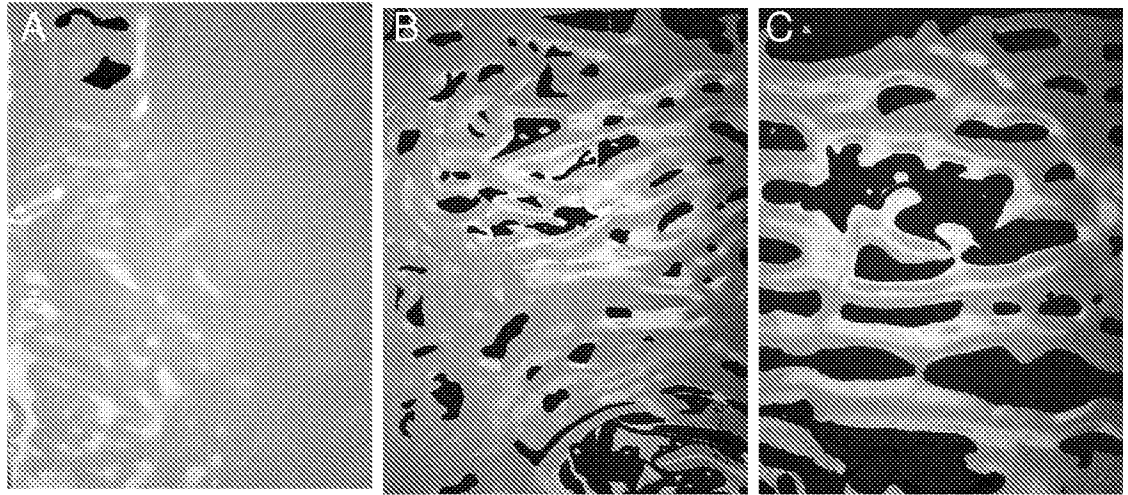


FIGURE 1

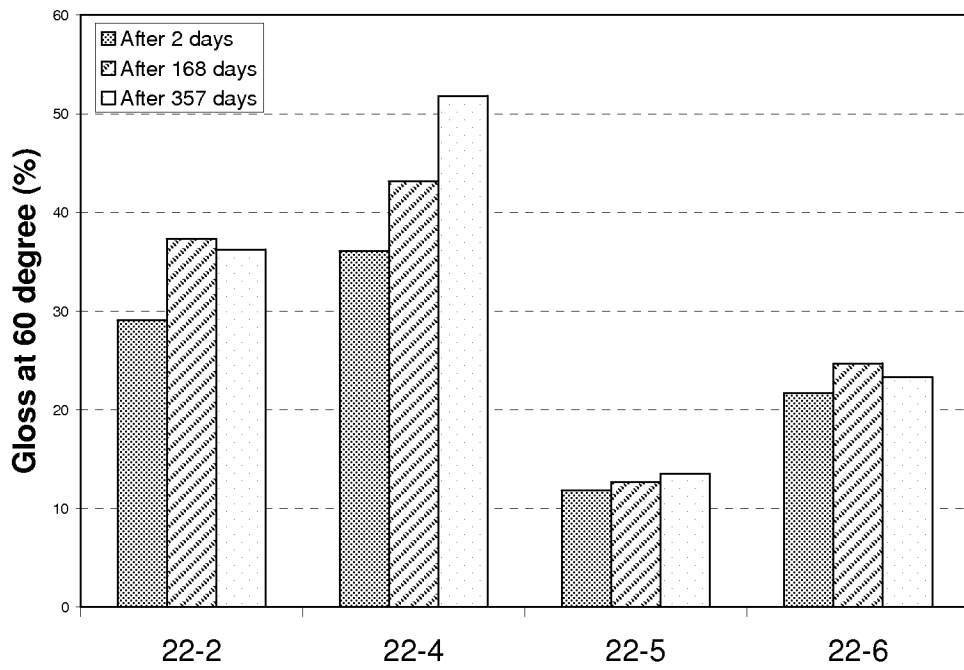


FIGURE 2

2/2

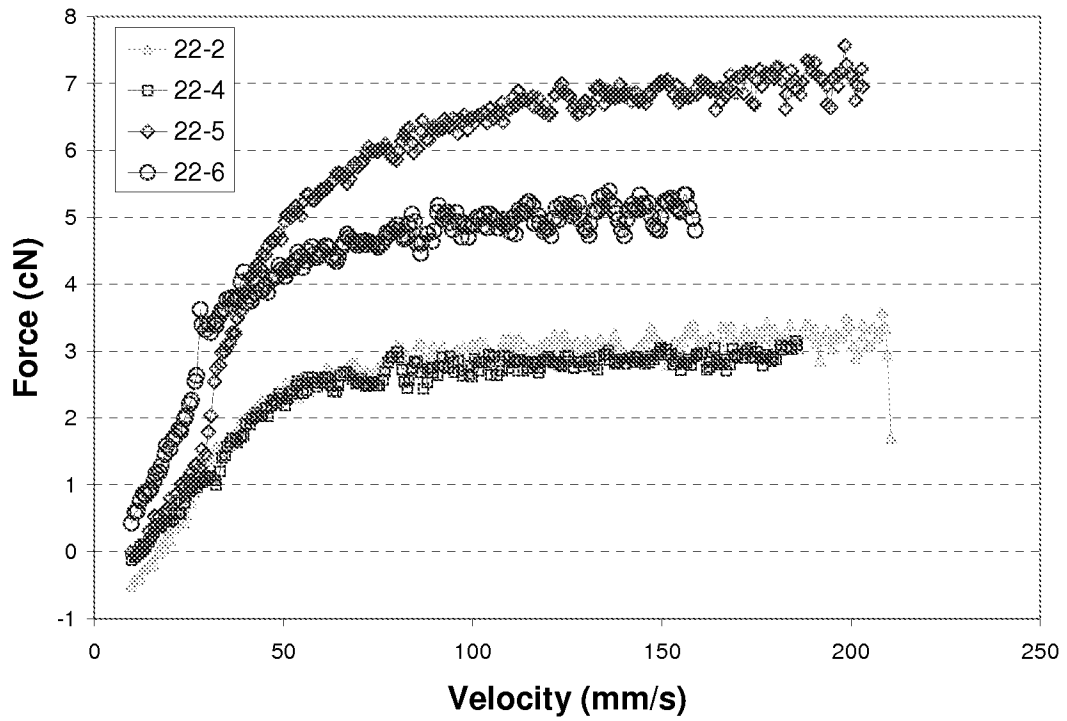


FIGURE 3

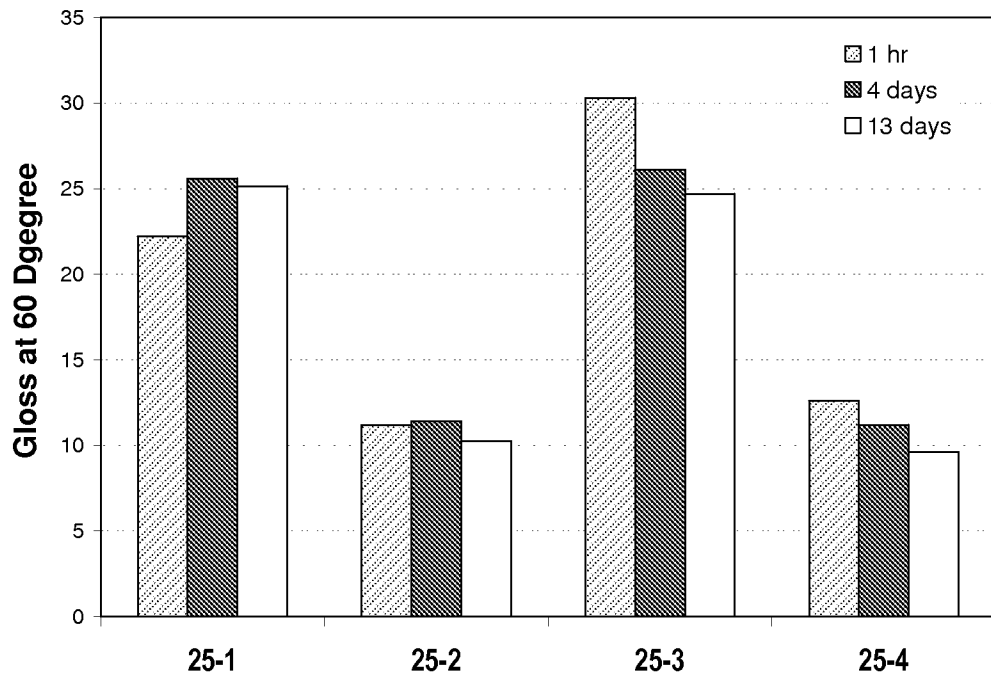


FIGURE 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/037892

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08L23/06 C08L23/04 C08L23/08
 ADD.

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

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C08L

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
 EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 99/10415 A1 (DOW CHEMICAL CO [US]; BABB DAVID A [US]; HOENIG WENDY D [US]; KAO CHE) 4 March 1999 (1999-03-04) abstract; claims 1-10	1
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 22 August 2011	Date of mailing of the international search report 07/09/2011
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Bergmans, Koen
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International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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