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(54) **Titre : PELLICULES INTERPOLYMERIQUES D'ETHYLENE**
(54) **Title: ETHYLENE INTERPOLYMER FILMS**

(57) **Abrégé/Abstract:**
This disclosure relates to multilayer films having improved caulkability. These multilayer films have at least one layer containing an ethylene interpolymer product, or a blend containing an ethylene interpolymer product, where the ethylene interpolymer product has: a Dilution Index (Y_d) greater than 0; total catalytic metal 2 3.0 ppm; ≥ 0.03 terminal vinyl unsaturations per 100 carbon atoms, and; optionally a Dimensionless Modulus (X d) greater than 0. The ethylene interpolymer products have a melt index from about 0.4 to about 100 dg/minute, a density from about 0.950 to about 0.970 g/cm^3, a polydispersity (M_w/M_n) from about 2 to about 25 and a $CDBI_{50}$ from about 55% to about 97%. Further, the ethylene interpolymer products are a blend of at least two ethylene interpolymers; where one ethylene interpolymer is produced with a single-site catalyst formulation and at least one ethylene interpolymer is produced with a heterogeneous catalyst formulation.

ETHYLENE INTERPOLYMER FILMS

ABSTRACT OF THE DISCLOSURE

This disclosure relates to multilayer films having improved caulkability. These multilayer films have at least one layer containing an ethylene interpolymer product, or a blend containing an ethylene interpolymer product, where the ethylene interpolymer product has: a Dilution Index (Y_d) greater than 0; total catalytic metal ≥ 3.0 ppm; ≥ 0.03 terminal vinyl unsaturations per 100 carbon atoms, and; optionally a Dimensionless Modulus (X_d) greater than 0. The ethylene interpolymer products have a melt index from about 0.4 to about 100 dg/minute, a density from about 0.950 to about 0.970 g/cm^3, a polydispersity (M_w/M_n) from about 2 to about 25 and a $CDBI_{50}$ from about 55% to about 97%. Further, the ethylene interpolymer products are a blend of at least two ethylene interpolymers; where one ethylene interpolymer is produced with a single-site catalyst formulation and at least one ethylene interpolymer is produced with a heterogeneous catalyst formulation.

ETHYLENE INTERPOLYMER FILMS

FIELD OF THE INVENTION

This disclosure relates to mono and multilayer films comprising at least one ethylene interpolymer product manufactured in a continuous solution polymerization process utilizing at least two reactors employing at least one single-site catalyst formulation and at least one heterogeneous catalyst formulation to produce films having improved properties.

BACKGROUND OF THE INVENTION

Ethylene interpolymer products are widely used in film applications. In film applications there is a need to improve film caulkability. The term "caulkability" refers to the ability of a film to seal through, or seal around contaminants. A film having good caulkability is highly desired, i.e. such films produce packages that do not leak. In the food packaging industry films that produce a packages of high integrity are valued because a package that leaks "a leaker" can be catastrophic, e.g. one leaker in a box containing multiple packages frequently results in the rejection of the entire box. In high speed packaging lines the ability of a film to seal through contamination is frequently challenged because the sealing area becomes contaminated with the food item being packaged (powders, liquids or pastes, etc.). Non-limiting examples of high speed food packaging processes include vertical and horizontal form-fill-seal packaging lines. In practice, it is common for the line speed of a packaging line to be limited by poor film caulkability. Generally, in the case of films having higher caulkability, the line speed of the packaging line can be increased (an obvious economic advantage) and fewer leakers are produced.

Herein, ethylene interpolymer products are disclosed that have improved caulkability.

The ethylene interpolymer products disclosed were produced in a solution polymerization process, where catalyst components, solvent, monomers and hydrogen are fed under pressure to one or more reactors. For ethylene homo polymerization, or ethylene copolymerization, reactor temperatures can range from about 80°C to about 300°C while pressures generally range from about 3MPag to about 45MPag and the ethylene interpolymer produced is dissolved in a solvent. The residence time of the solvent in the reactor is relatively short, for example, from about 1 second to about 20 minutes. The solution process can be operated under a wide range of process conditions that allow the production of a wide variety of ethylene interpolymers. Post reactor, the polymerization reaction is quenched to prevent further polymerization, by adding a catalyst deactivator, and passivated, by adding an acid scavenger. Once passivated, the polymer solution is forwarded to a polymer recovery operation where the ethylene interpolymer is separated from process solvent, unreacted residual ethylene and unreacted optional α-olefin(s).

SUMMARY OF THE INVENTION

This Application claims priority to Canadian Patent Application No. CA 2,868,640, filed October 21, 2014 and entitled "Solution Polymerization Process".

Embodiment of this disclosure include films having at least one layer, where this layer contains at least one ethylene interpolymer product comprising: (i) a first ethylene interpolymer; (ii) a second ethylene interpolymer, and; (iii) optionally a third ethylene interpolymer; where the ethylene interpolymer product has a Dilution Index, Y_d, greater than 0.

Embodiment of this disclosure include films having at least one layer, where this layer contains at least one ethylene interpolymer product comprising: (i) a first ethylene interpolymer; (ii) a second ethylene interpolymer, and; (iii) optionally a

third ethylene interpolymer; where the ethylene interpolymer has ≥ 0.03 terminal vinyl unsaturations per 100 carbon atoms.

Embodiment of this disclosure include films having at least one layer, where this layer contains at least one ethylene interpolymer product comprising: (i) a first ethylene interpolymer; (ii) a second ethylene interpolymer, and; (iii) optionally a third ethylene interpolymer; where the ethylene interpolymer product has ≥ 3 parts per million (ppm) of a total catalytic metal.

Further embodiment include films having at least one layer, where this layer contains at least one ethylene interpolymer product comprising: (i) a first ethylene interpolymer; (i) a first ethylene interpolymer; (ii) a second ethylene interpolymer, and; (iii) optionally a third ethylene interpolymer; where the ethylene interpolymer product has a Dilution Index, Y_d, greater than 0 and ≥ 0.03 terminal vinyl unsaturations per 100 carbon atoms or ≥ 3 parts per million (ppm) of a total catalytic metal or a Dimensionless Modulus, X_d, > 0.

Additional embodiment include films having at least one layer, where this layer contains at least one ethylene interpolymer product comprising: (i) a first ethylene interpolymer; (ii) a second ethylene interpolymer, and; (iii) optionally a third ethylene interpolymer; where the ethylene interpolymer product has ≥ 0.03 terminal vinyl unsaturations per 100 carbon atoms and ≥ 3 parts per million (ppm) of a total catalytic metal or a Dimensionless Modulus, X_d, > 0.

Embodiments include films having at least one layer, where this layer contains at least one ethylene interpolymer product comprising: (i) a first ethylene interpolymer; (ii) a second ethylene interpolymer, and; (iii) optionally a third ethylene interpolymer; where the ethylene interpolymer product has ≥ 3 parts per million (ppm) of a total catalytic metal and a Dimensionless Modulus, X_d, > 0.

Further embodiments include films having at least one layer, where this layer contains at least one ethylene interpolymer product comprising: (i) a first ethylene interpolymer; (ii) a second ethylene interpolymer, and; (iii) optionally a third ethylene interpolymer; where the ethylene interpolymer product has a Dilution Index, Y_d, greater than 0 and ≥ 0.03 terminal vinyl unsaturations per 100 carbon atoms and ≥ 3 parts per million (ppm) of a total catalytic metal or a Dimensionless Modulus, X_d, > 0.

Additional embodiments include films having at least one layer, where this layer contains at least one ethylene interpolymer product comprising: (i) a first ethylene interpolymer; (ii) a second ethylene interpolymer, and; (iii) optionally a third ethylene interpolymer; where the ethylene interpolymer product has a Dimensionless Modulus, X_d, > 0 and ≥ 3 parts per million (ppm) of a total catalytic metal and a Dilution Index, Y_d, greater than 0 or ≥ 0.03 terminal vinyl unsaturations per 100 carbon atoms

Embodiments also include films having at least one layer, where this layer contains at least one ethylene interpolymer product comprising: (i) a first ethylene interpolymer; (ii) a second ethylene interpolymer, and; (iii) optionally a third ethylene interpolymer; where the ethylene interpolymer product has a Dilution Index, Y_d, greater than 0, a Dimensionless Modulus, X_d, > 0, ≥ 3 parts per million (ppm) of a total catalytic metal and ≥ 0.03 terminal vinyl unsaturations per 100 carbon atoms.

The ethylene interpolymer products disclosed here have a melt index from about 0.4 to about 12 dg/minute, a density from about 0.900 to about 0.935 g/cm^3, a M_w/M_n from about 2 to about 25 and a $CDBI_{50}$ from about 20% to about 98%;

where melt index is measured according to ASTM D1238 (2.16 kg load and 190°C) and density is measured according to ASTM D792.

Further, the disclosed ethylene interpolymer products contain: (i) from about 15 to about 60 weight percent of a first ethylene interpolymer having a melt index from about 0.01 to about 200 dg/minute and a density from about 0.855 g/cm^3 to about 0.975 g/cm^3; (ii) from about 30 to about 85 weight percent of a second ethylene interpolymer having a melt index from about 0.3 to about 1000 dg/minute and a density from about 0.89 g/cm^3 to about 0.975 g/cm^3, and; (iii) optionally from about 0 to about 30 weight percent of a third ethylene interpolymer having a melt index from about 0.5 to about 2000 dg/minute and a density from about 0.89 to about 0.975 g/cm^3; where weight percent is the weight of the first, second or third ethylene polymer divided by the weight of ethylene interpolymer product.

Embodiments of this disclosure include films containing ethylene interpolymer products synthesized in a solution polymerization process containing from 0.1 to about 10 mole percent of one or more α-olefins.

Further, the first ethylene interpolymer (in the ethylene interpolymer product) is synthesized using a single-site catalyst formulation and the second ethylene interpolymer is synthesized using a first heterogeneous catalyst formulation. Embodiments of films may contain ethylene interpolymers where the third ethylene interpolymer is synthesized using a first heterogeneous catalyst formulation or a second heterogeneous catalyst formulation.

The second ethylene interpolymer (in the ethylene interpolymer product) may be synthesized using a first in-line Ziegler Natta catalyst formulation or a first batch Ziegler-Natta catalyst formulation; optionally, the third ethylene interpolymer is synthesized using the first in-line Ziegler Natta catalyst formulation or the first

batch Ziegler-Natta catalyst formulation. The optional third ethylene interpolymer may be synthesized using a second in-line Ziegler Natta catalyst formulation or a second batch Ziegler-Natta catalyst formulation.

Embodiments of this disclosure include films where the ethylene interpolymer product has ≤ 1 part per million (ppm) of a metal A; where metal A originates from the single-site catalyst formulation; non-limiting examples of metal A include titanium, zirconium or hafnium.

Further embodiments include films where the ethylene interpolymer product has a metal B and optionally a metal C; where the total amount of metal B and metal C is from about 3 to about 11 parts per million (ppm); where metal B originates from a first heterogeneous catalyst formulation and metal C originates form an optional second heterogeneous catalyst formation. Metals B and C are independently selected from the following non-limiting examples: titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, technetium, rhenium, iron, ruthenium or osmium. Metals B and C may be the same metal.

Additional embodiments of films containing ethylene interpolymer products include embodiments where the first ethylene interpolymer has a first M_w/M_n, the second ethylene interpolymer has a second M_w/M_n and the optional third ethylene has a third M_w/M_n; where the first M_w/M_n is lower than the second M_w/M_n and the optional third M_w/M_n. Embodiments also include films containing ethylene interpolymer products where the blending of the second ethylene interpolymer and the third ethylene interpolymer form an ethylene interpolymer blend having a fourth M_w/M_n; where the fourth M_w/M_n is not broader than the second M_w/M_n. Additional

ethylene interpolymer product embodiments are characterized as having both the second M_w/M_n and the third M_w/M_n less than about 4.0.

Further, embodiments of films contain ethylene interpolymer products where the first ethylene interpolymer has a first $CDBI_{50}$ from about 70 to about 98%, the second ethylene interpolymer has a second $CDBI_{50}$ from about 45 to about 98% and the optional third ethylene interpolymer has a third $CDBI_{50}$ from about 35 to about 98%. Other embodiments include ethylene interpolymer products where the first $CDBI_{50}$ is higher than the second $CDBI_{50}$; optionally the first $CDBI_{50}$ is higher than the third $CDBI_{50}$.

Embodiments in this disclosure also include multilayer films having improved caulkability. More specifically, multilayer films, containing ethylene interpolymer products in a sealant layer, where multilayer film has a hole size ≥ 95 μm (microns) and ≤ 115 μm, as determined in a caulkability test. Non-limiting examples of multilayer films include films that have from 2 to 11 layers.

BRIEF DESCRIPTION OF THE DRAWINGS

The following Figures are presented for the purpose of illustrating selected embodiments of this disclosure; it being understood, that the embodiments shown do not limit this disclosure.

Figure 1 compares the performance of multilayer films (nine layers) in the caulkability test; smaller hole size correlates with improved caulkability.

Figure 2 is a plot of Dilution Index (Y_d) (Y_d has dimensions of degrees (°)) and Dimensionless Modulus (X_d) for:

- Comparative S (open triangle, $Y_d = X_d = 0$) is an ethylene interpolymer comprising an ethylene interpolymer synthesized using an in-line Ziegler-Natta catalyst in a solution process (rheological reference);

- Examples 6, 101, 102, 103, 110, 115, 200, 201 (solid circle, $Y_d > 0$ and $X_d < 0$) are ethylene interpolymer products as described in this disclosure comprising a first ethylene interpolymer synthesized using a single-site catalyst formulation and a second ethylene interpolymer synthesized using an in-line Ziegler-Natta catalyst formulation in a solution process;

- Examples 120, 130 and 131 (solid square, $Y_d > 0$, $X_d > 0$) are ethylene interpolymer products as described in this disclosure;

- Comparatives D and E (open diamond, $Y_d < 0$, $X_d > 0$) are ethylene interpolymers comprising a first ethylene interpolymer synthesized using a single-site catalyst formation and a second ethylene interpolymer synthesized using a batch Ziegler-Natta catalyst formulation in a solution process, and;

- Comparative A (open square, $Y_d > 0$ and $X_d < 0$) is an ethylene interpolymer comprising a first and second ethylene interpolymer synthesized using a single-site catalyst formation in a solution process.

Figure 3 illustrates a typical Van Gurp Palmen (VGP) plot of phase angle [°] versus complex modulus [kPa].

Figure 4 plots the Storage modulus (G') and loss modulus (G") showing the cross over frequency ω_x and the two decade shift in phase angle to reach ω_c ($\omega_c = 0.01\ \omega_x$).

Figure 5 compares the amount of terminal vinyl unsaturations per 100 carbon atoms (terminal vinyl/100 C) in the ethylene interpolymer products of this disclosure (solid circles) with Comparatives B, C, E, E2, G, H, H2, I and J (open triangles).

Figure 6 compares the amount of total catalytic metal (ppm) in the ethylene interpolymer products of this disclosure (solid circles) with Comparatives B, C, E, E2, G, H, H2, I and J (open triangles).

Figure 7 illustrates the steps used to prepare a sample pouch for caulkability test.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Definition of Terms

Other than in the examples or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, extrusion conditions, etc., used in the specification and claims are to be understood as modified in all instances by the term "about". Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties that the various embodiments desire to obtain. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. The numerical values set forth in the specific examples are reported as precisely as possible. Any numerical values, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

It should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of "1 to 10" is intended to include all sub-ranges between and including the recited minimum value of 1 and the recited maximum value of 10; that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10.

Because the disclosed numerical ranges are continuous, they include every value between the minimum and maximum values. Unless expressly indicated otherwise, the various numerical ranges specified in this application are approximations.

All compositional ranges expressed herein are limited in total to and do not exceed 100 percent (volume percent or weight percent) in practice. Where multiple components can be present in a composition, the sum of the maximum amounts of each component can exceed 100 percent, with the understanding that, and as those skilled in the art readily understand, that the amounts of the components actually used will conform to the maximum of 100 percent.

In order to form a more complete understanding of this disclosure the following terms are defined and should be used with the accompanying figures and the description of the various embodiments throughout.

The term "Dilution Index (Y_d)", which has dimensions of degrees (°), and the "Dimensionless Modulus (X_d)" are based on rheological measurements and are fully described in this disclosure.

The term "hole size", which has dimensions of microns (μm), refers to an average diameter of a hole in a multilayer film as determined in the caulkability test; which is fully described herein. Smaller hole sizes are desired and correlate with improved caulkability.

As used herein, the term "monomer" refers to a small molecule that may chemically react and become chemically bonded with itself or other monomers to form a polymer.

As used herein, the term "α-olefin" is used to describe a monomer having a linear hydrocarbon chain containing from 3 to 20 carbon atoms having a double bond at one end of the chain.

As used herein, the term "ethylene polymer", refers to macromolecules produced from ethylene monomers and optionally one or more additional monomers; regardless of the specific catalyst or specific process used to make the ethylene polymer. In the polyethylene art, the one or more additional monomers are called "comonomer(s)" and often include α-olefins. The term "homopolymer" refers to a polymer that contains only one type of monomer. Common ethylene polymers include high density polyethylene (HDPE), medium density polyethylene (MDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), ultralow density polyethylene (ULDPE), plastomer and elastomers. The term ethylene polymer also includes polymers produced in a high pressure polymerization processes; non-limiting examples include low density polyethylene (LDPE), ethylene vinyl acetate copolymers (EVA), ethylene alkyl acrylate copolymers, ethylene acrylic acid copolymers and metal salts of ethylene acrylic acid (commonly referred to as ionomers). The term ethylene polymer also includes block copolymers which may include 2 to 4 comonomers. The term ethylene polymer also includes combinations of, or blends of, the ethylene polymers described above.

The term "ethylene interpolymer" refers to a subset of polymers within the "ethylene polymer" group that excludes polymers produced in high pressure polymerization processes; non-limiting examples of polymers produced in high pressure processes include LDPE and EVA (the latter is a copolymer of ethylene and vinyl acetate).

The term "heterogeneous ethylene interpolymers" refers to a subset of polymers in the ethylene interpolymer group that are produced using a

heterogeneous catalyst formulation; non-limiting examples of which include Ziegler-Natta or chromium catalysts.

The term "homogeneous ethylene interpolymer" refers to a subset of polymers in the ethylene interpolymer group that are produced using metallocene or single-site catalysts. Typically, homogeneous ethylene interpolymers have narrow molecular weight distributions, for example gel permeation chromatography (GPC) M_w/M_n values of less than 2.8; M_w and M_n refer to weight and number average molecular weights, respectively. In contrast, the M_w/M_n of heterogeneous ethylene interpolymers are typically greater than the M_w/M_n of homogeneous ethylene interpolymers. In general, homogeneous ethylene interpolymers also have a narrow comonomer distribution, i.e. each macromolecule within the molecular weight distribution has a similar comonomer content. Frequently, the composition distribution breadth index "CDBI" is used to quantify how the comonomer is distributed within an ethylene interpolymer, as well as to differentiate ethylene interpolymers produced with different catalysts or processes. The "$CDBI_{50}$" is defined as the percent of ethylene interpolymer whose composition is within 50% of the median comonomer composition; this definition is consistent with that described in U.S. Patent 5,206,075 assigned to Exxon Chemical Patents Inc. The $CDBI_{50}$ of an ethylene interpolymer can be calculated from TREF curves (Temperature Rising Elution Fractionation); the TREF method is described in Wild et al., J. Polym. Sci., Part B, Polym. Phys., Vol. 20 (3), pages 441-455. Typically the $CDBI_{50}$ of homogeneous ethylene interpolymers are greater than about 70%. In contrast, the $CDBI_{50}$ of α-olefin containing heterogeneous ethylene interpolymers are generally lower than the $CDBI_{50}$ of homogeneous ethylene interpolymers.

It is well known to those skilled in the art, that homogeneous ethylene interpolymers are frequently further subdivided into "linear homogeneous ethylene interpolymers" and "substantially linear homogeneous ethylene interpolymers". These two subgroups differ in the amount of long chain branching: more specifically, linear homogeneous ethylene interpolymers have less than about 0.01 long chain branches per 1000 carbon atoms; while substantially linear ethylene interpolymers have greater than about 0.01 to about 3.0 long chain branches per 1000 carbon atoms. A long chain branch is macromolecular in nature, i.e. similar in length to the macromolecule that the long chain branch is attached to. Hereafter, in this disclosure, the term "homogeneous ethylene interpolymer" refers to both linear homogeneous ethylene interpolymers and substantially linear homogeneous ethylene interpolymers.

Herein, the term "polyolefin" includes ethylene polymers and propylene polymers; non-limiting examples of propylene polymers include isotactic, syndiotactic and atactic propylene homopolymers, random propylene copolymers containing at least one comonomer and impact polypropylene copolymers or heterophasic polypropylene copolymers.

The term "thermoplastic" refers to a polymer that becomes liquid when heated, will flow under pressure and solidify when cooled. Thermoplastic polymers include ethylene polymers as well as other polymers commonly used in the plastic industry; non-limiting examples of other polymers commonly used in film applications include barrier resins (EVOH), tie resins, polyethylene terephthalate (PET), polyamides and the like.

As used herein the term "monolayer film" refers to a film containing a single layer of one or more thermoplastics.

As used herein the term "multilayer film" refers to a film comprised of more than one thermoplastic layer, or optionally non-thermoplastic layers. Non-limiting examples of non-thermoplastic materials include metals (foil) or cellulosic (paper) products. One or more of the thermoplastic layers within a multilayer film may be comprised of more than one thermoplastic.

As used herein, the term "tie resin" refers to a thermoplastic that when formed into an intermediate layer, or a "tie layer" within a multilayer film structure, promotes adhesion between adjacent film layers that are dissimilar in chemical composition.

In coextrusions the following nomenclature is typically used to designate a 5-layer coextruded film: A/B/C/D/E; wherein each uppercase letter refers to a chemically distinct layer. The central layer, layer C is typically called the "core layer"; similarly, three layer, seven layer, nine layer and eleven layer films, etc., have a central core layer. In a five layer multilayer film with the structure A/B/C/D/E, layers A and E are typically called the "skin layers" and layers B and D are typically called "intermediate layers". In the case of a five layer film with the structure A/B/C/B/A; the chemical composition of the two "A" skin layers are identical, similarly the chemical composition of the two intermediate "B" layers are identical.

As used herein, the term "sealant layer" refers to a layer of thermoplastic film that is capable of being attached to a second substrate, forming a leak proof seal.

As used herein, the term "adhesive lamination" and the term "extrusion lamination" describes continuous processes through which two or more substrates, or webs of material, are combined to form a multilayer product or sheet; wherein

the two or more webs are joined using an adhesive or a molten thermoplastic film, respectively.

As used herein, the term "extrusion coating" describes a continuous process through which a molten thermoplastic layer is combined with, or deposited on, a moving solid web or substrate. Non-limiting examples of substrates include paper, paperboard, foil, monolayer plastic film, multilayer plastic film or fabric. The molten thermoplastic layer could be monolayer or multilayer.

As used herein, the terms "hydrocarbyl", "hydrocarbyl radical" or "hydrocarbyl group" refers to linear or cyclic, aliphatic, olefinic, acetylenic and aryl (aromatic) radicals comprising hydrogen and carbon that are deficient by one hydrogen.

As used herein, an "alkyl radical" includes linear, branched and cyclic paraffin radicals that are deficient by one hydrogen radical; non-limiting examples include methyl ($-CH_3$) and ethyl ($-CH_2CH_3$) radicals. The term "alkenyl radical" refers to linear, branched and cyclic hydrocarbons containing at least one carbon-carbon double bond that is deficient by one hydrogen radical.

Herein the term "R1" and its superscript form "^{R1}" refers to a first reactor in a continuous solution polymerization process; it being understood that R1 is distinctly different from the symbol R^1; the latter is used in chemical formula, e.g. representing a hydrocarbyl group. Similarly, the term "R2" and it's superscript form "^{R2}" refers to a second reactor, and; the term "R3" and it's superscript form "^{R3}" refers to a third reactor.

Catalysts

Organometallic catalyst formulations that are efficient in polymerizing olefins are well known in the art. In the embodiments disclosed herein, at least two

catalyst formulations are employed in a continuous solution polymerization process. One of the catalyst formulations is a single-site catalyst formulation that produces a first ethylene interpolymer. The other catalyst formulation is a heterogeneous catalyst formulation that produces a second ethylene interpolymer. Optionally a third ethylene interpolymer is produced using the heterogeneous catalyst formulation that was used to produce the second ethylene interpolymer, or a different heterogeneous catalyst formulation may be used to produce the third ethylene interpolymer. In the continuous solution process, the at least one homogeneous ethylene interpolymer and the at least one heterogeneous ethylene interpolymer are solution blended and an ethylene interpolymer product is produced.

Single Site Catalyst Formulation

The catalyst components which make up the single site catalyst formulation are not particularly limited, i.e. a wide variety of catalyst components can be used. One non-limiting embodiment of a single site catalyst formulation comprises the following three or four components: a bulky ligand-metal complex; an alumoxane co-catalyst; an ionic activator and optionally a hindered phenol. In Table 2A of this disclosure: "(i)" refers to the amount of "component (i)", i.e. the bulky ligand-metal complex added to R1; "(ii)" refers to "component (ii)", i.e. the alumoxane co-catalyst; "(iii)" refers to "component (iii)" i.e. the ionic activator, and; "(iv)" refers to "component (iv)", i.e. the optional hindered phenol.

Non-limiting examples of component (i) are represented by formula (I):

$$(L^A)_aM(PI)_b(Q)_n \qquad (I)$$

wherein (L^A) represents a bulky ligand; M represents a metal atom; PI represents a phosphinimine ligand; Q represents a leaving group; a is 0 or 1; b is 1 or 2; (a+b) = 2; n is 1 or 2, and; the sum of (a+b+n) equals the valance of the metal M.

Non-limiting examples of the bulky ligand L^A in formula (I) include unsubstituted or substituted cyclopentadienyl ligands or cyclopentadienyl-type ligands, heteroatom substituted and/or heteroatom containing cyclopentadienyl-type ligands. Additional non-limiting examples include, cyclopentaphenanthreneyl ligands, unsubstituted or substituted indenyl ligands, benzindenyl ligands, unsubstituted or substituted fluorenyl ligands, octahydrofluorenyl ligands, cyclooctatetraendiyl ligands, cyclopentacyclododecene ligands, azenyl ligands, azulene ligands, pentalene ligands, phosphoyl ligands, phosphinimine, pyrrolyl ligands, pyrozolyl ligands, carbazolyl ligands, borabenzene ligands and the like, including hydrogenated versions thereof, for example tetrahydroindenyl ligands. In other embodiments, L^A may be any other ligand structure capable of η-bonding to the metal M, such embodiments include both η^3-bonding and η^5-bonding to the metal M. In other embodiments, L^A may comprise one or more heteroatoms, for example, nitrogen, silicon, boron, germanium, sulfur and phosphorous, in combination with carbon atoms to form an open, acyclic, or a fused ring, or ring system, for example, a heterocyclopentadienyl ancillary ligand. Other non-limiting embodiments for L^A include bulky amides, phosphides, alkoxides, aryloxides, imides, carbolides, borollides, porphyrins, phthalocyanines, corrins and other polyazomacrocycles.

Non-limiting examples of metal M in formula (I) include Group 4 metals, titanium, zirconium and hafnium.

The phosphinimine ligand, PI, is defined by formula (II):

$$(R^p)_3 P = N - \qquad (II)$$

wherein the R^p groups are independently selected from: a hydrogen atom; a halogen atom; C_{1-20} hydrocarbyl radicals which are unsubstituted or substituted with one or more halogen atom(s); a C_{1-8} alkoxy radical; a C_{6-10} aryl radical; a C_{6-10} aryloxy radical; an amido radical; a silyl radical of formula $-Si(R^s)_3$, wherein the R^s groups are independently selected from, a hydrogen atom, a C_{1-8} alkyl or alkoxy radical, a C_{6-10} aryl radical, a C_{6-10} aryloxy radical, or a germanyl radical of formula $-Ge(R^G)_3$, wherein the R^G groups are defined as R^s is defined in this paragraph.

The leaving group Q is any ligand that can be abstracted from formula (I) forming a catalyst species capable of polymerizing one or more olefin(s). An equivalent term for Q is an "activatable ligand", i.e. equivalent to the term "leaving group". In some embodiments, Q is a monoanionic labile ligand having a sigma bond to M. Depending on the oxidation state of the metal, the value for n is 1 or 2 such that formula (I) represents a neutral bulky ligand-metal complex. Non-limiting examples of Q ligands include a hydrogen atom, halogens, C_{1-20} hydrocarbyl radicals, C_{1-20} alkoxy radicals, C_{5-10} aryl oxide radicals; these radicals may be linear, branched or cyclic or further substituted by halogen atoms, C_{1-10} alkyl radicals, C_{1-10} alkoxy radicals, C_{6-10} arly or aryloxy radicals. Further non-limiting examples of Q ligands include weak bases such as amines, phosphines, ethers, carboxylates, dienes, hydrocarbyl radicals having from 1 to 20 carbon atoms. In another embodiment, two Q ligands may form part of a fused ring or ring system.

Further embodiments of component (i) of the single site catalyst formulation include structural, optical or enantiomeric isomers (meso and racemic isomers) and

mixtures thereof of the bulky ligand-metal complexes described in formula (I) above.

The second single site catalyst component, component (ii), is an alumoxane co-catalyst that activates component (i) to a cationic complex. An equivalent term for "alumoxane" is "aluminoxane"; although the exact structure of this co-catalyst is uncertain, subject matter experts generally agree that it is an oligomeric species that contain repeating units of the general formula (III):

$$(R)_2AlO\text{-}(Al(R)\text{-}O)_n\text{-}Al(R)_2 \qquad (III)$$

where the R groups may be the same or different linear, branched or cyclic hydrocarbyl radicals containing 1 to 20 carbon atoms and n is from 0 to about 50. A non-limiting example of an alumoxane is methyl aluminoxane (or MAO) wherein each R group in formula (III) is a methyl radical.

The third catalyst component (iii) of the single site catalyst formation is an ionic activator. In general, ionic activators are comprised of a cation and a bulky anion; wherein the latter is substantially non-coordinating. Non-limiting examples of ionic activators are boron ionic activators that are four coordinate with four ligands bonded to the boron atom. Non-limiting examples of boron ionic activators include the following formulas (IV) and (V) shown below;

$$[R^5]^+[B(R^7)_4]^- \qquad (IV)$$

where B represents a boron atom, R^5 is an aromatic hydrocarbyl (e.g. triphenyl methyl cation) and each R^7 is independently selected from phenyl radicals which are unsubstituted or substituted with from 3 to 5 substituents selected from fluorine atoms, $C_{1\text{-}4}$ alkyl or alkoxy radicals which are unsubstituted or substituted by fluorine atoms; and a silyl radical of formula $-Si(R^9)_3$, where each R^9 is

independently selected from hydrogen atoms and C_{1-4} alkyl radicals, and;

compounds of formula (V);

$$[(R^8)_tZH]^+[B(R^7)_4]^- \qquad (V)$$

where B is a boron atom, H is a hydrogen atom, Z is a nitrogen or phosphorus atom, t is 2 or 3 and R^8 is selected from C_{1-8} alkyl radicals, phenyl radicals which are unsubstituted or substituted by up to three C_{1-4} alkyl radicals, or one R^8 taken together with the nitrogen atom may form an anilinium radical and R^7 is as defined above in formula (IV).

In both formula (IV) and (V), a non-limiting example of R^7 is a pentafluorophenyl radical. In general, boron ionic activators may be described as salts of tetra(perfluorophenyl) boron; non-limiting examples include anilinium, carbonium, oxonium, phosphonium and sulfonium salts of tetra(perfluorophenyl)boron with anilinium and trityl (or triphenylmethylium). Additional non-limiting examples of ionic activators include: triethylammonium tetra(phenyl)boron, tripropylammonium tetra(phenyl)boron, tri(n-butyl)ammonium tetra(phenyl)boron, trimethylammonium tetra(p-tolyl)boron, trimethylammonium tetra(o-tolyl)boron, tributylammonium tetra(pentafluorophenyl)boron, tripropylammonium tetra(o,p-dimethylphenyl)boron, tributylammonium tetra(m,m-dimethylphenyl)boron, tributylammonium tetra(p-trifluoromethylphenyl)boron, tributylammonium tetra(pentafluorophenyl)boron, tri(n-butyl)ammonium tetra(o-tolyl)boron, N,N-dimethylanilinium tetra(phenyl)boron, N,N-diethylanilinium tetra(phenyl)boron, N,N-diethylanilinium tetra(phenyl)n-butylboron, N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron, di-(isopropyl)ammonium tetra(pentafluorophenyl)boron, dicyclohexylammonium tetra(phenyl)boron, triphenylphosphonium tetra(phenyl)boron, tri(methylphenyl)phosphonium

tetra(phenyl)boron, tri(dimethylphenyl)phosphonium tetra(phenyl)boron, tropillium tetrakispentafluorophenyl borate, triphenylmethylium tetrakispentafluorophenyl borate, benzene(diazonium)tetrakispentafluorophenyl borate, tropillium tetrakis(2,3,5,6-tetrafluorophenyl)borate, triphenylmethylium tetrakis(2,3,5,6-tetrafluorophenyl)borate, benzene(diazonium) tetrakis(3,4,5-trifluorophenyl)borate, tropillium tetrakis(3,4,5 -trifluorophenyl)borate, benzene(diazonium) tetrakis(3,4,5-trifluorophenyl)borate, tropillium tetrakis(1,2,2-trifluoroethenyl)borate, triphenylmethylium tetrakis(1 ,2,2-trifluoroethenyl)borate, benzene(diazonium) tetrakis(1,2,2-trifluoroethenyl)borate, tropillium tetrakis(2,3,4,5-tetrafluorophenyl)borate, triphenylmethylium tetrakis(2,3,4,5-tetrafluorophenyl)borate, and benzene(diazonium) tetrakis(2,3,4,5 tetrafluorophenyl)borate. Readily available commercial ionic activators include N,N-dimethylanilinium tetrakispentafluorophenyl borate, and triphenylmethylium tetrakispentafluorophenyl borate.

The optional fourth catalyst component of the single site catalyst formation is a hindered phenol, component (iv). Non-limiting example of hindered phenols include butylated phenolic antioxidants, butylated hydroxytoluene, 2,4-di-tertiarybutyl-6-ethyl phenol, 4,4'-methylenebis (2,6-di-tertiary-butylphenol), 1,3, 5-trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxybenzyl) benzene and octadecyl-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate.

To produce an active single site catalyst formulation the quantity and mole ratios of the three or four components, (i) through (iv) are optimized as described below.

Heterogeneous Catalyst Formulations

A number of heterogeneous catalyst formulations are well known to those skilled in the art, including, as non-limiting examples, Ziegler-Natta and chromium catalyst formulations.

In this disclosure, embodiments include an in-line and batch Ziegler-Natta catalyst formulations. The term "in-line Ziegler-Natta catalyst formulation" refers to the continuous synthesis of a small quantity of active Ziegler-Natta catalyst and immediately injecting this catalyst into at least one continuously operating reactor, where the catalyst polymerizes ethylene and one or more optional α-olefins to form an ethylene interpolymer. The terms "batch Ziegler-Natta catalyst formulation" or "batch Ziegler-Natta procatalyst" refer to the synthesis of a much larger quantity of catalyst or procatalyst in one or more mixing vessels that are external to, or isolated from, the continuously operating solution polymerization process. Once prepared, the batch Ziegler-Natta catalyst formulation, or batch Ziegler-Natta procatalyst, is transferred to a catalyst storage tank. The term "procatalyst" refers to an inactive catalyst formulation (inactive with respect to ethylene polymerization); the procatalyst is converted into an active catalyst by adding an alkyl aluminum co-catalyst. As needed, the procatalyst is pumped from the storage tank to at least one continuously operating reactor, where an active catalyst is formed and polymerizes ethylene and one or more optional α-olefins to form an ethylene interpolymer. The procatalyst may be converted into an active catalyst in the reactor or external to the reactor.

A wide variety of chemical compounds can be used to synthesize an active Ziegler-Natta catalyst formulation. The following describes various chemical compounds that may be combined to produce an active Ziegler-Natta catalyst

formulation. Those skilled in the art will understand that the embodiments in this disclosure are not limited to the specific chemical compound disclosed.

An active Ziegler-Natta catalyst formulation may be formed from: a magnesium compound, a chloride compound, a metal compound, an alkyl aluminum co-catalyst and an aluminum alkyl. In Table 2A of this disclosure: "(v)" refers to "component (v)" the magnesium compound; the term "(vi)" refers to the "component (vi)" the chloride compound; "(vii)" refers to "component (vii)" the metal compound; "(viii)" refers to "component (viii)" alkyl aluminum co-catalyst, and; "(ix)" refers to "component (ix)" the aluminum alkyl. As will be appreciated by those skilled in the art, Ziegler-Natta catalyst formulations may contain additional components; a non-limiting example of an additional component is an electron donor, e.g. amines or ethers.

A non-limiting example of an active in-line Ziegler-Natta catalyst formulation can be prepared as follows. In the first step, a solution of a magnesium compound (component (v)) is reacted with a solution of the chloride compound (component (vi)) to form a magnesium chloride support suspended in solution. Non-limiting examples of magnesium compounds include $Mg(R^1)_2$; wherein the R^1 groups may be the same or different, linear, branched or cyclic hydrocarbyl radicals containing 1 to 10 carbon atoms. Non-limiting examples of chloride compounds include R^2Cl; wherein R^2 represents a hydrogen atom, or a linear, branched or cyclic hydrocarbyl radical containing 1 to 10 carbon atoms. In the first step, the solution of magnesium compound may also contain an aluminum alkyl (component (ix)). Non-limiting examples of aluminum alkyl include $Al(R^3)_3$, wherein the R^3 groups may be the same or different, linear, branched or cyclic hydrocarbyl radicals containing from 1 to 10 carbon atoms. In the second step a solution of the metal compound

(component (vii)) is added to the solution of magnesium chloride and the metal compound is supported on the magnesium chloride. Non-limiting examples of suitable metal compounds include $M(X)_n$ or $MO(X)_n$; where M represents a metal selected from Group 4 through Group 8 of the Periodic Table, or mixtures of metals selected from Group 4 through Group 8; O represents oxygen, and; X represents chloride or bromide; n is an integer from 3 to 6 that satisfies the oxidation state of the metal. Additional non-limiting examples of suitable metal compounds include Group 4 to Group 8 metal alkyls, metal alkoxides (which may be prepared by reacting a metal alkyl with an alcohol) and mixed-ligand metal compounds that contain a mixture of halide, alkyl and alkoxide ligands. In the third step a solution of an alkyl aluminum co-catalyst (component (viii)) is added to the metal compound supported on the magnesium chloride. A wide variety of alkyl aluminum co-catalysts are suitable, as expressed by formula (VI):

$$Al(R^4)_p(OR^5)_q(X)_r \qquad (VI)$$

wherein the R^4 groups may be the same or different, hydrocarbyl groups having from 1 to 10 carbon atoms; the OR^5 groups may be the same or different, alkoxy or aryloxy groups wherein R^5 is a hydrocarbyl group having from 1 to 10 carbon atoms bonded to oxygen; X is chloride or bromide, and; (p+q+r) = 3, with the proviso that p is greater than 0. Non-limiting examples of commonly used alkyl aluminum co-catalysts include trimethyl aluminum, triethyl aluminum, tributyl aluminum, dimethyl aluminum methoxide, diethyl aluminum ethoxide, dibutyl aluminum butoxide, dimethyl aluminum chloride or bromide, diethyl aluminum chloride or bromide, dibutyl aluminum chloride or bromide and ethyl aluminum dichloride or dibromide.

The process described in the paragraph above, to synthesize an active in-line Ziegler-Natta catalyst formulation, can be carried out in a variety of solvents;

non-limiting examples of solvents include linear or branched C_5 to C_{12} alkanes or mixtures thereof. To produce an active in-line Ziegler-Natta catalyst formulation the quantity and mole ratios of the five components, (v) through (ix), are optimized as described below.

Additional embodiments of heterogeneous catalyst formulations include formulations where the "metal compound" is a chromium compound; non-limiting examples include silyl chromate, chromium oxide and chromocene. In some embodiments, the chromium compound is supported on a metal oxide such as silica or alumina. Heterogeneous catalyst formulations containing chromium may also include co-catalysts; non-limiting examples of co-catalysts include trialkylaluminum, alkylaluminoxane and dialkoxyalkylaluminum compounds and the like.

Solution Polymerization Process: In-line Heterogeneous Catalyst Formulation

The ethylene interpolymer products disclosed herein, useful to manufacture monolayer or multilayer films having improved caulkability, were produced in a continuous solution polymerization process. This solution process has been fully described in Canadian Patent Application No. CA 2,868,640, filed October 21, 2014 and entitled "Solution Polymerization Process"; which is incorporated by reference into this application in its' entirety.

Embodiments of this process includes at least two continuously stirred reactors, R1 and R2 and an optional tubular reactor R3. Feeds (solvent, ethylene, at least two catalyst formulations, optional hydrogen and optional α-olefin) are feed to at least two reactor continuously. A single site catalyst formulation is injected into R1 and a first heterogeneous catalyst formation is injected into R2 and optionally R3. Optionally, a second heterogeneous catalyst formulation is injected

into R3. The single site catalyst formulation includes an ionic activator (component (iii)), a bulky ligand-metal complex (component (i)), an alumoxane co-catalyst (component (ii)) and an optional hindered phenol (component (iv)), respectively.

R1 and R2 may be operated in series or parallel modes of operation. To be more clear, in series mode 100% of the effluent from R1 flows directly into R2. In parallel mode, R1 and R2 operate independently and the effluents from R1 and R2 are combined downstream of the reactors.

A heterogeneous catalyst formulation is injected into R2. In one embodiment a first in-line Ziegler-Natta catalyst formulation is injected into R2. A first in-line Ziegler-Natta catalyst formation is formed within a first heterogeneous catalyst assembly by optimizing the following molar ratios: (aluminum alkyl)/(magnesium compound) or (ix)/(v); (chloride compound)/(magnesium compound) or (vi)/(v); (alkyl aluminum co-catalyst)/(metal compound) or (viii)/(vii), and; (aluminum alkyl)/(metal compound) or (ix)/(vii); as well as the time these compounds have to react and equilibrate. Within the first heterogeneous catalyst assembly the time between the addition of the chloride compound and the addition of the metal compound (component (vii)) is controlled; hereafter HUT-1 (the first Hold-Up-Time). The time between the addition of component (vii) and the addition of the alkyl aluminum co-catalyst, component (viii), is also controlled; hereafter HUT-2 (the second Hold-Up-Time). In addition, the time between the addition of the alkyl aluminum co-catalyst and the injection of the in-line Ziegler-Natta catalyst formulation into R2 is controlled; hereafter HUT-3 (the third Hold-Up-Time). Optionally, 100% the alkyl aluminum co-catalyst, may be injected directly into R2. Optionally, a portion of the alkyl aluminum co-catalyst may be injected into the first heterogeneous catalyst assembly and the remaining portion injected directly into

R2. The quantity of in-line heterogeneous catalyst formulation added to R2 is expressed as the parts-per-million (ppm) of metal compound (component (vii)) in the reactor solution, hereafter "R2 (vii) (ppm)". Injection of the in-line heterogeneous catalyst formulation into R2 produces a second ethylene interpolymer in a second exit stream (exiting R2). Optionally the second exit stream is deactivated by adding a catalyst deactivator. If the second exit stream is not deactivated the second exit stream enters reactor R3. One embodiment of a suitable R3 design is a tubular reactor. Optionally, one or more of the following fresh feeds may be injected into R3; solvent, ethylene, hydrogen, α-olefin and a first or second heterogeneous catalyst formulation; the latter is supplied from a second heterogeneous catalyst assembly. The chemical composition of the first and second heterogeneous catalyst formulations may be the same, or different, i.e. the catalyst components ((v) through (ix)), mole ratios and hold-up-times may differ in the first and second heterogeneous catalyst assemblies. The second heterogeneous catalyst assembly generates an efficient catalyst by optimizing hold-up-times and the molar ratios of the catalyst components.

In reactor R3, a third ethylene interpolymer may, or may not, form. A third ethylene interpolymer will not form if a catalyst deactivator is added upstream of reactor R3. A third ethylene interpolymer will be formed if a catalyst deactivator is added downstream of R3. The optional third ethylene interpolymer may be formed using a variety of operational modes (with the proviso that catalyst deactivator is not added upstream). Non-limiting examples of operational modes include: (a) residual ethylene, residual optional α-olefin and residual active catalyst entering R3 react to form the third ethylene interpolymer, or; (b) fresh process solvent, fresh ethylene and optionally fresh α-olefin are added to R3 and the residual active

catalyst entering R3 forms the third ethylene interpolymer, or; (c) a second in-line heterogeneous catalyst formulation is added to R3 to polymerize residual ethylene and residual optional α-olefin to form the third ethylene interpolymer, or; (d) fresh process solvent, ethylene, optional α-olefin and a second in-line heterogeneous catalyst formulation are added to R3 to form the third ethylene interpolymer.

In series mode, R3 produces a third exit stream (the stream exiting R3) containing the first ethylene interpolymer, the second ethylene interpolymer and optionally a third ethylene interpolymer. A catalyst deactivator may be added to the third exit stream producing a deactivated solution; with the proviso a catalyst deactivator is not added if a catalyst deactivator was added upstream of R3.

The deactivated solution passes through a pressure let down device, a heat exchanger and a passivator is added forming a passivated solution. The passivated solution passes through a series of vapor liquid separators and ultimately the ethylene interpolymer product enters polymer recover. Non-limiting examples of polymer recovery operations include one or more gear pump, single screw extruder or twin screw extruder that forces the molten ethylene interpolymer product through a pelletizer.

Embodiments of the manufactured articles disclosed herein, may also be formed from ethylene interpolymer products synthesized using a batch Ziegler-Natta catalyst. Typically, a first batch Ziegler-Natta procatalyst is injected into R2 and the procatalyst is activated within R2 by injecting an alkyl aluminum co-catalyst forming a first batch Ziegler-Natta catalyst. Optionally, a second batch Ziegler-Natta procatalyst is injected into R3.

A variety of solvents may be used as the process solvent; non-limiting examples include linear, branched or cyclic C_5 to C_{12} alkanes. Non-limiting examples of α-olefins include C_3 to C_{10} α-olefins.

In the continuous polymerization process, polymerization is terminated by adding a catalyst deactivator. The catalyst deactivator substantially stops the polymerization reaction by changing active catalyst species to inactive forms. Prior to entering the vapor/liquid separator, a passivator or acid scavenger is added to the deactivated solution. Suitable passivators are well known in the art, non-limiting examples include alkali or alkaline earth metal salts of carboxylic acids or hydrotalcites.

In this disclosure, the number of solution reactors is not particularly important; with the proviso that the continuous solution polymerization process comprises at least two reactors that employ at least one single-site catalyst formulation and at least one heterogeneous catalyst formulation.

<u>First Ethylene Interpolymer</u>

The first ethylene interpolymer is produced with a single-site catalyst formulation. If the optional α-olefin is not added to reactor 1 (R1), then the ethylene interpolymer produced in R1 is an ethylene homopolymer. If an α-olefin is added, the following weight ratio is one parameter to control the density of the first ethylene interpolymer: $((\alpha\text{-olefin})/(\text{ethylene}))^{R1}$. The symbol "$\sigma^1$" refers to the density of the first ethylene interpolymer produced in R1. The upper limit on σ^1 may be about 0.975 g/cm^3; in some cases about 0.965 g/cm^3 and; in other cases about 0.955 g/cm^3. The lower limit on σ^1 may be about 0.855 g/cm^3, in some cases about 0.865 g/cm^3, and; in other cases about 0.875 g/cm^3.

Methods to determine the $CDBI_{50}$ (Composition Distribution Branching Index) of an ethylene interpolymer are well known to those skilled in the art. The $CDBI_{50}$, expressed as a percent, is defined as the percent of the ethylene interpolymer whose comonomer composition is within 50% of the median comonomer composition. It is also well known to those skilled in the art that the $CDBI_{50}$ of ethylene interpolymers produced with single-site catalyst formulations are higher relative to the $CDBI_{50}$ of α-olefin containing ethylene interpolymers produced with heterogeneous catalyst formulations. The upper limit on the $CDBI_{50}$ of the first ethylene interpolymer (produced with a single-site catalyst formulation) may be about 98%, in other cases about 95% and in still other cases about 90%. The lower limit on the $CDBI_{50}$ of the first ethylene interpolymer may be about 70%, in other cases about 75% and in still other cases about 80%.

As is well known to those skilled in the art the M_w/M_n of ethylene interpolymers produced with single site catalyst formulations are lower relative to ethylene interpolymers produced with heterogeneous catalyst formulations. Thus, in the embodiments disclosed, the first ethylene interpolymer has a lower M_w/M_n relative to the second ethylene interpolymer; where the second ethylene interpolymer is produced with a heterogeneous catalyst formulation. The upper limit on the M_w/M_n of the first ethylene interpolymer may be about 2.8, in other cases about 2.5 and in still other cases about 2.2. The lower limit on the M_w/M_n the first ethylene interpolymer may be about 1.7, in other cases about 1.8 and in still other cases about 1.9.

The first ethylene interpolymer contains catalyst residues that reflect the chemical composition of the single-site catalyst formulation used. Those skilled in the art will understand that catalyst residues are typically quantified by the parts per

million of metal in the first ethylene interpolymer, where metal refers to the metal in component (i), i.e. the metal in the "bulky ligand-metal complex"; hereafter (and in the claims) this metal will be referred to "metal A". As recited earlier in this disclosure, non-limiting examples of metal A include Group 4 metals, titanium, zirconium and hafnium. The upper limit on the ppm of metal A in the first ethylene interpolymer may be about 1.0 ppm, in other cases about 0.9 ppm and in still other cases about 0.8 ppm. The lower limit on the ppm of metal A in the first ethylene interpolymer may be about 0.01 ppm, in other cases about 0.1 ppm and in still other cases about 0.2 ppm.

The amount of hydrogen added to R1 can vary over a wide range allowing the continuous solution process to produce first ethylene interpolymers that differ greatly in melt index, hereafter I_2^1 (melt index is measured at 190°C using a 2.16 kg load following the procedures outlined in ASTM D1238). The quantity of hydrogen added to R1 is expressed as the parts-per-million (ppm) of hydrogen in R1 relative to the total mass in reactor R1; hereafter H_2^{R1} (ppm). The upper limit on I_2^1 may be about 200 dg/min, in some cases about 100 dg/min; in other cases about 50 dg/min, and; in still other cases about 1 dg/min. The lower limit on I_2^1 may be about 0.01 dg/min, in some cases about 0.05 dg/min; in other cases about 0.1 dg/min, and; in still other cases about 0.5 dg/min.

The upper limit on the weight percent (wt%) of the first ethylene interpolymer in the ethylene interpolymer product may be about 60 wt%, in other cases about 55 wt% and in still other cases about 50 wt%. The lower limit on the wt % of the first ethylene interpolymer in the ethylene interpolymer product may be about 15 wt%; in other cases about 25 wt% and in still other cases about 30 wt%.

Second Ethylene Interpolymer

If optional α-olefin is not added to reactor 2 (R2) either by adding fresh α-olefin to R2 (or carried over from R1) then the ethylene interpolymer produced in R2 is an ethylene homopolymer. If an optional α-olefin is present in R2, the following weight ratio is one parameter to control the density of the second ethylene interpolymer produced in R2: $((\alpha\text{-olefin})/(\text{ethylene}))^{R2}$. Hereafter, the symbol "σ^2" refers to the density of the ethylene interpolymer produced in R2. The upper limit on σ^2 may be about 0.975 g/cm^3; in some cases about 0.965 g/cm^3 and; in other cases about 0.955 g/cm^3. Depending on the heterogeneous catalyst formulation used, the lower limit on σ^2 may be about 0.89 g/cm^3, in some cases about 0.90 g/cm^3, and; in other cases about 0.91 g/cm^3.

A heterogeneous catalyst formulation is used to produce the second ethylene interpolymer. If the second ethylene interpolymer contains an α-olefin, the $CDBI_{50}$ of the second ethylene interpolymer is lower relative to the $CDBI_{50}$ of the first ethylene interpolymer that was produced with a single-site catalyst formulation. In an embodiment of this disclosure, the upper limit on the $CDBI_{50}$ of the second ethylene interpolymer (that contains an α-olefin) may be about 70%, in other cases about 65% and in still other cases about 60%. In an embodiment of this disclosure, the lower limit on the $CDBI_{50}$ of the second ethylene interpolymer (that contains an α-olefin) may be about 45%, in other cases about 50% and in still other cases about 55%. If an α-olefin is not added to the continuous solution polymerization process the second ethylene interpolymer is an ethylene homopolymer. In the case of a homopolymer, which does not contain α-olefin, one can still measure a $CDBI_{50}$ using TREF. In the case of a homopolymer, the upper limit on the $CDBI_{50}$ of the second ethylene interpolymer may be about 98%, in other cases about 96% and in

still other cases about 95%, and; the lower limit on the $CDBI_{50}$ may be about 88%, in other cases about 89% and in still other cases about 90%. It is well known to those skilled in the art that as the α-olefin content in the second ethylene interpolymer approaches zero, there is a smooth transition between the recited $CDBI_{50}$ limits for the second ethylene interpolymers (that contain an α-olefin) and the recited $CDBI_{50}$ limits for the second ethylene interpolymers that are ethylene homopolymers. Typically, the $CDBI_{50}$ of the first ethylene interpolymer is higher than the $CDBI_{50}$ of the second ethylene interpolymer.

The M_w/M_n of second ethylene interpolymer is higher than the M_w/M_n of the first ethylene interpolymer. The upper limit on the M_w/M_n of the second ethylene interpolymer may be about 4.4, in other cases about 4.2 and in still other cases about 4.0. The lower limit on the M_w/M_n of the second ethylene interpolymer may be about 2.2. M_w/M_n's of 2.2 are observed when the melt index of the second ethylene interpolymer is high, or when the melt index of the ethylene interpolymer product is high, e.g. greater than 10 g/10 minutes. In other cases the lower limit on the M_w/M_n of the second ethylene interpolymer may be about 2.4 and in still other cases about 2.6.

The second ethylene interpolymer contains catalyst residues that reflect the chemical composition of heterogeneous catalyst formulation. Those skilled in the art with understand that heterogeneous catalyst residues are typically quantified by the parts per million of metal in the second ethylene interpolymer, where the metal refers to the metal originating from component (vii), i.e. the "metal compound"; hereafter (and in the claims) this metal will be referred to as "metal B". As recited earlier in this disclosure, non-limiting examples of metal B include metals selected from Group 4 through Group 8 of the Periodic Table, or mixtures of metals selected

from Group 4 through Group 8. The upper limit on the ppm of metal B in the second ethylene interpolymer may be about 12 ppm, in other cases about 10 ppm and in still other cases about 8 ppm. The lower limit on the ppm of metal B in the second ethylene interpolymer may be about 0.5 ppm, in other cases about 1 ppm and in still other cases about 3 ppm. While not wishing to be bound by any particular theory, in series mode of operation it is believed that the chemical environment within the second reactor deactivates the single site catalyst formulation, or; in parallel mode of operation the chemical environment within R2 deactivates the single site catalyst formation.

The amount of hydrogen added to R2 can vary over a wide range which allows the continuous solution process to produce second ethylene interpolymers that differ greatly in melt index, hereafter I_2^2. The quantity of hydrogen added is expressed as the parts-per-million (ppm) of hydrogen in R2 relative to the total mass in reactor R2; hereafter H_2^{R2} (ppm). The upper limit on I_2^2 may be about 1000 dg/min; in some cases about 750 dg/min; in other cases about 500 dg/min, and; in still other cases about 200 dg/min. The lower limit on I_2^2 may be about 0.3 dg/min, in some cases about 0.4 dg/min, in other cases about 0.5 dg/min, and; in still other cases about 0.6 dg/min.

The upper limit on the weight percent (wt%) of the second ethylene interpolymer in the ethylene interpolymer product may be about 85 wt%, in other cases about 80 wt% and in still other cases about 70 wt%. The lower limit on the wt % of the second ethylene interpolymer in the ethylene interpolymer product may be about 30 wt%; in other cases about 40 wt% and in still other cases about 50 wt%.

Third Ethylene Interpolymer

A third ethylene interpolymer is not produced in R3 if a catalyst deactivator is added upstream of R3. If a catalyst deactivator is not added and optional α-olefin is not present then the third ethylene interpolymer produced in R3 is an ethylene homopolymer. If a catalyst deactivator is not added and optional α-olefin is present in R3, the following weight ratio determines the density of the third ethylene interpolymer: $((\alpha\text{-olefin})/(\text{ethylene}))^{R3}$. In the continuous solution polymerization process $((\alpha\text{-olefin})/(\text{ethylene}))^{R3}$ is one of the control parameter used to produce a third ethylene interpolymer with a desired density. Hereafter, the symbol "σ^3" refers to the density of the ethylene interpolymer produced in R3. The upper limit on σ^3 may be about 0.975 g/cm^3; in some cases about 0.965 g/cm^3 and; in other cases about 0.955 g/cm^3. Depending on the heterogeneous catalyst formulations used, the lower limit on σ^3 may be about 0.89 g/cm^3, in some cases about 0.90 g/cm^3, and; in other cases about 0.91 g/cm^3. Optionally, a second heterogeneous catalyst formulation may be added to R3. In other cases (i.e. α-olefin containing ethylene interpolymer products) the upper limit on the $CDBI_{50}$ of the optional third ethylene interpolymer may be about 65%, in other cases about 60% and in still other cases about 55%. The $CDBI_{50}$ of an α-olefin containing optional third ethylene interpolymer will be lower than the $CDBI_{50}$ of the first ethylene interpolymer produced with the single-site catalyst formulation. Typically, the lower limit on the $CDBI_{50}$ of the optional third ethylene interpolymer (containing an α-olefin) may be about 35%, in other cases about 40% and in still other cases about 45%. If an α-olefin is not added to the continuous solution polymerization process the optional third ethylene interpolymer is an ethylene homopolymer. In the case of an ethylene homopolymer the upper limit on the $CDBI_{50}$ may be about 98%, in other cases

about 96% and in still other cases about 95%, and; the lower limit on the $CDBI_{50}$ may be about 88%, in other cases about 89% and in still other cases about 90%. Typically, the $CDBI_{50}$ of the first ethylene interpolymer is higher than the $CDBI_{50}$ of the third ethylene interpolymer and second ethylene interpolymer.

The upper limit on the M_w/M_n of the optional third ethylene interpolymer may be about 5.0, in other cases about 4.8 and in still other cases about 4.5. The lower limit on the M_w/M_n of the optional third ethylene interpolymer may be about 2.2, in other cases about 2.4 and in still other cases about 2.6. The M_w/M_n of the optional third ethylene interpolymer is higher than the M_w/M_n of the first ethylene interpolymer. When blended together, the second and third ethylene interpolymer have a fourth M_w/M_n which is not broader than the M_w/M_n of the second ethylene interpolymer.

The catalyst residues in the optional third ethylene interpolymer reflect the chemical composition of the heterogeneous catalyst formulation(s) used, i.e. the first and optionally a second heterogeneous catalyst formulation. The chemical compositions of the first and second heterogeneous catalyst formulations may be the same or different; for example a first component (vii) and a second component (vii) may be used to synthesize the first and second heterogeneous catalyst formulation. As recited above, "metal B" refers to the metal that originates from the first component (vii). Hereafter, "metal C" refers to the metal that originates from the second component (vii). Metal B and optional metal C may be the same, or different. Non-limiting examples of metal B and metal C include metals selected from Group 4 through Group 8 of the Periodic Table, or mixtures of metals selected from Group 4 through Group 8. The upper limit on the ppm of (metal B + metal C) in the optional third ethylene interpolymer may be about 12 ppm, in other cases

about 10 ppm and in still other cases about 8 ppm. The lower limit on the ppm of (metal B + metal C) in the optional third ethylene interpolymer may be about 0.5 ppm, in other cases about 1 ppm and in still other cases about 3 ppm.

Optionally hydrogen may be added to R3. Adjusting the amount of hydrogen in R3, hereafter H_2^{R3} (ppm), allows the continuous solution process to produce third ethylene interpolymers that differ widely in melt index, hereafter I_2^3. The upper limit on I_2^3 may be about 2000 dg/min; in some cases about 1500 dg/min; in other cases about 1000 dg/min, and; in still other cases about 500 dg/min. The lower limit on I_2^3 may be about 0.5 dg/min, in some cases about 0.6 dg/min, in other cases about 0.7 dg/min, and; in still other cases about 0.8 dg/min.

The upper limit on the weight percent (wt%) of the optional third ethylene interpolymer in the ethylene interpolymer product may be about 30 wt%, in other cases about 25 wt% and in still other cases about 20 wt%. The lower limit on the wt % of the optional third ethylene interpolymer in the ethylene interpolymer product may be 0 wt%; in other cases about 5 wt% and in still other cases about 10 wt%.

Ethylene Interpolymer Product

The upper limit on the density of the ethylene interpolymer product may be about 0.940 g/cm^3; in some cases about 0.937 g/cm^3 and; in other cases about 0.935 g/cm^3. The lower limit on the density of the ethylene interpolymer product may be about 0.890 g/cm^3, in some cases about 0.895 g/cm^3, and; in other cases about 0.900 g/cm^3.

The upper limit on the $CDBI_{50}$ of the ethylene interpolymer product may be about 97%, in other cases about 90% and in still other cases about 85%. An ethylene interpolymer product with a $CDBI_{50}$ of 97% may result if an α-olefin is not added to the continuous solution polymerization process; in this case, the ethylene

interpolymer product is an ethylene homopolymer. The lower limit on the $CDBI_{50}$ of an ethylene interpolymer may be about 20%, in other cases about 40% and in still other cases about 60%.

The upper limit on the M_w/M_n of the ethylene interpolymer product may be about 25, in other cases about 15 and in still other cases about 9. The lower limit on the M_w/M_n of the ethylene interpolymer product may be 2.0, in other cases about 2.2 and in still other cases about 2.4.

The catalyst residues in the ethylene interpolymer product reflect the chemical compositions of: the single-site catalyst formulation employed in R1; the first heterogeneous catalyst formulation employed in R2, and; optionally the first or optionally the first and second heterogeneous catalyst formulation employed in R3. In this disclosure, catalyst residues were quantified by measuring the parts per million of catalytic metal in the ethylene interpolymer products. In addition, the elemental quantities (ppm) of magnesium, chlorine and aluminum were quantified. Catalytic metals originate from two or optionally three sources, specifically: 1) "metal A" that originates from component (i) that was used to form the single-site catalyst formulation; (2) "metal B" that originates from the first component (vii) that was used to form the first heterogeneous catalyst formulation, and; (3) optionally "metal C" that originates from the second component (vii) that was used to form the optional second heterogeneous catalyst formulation. Metals A, B and C may be the same or different. In this disclosure the term "total catalytic metal" is equivalent to the sum of catalytic metals A+B+C. Further, in this disclosure the terms "first total catalytic metal" and "second total catalyst metal" are used to differentiate between the first ethylene interpolymer product of this disclosure and a comparative "polyethylene composition" that were produced using different catalyst formulations.

The upper limit on the ppm of metal A in the ethylene interpolymer product may be about 0.6 ppm, in other cases about 0.5 ppm and in still other cases about 0.4 ppm. The lower limit on the ppm of metal A in the ethylene interpolymer product may be about 0.001 ppm, in other cases about 0.01 ppm and in still other cases about 0.03 ppm. The upper limit on the ppm of (metal B + metal C) in the ethylene interpolymer product may be about 11 ppm, in other cases about 9 ppm and in still other cases about 7 ppm. The lower limit on the ppm of (metal B + metal C) in the ethylene interpolymer product may be about 0.5 ppm, in other cases about 1 ppm and in still other cases about 3 ppm.

In some embodiments, ethylene interpolymers may be produced where the catalytic metals (metal A, metal B and metal C) are the same metal; a non-limiting example would be titanium. In such embodiments, the ppm of (metal B + metal C) in the ethylene interpolymer product is calculated using equation (VII):

$$ppm^{(B+C)} = ((ppm^{(A+B+C)} - (f^A \times ppm^A))/(1-f^A) \qquad \text{(VII)}$$

where: $ppm^{(B+C)}$ is the calculated ppm of (metal B + metal C) in the ethylene interpolymer product; $ppm^{(A+B+C)}$ is the total ppm of catalyst residue in the ethylene interpolymer product as measured experimentally, i.e. (metal A ppm + metal B ppm + metal C ppm); f^A represents the weight fraction of the first ethylene interpolymer in the ethylene interpolymer product, f^A may vary from about 0.15 to about 0.6, and; ppm^A represents the ppm of metal A in the first ethylene interpolymer. In equation (VII) ppm^A is assumed to be 0.35 ppm.

Embodiments of the ethylene interpolymer products disclosed herein have lower catalyst residues relative to the polyethylene polymers described in US 6,277,931. Higher catalyst residues in U.S. 6,277,931 increase the complexity of the continuous solution polymerization process; an example of increased

complexity includes additional purification steps to remove catalyst residues from the polymer. In contrast, in the present disclosure, catalyst residues are not removed. In this disclosure, the upper limit on the "total catalytic metal", i.e. the total ppm of (metal A ppm + metal B ppm + optional metal C ppm) in the ethylene interpolymer product may be about 11 ppm, in other cases about 9 ppm and in still other cases about 7, and; the lower limit on the total ppm of catalyst residuals (metal A + metal B + optional metal C) in the ethylene interpolymer product may be about 0.5 ppm, in other cases about 1 ppm and in still other cases about 3 ppm.

The upper limit on melt index of the ethylene interpolymer product may be about 15 dg/min, in some cases about 13 dg/min and in other cases about 12 dg/min. The lower limit on the melt index of the ethylene interpolymer product may be about 0.3 dg/min, in some cases about 0.4 dg/min and in other cases about 0.5.

A computer generated ethylene interpolymer product is illustrated in Table 1; this simulations was based on fundamental kinetic models (with kinetic constants specific for each catalyst formulation) as well as feeds, mole ratios and reactor conditions. The simulation was based on the configuration of the solution pilot plant as described below; which was used to produce Examples 2 of ethylene interpolymer product disclosed herein. Simulated Example 13 was synthesized using a single-site catalyst formulation (PIC-1) in R1 and an in-line Ziegler-Natta catalyst formulation in R2 and R3. Table 1 discloses a non-limiting example of the density, melt index and molecular weights of the first, second and third ethylene interpolymers produced in the three reactors (R1, R2 and R3); these three interpolymers are combined to produce Simulated Example 13 (the ethylene polymer product). As shown in Table 1, the Simulated Example 13 product has a density of 0.9169 g/cm^3, a melt index of 1.0 dg/min, a branch frequency of 12.1 (the

number of C_6-branches per 1000 carbon atoms (1-octene comonomer)) and a M_w/M_n of 3.11. Simulated Example 13 comprises: a first, second and third ethylene interpolymer having a first, second and third melt index of 0.31 dg/min, 1.92 dg/min and 4.7 dg/min, respectively; a first, second and third density of 0.9087 g/cm^3, 0.9206 g/cm^3 and 0.9154 g/cm^3, respectively; a first, second and third M_w/M_n of 2.03 M_w/M_n, 3.29 M_w/M_n and 3.28 M_w/M_n, respectively, and; a first, second and third $CDBI_{50}$ of 90 to 95%, 55 to 60% and 45 to 55%, respectively. The simulated production rate of Simulated Example 13 was 90.9 kg/hr and the R3 exit temperature was 217.1°C.

Ethylene Interpolymer Products Suitable for Multilayer Films

Tables 2A through 2C summarize process conditions that were used to produce Example 2 and Comparative Example 2. The production rates of Examples 2 was 17.6 percent higher relative to Comparative Example 2. In Examples 2 a single-site catalyst formulation was employed in reactor 1 and an in-line Ziegler-Natta catalyst formulations was employed in reactor 2, producing an ethylene interpolymer products having production rate from 94.8 kg/hr. In contrast, in Comparative Example 2 a single-site catalyst formulation was used in both reactors 1 and 2, producing "a comparative ethylene interpolymer", Comparative Example 2, at a maximum production rate of 80.6 kg/hr. In Examples 2 and Comparative Example 2, reactors 1 and 2 were configured in series, i.e. the effluent from reactor 1 flowed directly into reactor 2. Table 2B and 2C document additional solution process parameter recorded during the production of Example 2 and Comparative Example 2. Table 3 summarizes the density, melt flow properties and molecular weights of Example 2 and Comparative Example 2.

Table 4 compares the materials that were used to prepare 9-layer films for caulkability testing, i.e. measuring the "hole size" and quantifying the caulkability of the material used in the sealant layer. Examples 200 and 201 are embodiments of the ethylene interpolymers claimed herein. Comparative C is a commercial product available from The Dow Chemical Company designated Elite 5400G; which is produced in a series dual reactor solution process using a single-site catalyst is the first reactor and a batch Ziegler-Natta catalyst in the second reactor. Comparative BA, BC, BD are commercial products available from NOVA Chemicals designated SURPASS FPs117-C, FPs016-C and FPs116-CX01; which were produced in a series dual reactor solution process using a single-site catalyst in both reactors. Comparative AE is a commercial product called IMPACT D143 available from the Chevron Phillips Chemical Company; which is a single reactor slurry product produced with a single-site catalyst. Comparatives BE and S are commercial product available from NOVA Chemicals Corporation produced in a one solution reactor using an in-line Ziegler-Natta catalyst. Comparative BB, available from The Dow Chemical Company, Attane 4201G, is produced in one solution reactor using a batch Ziegler-Natta catalyst. Comparative BF is a single reactor gas phase product called PF-0118-F, produced with a batch Ziegler-Natta catalyst, available from NOVA Chemicals Corporation. EVA is Elvax 3135X available from DuPont Packaging & Industrial Polymers, which is poly(ethylene-co-vinyl acetate) produced in a high pressure process. The final sealant tested was an Ionomer, Surlyn 1601-2 available from DuPont Packaging & Industrial Polymers. Ionomers are poly(ethylene-co-methacrylic acid) copolymers, produced in a high pressure process, in a subsequent process step a portion of the acidic groups are neutralized with metal cations. Thus ionomers contain ionic groups and define a

unique class of sealant; i.e. distinctly different relative to the ethylene interpolymer products disclosed herein. Ionomers are generally regarded, by those of ordinary experience in the art, as sealants having high caulkability. The packaging industry is demanding ethylene interpolymer products that perform as well as ionomers.

The remaining materials in Table 4 are a maleic anhydride grafted polyethylene, Bynel 41E710, available from DuPont Packaging & Industrial Polymers. Bynel was used to formulate a tie-layer between the various ethylene interpolymer-like layers of the 9-layer film ethylene interpolymers and Nylon, i.e. Ultramid C40 L 01 available from BASF Corporation.

Table 5 shows the construction of the 9-layer films that were evaluated in the caulkability test. A consistent 9-layer structure was used, with the exception that the composition of the sealant layer (layer 1) was changed from sample to sample. The 9-layer films were consistently 3.5-mil in total thickness. The sealant layer contained a consistent amount of additives, i.e. antiblock, slip and processing aid; these additives were introduced by gravimetrically feeding 8.5 wt% of an additive containing masterbatch to extruder 1, along with 91.5 wt% of the sealant material.

Table 6 summarizes results from the caulkability test. This test is fully described below in the experimental section of this disclosure. In brief, the caulkability test uses a Leak Test (ASTM F2054-13) to calculate an average hole diameter, "hole size". In this disclosure the "hole size" is used to quantify the caulkability of the sealant in layer 1 of the 9-layer multilayer films. Hole size quantifies the sealants caulkability or the ability of the sealant flow around a contaminant (a copper wire) and form a heats seal with high integrity. The copper wire simulates the presence of a contaminant in the sealing area. As shown in

Table 6 and Figure 1, the ethylene interpolymer product Example 201, disclosed herein, is the best performing poly(ethylene-co-α-olefin).

Dilution Index (Y_d) of Ethylene Interpolymer Products

In Figure 2 the Dilution Index (Y_d), having dimensions of ° (degrees)) and Dimensionless Modulus (X_d) are plotted for several embodiments of the ethylene interpolymer products disclosed herein (the solid symbols), as well as comparative ethylene interpolymer products, i.e. Comparative A, D, E and S. Further, Figure 2 defines the following three quadrants:

- Type I: $Y_d > 0$ and $X_d < 0$;
- Type II: $Y_d > 0$ and $X_d > 0$, and;
- Type III: $Y_d < 0$ and $X_d > 0$.

The data plotted in Figure 2 is also tabulated in Table 7. In Figure 2, Comparative S (open triangle) was used as the rheological reference in the Dilution Index test protocol. Comparative S is an ethylene interpolymer product comprising an ethylene interpolymer synthesized using an in-line Ziegler-Natta catalyst in one solution reactor, i.e. SCLAIR® FP120-C which is an ethylene/1-octene interpolymer available from NOVA Chemicals Corporation (Calgary, Alberta, Canada). Comparatives D and E (open diamonds, $Y_d < 0$, $X_d > 0$) are ethylene interpolymer products comprising a first ethylene interpolymer synthesized using a single-site catalyst formation and a second ethylene interpolymer synthesized using a batch Ziegler-Natta catalyst formulation employing a dual reactor solution process, i.e. Elite® 5100G and Elite® 5400G, respectively, both ethylene/1-octene interpolymers available from The Dow Chemical Company (Midland, Michigan, USA). Comparative A (open square, $Y_d > 0$ and $X_d < 0$) was an ethylene interpolymer product comprising a first and second ethylene interpolymer synthesized using a

single-site catalyst formation in a dual reactor solution process, i.e. SURPASS® FPs117-C which is an ethylene/1-octene interpolymer available from NOVA Chemicals Corporation (Calgary, Alberta, Canada).

The following defines the Dilution Index (Y_d) and Dimensionless Modulus (X_d). In addition to having molecular weights, molecular weight distributions and branching structures, blends of ethylene interpolymers may exhibit a hierarchical structure in the melt phase. In other words, the ethylene interpolymer components may be, or may not be, homogeneous down to the molecular level depending on interpolymer miscibility and the physical history of the blend. Such hierarchical physical structure in the melt is expected to have a strong impact on flow and hence on processing and converting; as well as the end-use properties of manufactured articles. The nature of this hierarchical physical structure between interpolymers can be characterized.

The hierarchical physical structure of ethylene interpolymers can be characterized using melt rheology. A convenient method can be based on the small amplitude frequency sweep tests. Such rheology results are expressed as the phase angle δ as a function of complex modulus G^*, referred to as van Gurp-Palmen plots (as described in M. Van Gurp, J. Palmen, Rheol. Bull. (1998) 67(1): 5-8, and; Dealy J, Plazek D. Rheol. Bull. (2009) 78(2): 16-31). For a typical ethylene interpolymer, the phase angle δ increases toward its upper bound of 90° with G^* becoming sufficiently low. A typical VGP plot is shown in Figure 3. The VGP plots are a signature of resin architecture. The rise of δ toward 90° is monotonic for an ideally linear, monodisperse interpolymer. The $\delta(G^*)$ for a branched interpolymer or a blend containing a branched interpolymer may show an inflection point that reflects the topology of the branched interpolymer (see S. Trinkle, P. Walter, C.

Friedrich, Rheo. Acta (2002) 41: 103-113). The deviation of the phase angle δ from the monotonic rise may indicate a deviation from the ideal linear interpolymer either due to presence of long chain branching if the inflection point is low (e.g., $\delta \leq$ 20°) or a blend containing at least two interpolymers having dissimilar branching structure if the inflection point is high (e.g., $\delta \geq 70°$).

For commercially available linear low density polyethylenes, inflection points are not observed; with the exception of some commercial polyethylenes that contain a small amount of long chain branching (LCB). To use the VGP plots regardless of presence of LCB, an alternative is to use the point where the frequency ω_c is two decades below the cross-over frequency ω_c, i.e., $\omega_c = 0.01\omega_x$. The cross-over point is taken as the reference as it is known to be a characteristic point that correlates with MI, density and other specifications of an ethylene interpolymer. The cross-over modulus is related to the plateau modulus for a given molecular weight distribution (see S. Wu. J Polym Sci, Polym Phys Ed (1989) 27:723; M.R. Nobile, F. Cocchini. Rheol Acta (2001) 40:111). The two decade shift in phase angle δ is to find the comparable points where the individual viscoelastic responses of constituents could be detected; to be more clear, this two decade shift is shown in Figure 4. The complex modulus G_c^* for this point is normalized to the cross-over modulus, $G_x^*/(\sqrt{2})$, as $(\sqrt{2})G_c^*/G_x^*$, to minimize the variation due to overall molecular weight, molecular weight distribution and the short chain branching. As a result, the coordinates on VGP plots for this low frequency point at $\omega_c = 0.01\omega_x$, namely $(\sqrt{2})G_c^*/G_x^*$ and δ_c, characterize the contribution due to blending. Similar to the inflection points, the closer the $((\sqrt{2})G_c^*/G_x^*, \delta_c)$ point is toward the 90° upper bound, the more the blend behaves as if it were an ideal single component.

As an alternative way to avoid interference due to the molecular weight, molecular weight distribution and the short branching of the ethylene δ_c interpolymer ingredients, the coordinates (G_c^*, δ_c) are compared to a reference sample of interest to form the following two parameters:

- "Dilution Index (Y_d)"

$$Y_d = \delta_c - (C_0 - C_1 e^{C_2 \ln G_c^*})$$

- "Dimensionless Modulus (X_d)"

$$X_d = G^*_{0.01\omega_c}/G_r^*$$

The constants C_0, C_1, and C_2 are determined by fitting the VGP data $\delta(G^*)$ of the reference sample to the following equation:

$$\delta = C_0 - C_1 e^{C_2 \ln G^*}$$

G_r^* is the complex modulus of this reference sample at its $\delta_c = \delta(0.01\omega_x)$. When an ethylene interpolymer, synthesized with an in-line Ziegler-Natta catalyst employing one solution reactor, having a density of 0.920 g/cm^3 and a melt index (MI or I_2) of 1.0 dg/min is taken as a reference sample, the constants are:

C_0 = 93.43°

C_1 = 1.316°

C_2 = 0.2945

G_r^* = 9432 Pa.

The values of these constants can be different if the rheology test protocol differs from that specified herein.

These regrouped coordinates (X_d, Y_d) from (G_c^*, δ_c) allows comparison between ethylene interpolymer products disclosed herein with Comparative examples. The Dilution Index (Y_d) reflects whether the blend behaves like a simple

blend of linear ethylene interpolymers (lacking hierarchical structure in the melt) or shows a distinctive response that reflects a hierarchical physical structure within the melt. The lower the Y_d, the more the sample shows separate responses from the ethylene interpolymers that comprise the blend; the higher the Y_d the more the sample behaves like a single component, or single ethylene interpolymer.

Returning to Figure 2: Type I (upper left quadrant) ethylene interpolymer products of this disclosure (solid symbols) have $Y_d > 0$; in contrast, Type III (lower right quadrant) comparative ethylene interpolymers, Comparative D and E have $Y_d < 0$. In the case of Type I ethylene interpolymer products (solid circles), the first ethylene interpolymer (single-site catalyst) and the second ethylene interpolymer (in-line Ziegler Natta catalyst) behave as a simple blend of two ethylene interpolymers and a hierarchical structure within the melt does not exist. However, in the case of Comparatives D and E (open diamonds), the melt comprising a first ethylene interpolymer (single-site catalyst) and a second ethylene interpolymer (batch Ziegler Natta catalyst) possesses a hierarchical structure.

The ethylene interpolymer products of this disclosure fall into one of two quadrants: Type I with $X_d < 0$, or; Type II with $X_d > 0$. The Dimensionless Modulus (X_d), reflects differences (relative to the reference sample) that are related to the overall molecular weight, molecular weight distribution (M_w/M_n) and short chain branching. Not wishing to be bound by theory, conceptually, the Dimensionless Modulus (X_d) may be considered to be related to the M_w/M_n and the radius of gyration ($\langle R_g \rangle^2$) of the ethylene interpolymer in the melt; conceptually, increasing X_d has similar effects as increasing M_w/M_n and/or $\langle R_g \rangle^2$, without the risk of including lower molecular weight fraction and sacrificing certain related properties.

Relative to Comparative A (recall that Comparative A comprises a first and second ethylene interpolymer synthesized with a single-site catalyst) the solution process disclosed herein enables the manufacture of ethylene interpolymer products having higher X_d. Not wishing to be bound by theory, as X_d increases the macromolecular coils of higher molecular weight fraction are more expanded (conceptually higher $<R_g>^2$) and upon crystallization the probability of tie chain formation is increased resulting in higher toughness properties; the polyethylene art is replete with disclosures that correlate higher toughness (higher dart impact in manufactured film articles and improved ESCR and/or PENT in manufactured molding articles, e.g. containers and lids) with an increasing probability of tie chain formation.

In the Dilution Index testing protocol, the upper limit on Y_d may be about 20, in some cases about 15 and is other cases about 13. The lower limit on Y_d may be about -30, in some cases -25, in other cases -20 and in still other cases -15. In the Dilution Index testing protocol, the upper limit on X_d is 1.0, in some cases about 0.95 and in other cases about 0.9. The lower limit on X_d is -2, in some cases -1.5 and in still other cases -1.0.

Terminal Vinyl Unsaturation of Ethylene Interpolymer Products

The ethylene interpolymer products of this disclosure are further characterized by a terminal vinyl unsaturation greater than or equal to 0.03 terminal vinyl groups per 100 carbon atoms (≥ 0.03 terminal vinyls/100 C); as determine via Fourier Transform Infrared (FTIR) spectroscopy according to ASTM ASTM D3124-98 and ASTM D6248-98.

Figure 5 compares the terminal vinyl/100 C content of the ethylene interpolymers of this disclosure with several Comparatives. The data shown in

Figure 5 is also tabulated in Tables 8A and 8B. All of the comparatives in Figure 5 and Tables 8A and 8B are Elite® products available from The Dow Chemical Company (Midland, Michigan, USA); Elite products are ethylene interpolymers produced in a dual reactor solution process and comprise an interpolymer synthesized using a single-site catalyst and an interpolymer synthesized using a batch Ziegler-Natta catalyst: Comparative B is Elite 5401G; Comparative C is Elite 5400G; Comparative E and E2 are Elite 5500G; Comparative G is Elite 5960; Comparative H and H2 are Elite 5100G; Comparative I is Elite 5940G, and; Comparative J is Elite 5230G.

As shown in Figure 5 the average terminal vinyl content in the ethylene interpolymer of this disclosure was 0.045 terminal vinyls/100 C; in contrast, the average terminal vinyl content in the Comparative samples was 0.023 terminal vinyls/100 C. Statistically, at the 99.999% confidence level, the ethylene interpolymers of this disclosure are significantly different from the Comparatives; i.e. a t-Test assuming equal variances shows that the means of the two populations (0.045 and 0.023 terminal vinyls/100 C) are significantly different at the 99.999% confidence level (t(obs) = 12.891 > 3.510 t(crit two tail); or p-value = 4.84×10^{-17} < 0.001 α (99.999% confidence)).

Catalyst Residues (Total Catalytic Metal)

The ethylene interpolymer products of this disclosure are further characterized by having ≥ 3 parts per million (ppm) of total catalytic metal (Ti); where the quantity of catalytic metal was determined by Neutron Activation Analysis (N.A.A.) as specified herein.

Figure 6 compares the total catalytic metal content of the disclosed ethylene interpolymers with several Comparatives; Figure 6 data is also tabulated in Tables

9A and 9B. All of the comparatives in Figure 6 and Tables 9A and 9B are Elite® products available from The Dow Chemical Company (Midland, Michigan, USA), for additional detail see the section above.

As shown in Figure 6 the average total catalytic metal content in the ethylene interpolymers of this disclosure was 7.02 ppm of titanium; in contrast, the average total catalytic metal content in the Comparative samples was 1.63 ppm of titanium. Statistically, at the 99.999% confidence level, the ethylene interpolymers of this disclosure are significantly different from the Comparatives, i.e. a t-Test assuming equal variances shows that the means of the two populations (7.02 and 1.63 ppm titanium) are significantly different at the 99.999% confidence level, i.e. (t(obs) = 12.71 > 3.520 t(crit two tail); or p-value = $1.69 \times 10^{-16} < 0.001$ α (99.999% confidence)).

Flexible Manufactured Articles

The ethylene interpolymer products disclosed herein, are well suited for use in mono and multilayer films; particularly packaging films where high caulkability and seal through contamination is desired. Non-limiting examples of processes to prepare such films include blown film and cast film processes.

Depending on the end-use application, the disclosed ethylene interpolymer products may be converted into films that span a wide range of thicknesses. Non-limiting examples include, food packaging films where thicknesses may range from about 0.5 mil (13 µm) to about 4 mil (102 µm), and; in heavy duty sack applications film thickness may range from about 2 mil (51µm) to about 10 mil (254 µm).

The disclosed ethylene interpolymer products may also be used in monolayer films; where the monolayer may contain more than one ethylene interpolymer product and/or additional thermoplastics; non-limiting examples of

thermoplastics include ethylene polymers and propylene polymers. The lower limit on the weight percent of the ethylene interpolymer product having improved color in a monolayer film may be about 3 wt%, in other cases about 10 wt% and in still other cases about 30 wt%. The upper limit on the weight percent of the ethylene interpolymer product having improved color in the monolayer film may be 100 wt%, in other cases about 90 wt% and in still other cases about 70 wt%.

The ethylene interpolymer products disclosed herein may also be used in one or more layers of a multilayer film; non-limiting examples of multilayer films include three, five, seven, nine, eleven or more layers. The thickness of a specific layer (containing an ethylene interpolymer product having improved color) within a multilayer film may be about 1%, in other cases about 3% and in still other cases about 5% of the total multilayer film thickness. In other embodiments, the thickness of a specific layer (containing the ethylene interpolymer product having improved color) within a multilayer film may be about 99%, in other cases about 97% and in still other cases about 95% of the total multilayer film thickness. Each individual layer of a multilayer film may contain more than one ethylene interpolymer product and/or additional thermoplastics.

Additional embodiments include laminations and coatings, wherein mono or multilayer films containing the disclosed ethylene interpolymer products are extrusion laminated or adhesively laminated or extrusion coated. In extrusion lamination or adhesive lamination, two or more substrates are bonded together with a thermoplastic or an adhesive, respectively. In extrusion coating, a thermoplastic is applied to the surface of a substrate. These processes are well known to those experienced in the art.

Additional non-limiting examples where the disclosed ethylene interpolymer products are useful in monolayer or multilayer films include: fresh and frozen food packaging (including liquids, gels or solids), stand-up pouches, retortable packaging and bag-in-box packaging; barrier films (oxygen, moisture, aroma, oil, etc.) and modified atmosphere packaging; light and heavy duty shrink films and wraps, collation shrink film, pallet shrink film, shrink bags, shrink bundling and shrink shrouds; light and heavy duty stretch films, hand stretch wrap, machine stretch wrap and stretch hood films; high clarity films; heavy-duty sacks; household wrap, overwrap films and sandwich bags; industrial and institutional films, trash bags, can liners, magazine overwrap, newspaper bags, mail bags, sacks and envelopes, bubble wrap, carpet film, furniture bags, garment bags, coin bags, auto panel films; medical applications such as gowns, draping and surgical garb; construction films and sheeting, asphalt films, insulation bags, masking film, landscaping film and bags; geomembrane liners for municipal waste disposal and mining applications; batch inclusion bags; agricultural films, mulch film and green house films; in-store packaging, self-service bags, boutique bags, grocery bags, carry-out sacks and t-shirt bags; oriented films, machine direction and biaxially oriented films and functional film layers in oriented polypropylene (OPP) films, e.g. sealant and/or toughness layers. Additional manufactured articles comprising one or more films containing at least one ethylene interpolymer product having improved color include laminates and/or multilayer films; sealants and tie layers in multilayer films and composites; laminations with paper; aluminum foil laminates or laminates containing vacuum deposited aluminum; polyamide laminates; polyester laminates; extrusion coated laminates, and; hot-melt adhesive formulations. The manufactured articles summarized in this paragraph contain at least one film

(monolayer or multilayer) comprising at least one embodiment of the disclosed ethylene interpolymer products.

Desired film physical properties (monolayer or multilayer) typically depend on the application of interest. Non-limiting examples of desirable film properties include: high caulkability, good seal through contamination, good hot tack, low heat sealing initiation, good optical properties (gloss, haze and clarity), dart impact, Elmendorf tear, modulus (1% and 2% secant modulus), puncture-propagation tear resistance and tensile properties (yield strength, break strength, elongation at break, toughness, etc.).

Additives and Adjuvants

The mono and multilayer films disclosed here, containing at least one layer comprising at least one ethylene interpolymer product may optionally include, depending on its intended use, additives and adjuvants. Non-limiting examples of additives and adjuvants include, anti-blocking agents, antioxidants, heat stabilizers, slip agents, processing aids, anti-static additives, colorants, dyes, filler materials, light stabilizers, heat stabilizers, light absorbers, lubricants, pigments, plasticizers, nucleating agents and combinations thereof. Non-limiting examples of suitable primary antioxidants include Irganox 1010 [CAS Reg. No. 6683-19-8] and Irganox 1076 [CAS Reg. No. 2082-79-3]; both available from BASF Corporation, Florham Park, NJ, U.S.A. Non-limiting examples of suitable secondary antioxidants include Irgafos 168 [CAS Reg. No. 31570-04-4], available from BASF Corporation, Florham Park, NJ, U.S.A.; Weston 705 [CAS Reg. No. 939402-02-5], available from Addivant, Danbury CT, U.S.A. and; Doverphos Igp-11 [CAS Reg. No. 1227937-46-3] available form Dover Chemical Corporation, Dover OH, U.S.A.

Testing Methods

Prior to testing, each specimen was conditioned for at least 24 hours at 23 ±2°C and 50 ±10% relative humidity and subsequent testing was conducted at 23 ±2°C and 50 ±10% relative humidity. Herein, the term "ASTM conditions" refers to a laboratory that is maintained at 23 ±2°C and 50 ±10% relative humidity; and specimens to be tested were conditioned for at least 24 hours in this laboratory prior to testing. ASTM refers to the American Society for Testing and Materials.

Density

Ethylene interpolymer product densities were determined using ASTM D792-13 (November 1, 2013).

Melt Index

Ethylene interpolymer product melt index was determined using ASTM D1238 (August 1, 2013). Melt indexes, I_2, I_6, I_{10} and I_{21} were measured at 190°C, using weights of 2.16 kg, 6.48 kg, 10 kg and a 21.6 kg respectively. Herein, the term "stress exponent" or its acronym "S.Ex.", is defined by the following relationship:

$$S.Ex. = \log (I_6/I_2)/\log(6480/2160)$$

wherein I_6 and I_2 are the melt flow rates measured at 190°C using 6.48 kg and 2.16 kg loads, respectively. In this disclosure, melt index was expressed using the units of g/10 minutes or g/10 min or dg/minutes or dg/min; these units are equivalent.

Gel Permeation Chromatography (GPC)

Ethylene interpolymer product molecular weights, M_n, M_w and M_z, as well the as the polydispersity (M_w/M_n), were determined using ASTM D6474-12 (December 15, 2012). This method illuminates the molecular weight distributions of ethylene interpolymer products by high temperature gel permeation chromatography (GPC).

The method uses commercially available polystyrene standards to calibrate the GPC.

Unsaturation Content

The quantity of unsaturated groups, i.e. double bonds, in an ethylene interpolymer product was determined according to ASTM D3124-98 (vinylidene unsaturation, published March 2011) and ASTM D6248-98 (vinyl and trans unsaturation, published July 2012). An ethylene interpolymer sample was: a) first subjected to a carbon disulfide extraction to remove additives that may interfere with the analysis; b) the sample (pellet, film or granular form) was pressed into a plaque of uniform thickness (0.5 mm), and; c) the plaque was analyzed by FTIR.

Comonomer Content

The quantity of comonomer in an ethylene interpolymer product was determined by FTIR (Fourier Transform Infrared spectroscopy) according to ASTM D6645-01 (published January 2010).

Composition Distribution Branching Index (CDBI)

The "Composition Distribution Branching Index" or "CDBI" of the disclosed Examples and Comparative Examples were determined using a crystal-TREF unit commercially available form Polymer ChAR (Valencia, Spain). The acronym "TREF" refers to Temperature Rising Elution Fractionation. A sample of ethylene interpolymer product (80 to 100 mg) was placed in the reactor of the Polymer ChAR crystal-TREF unit, the reactor was filled with 35 ml of 1,2,4-trichlorobenzene (TCB), heated to 150°C and held at this temperature for 2 hours to dissolve the sample. An aliquot of the TCB solution (1.5 mL) was then loaded into the Polymer ChAR TREF column filled with stainless steel beads and the column was equilibrated for 45 minutes at 110°C. The ethylene interpolymer product was then crystallized from

the TCB solution, in the TREF column, by slowly cooling the column from 110°C to 30°C using a cooling rate of 0.09°C per minute. The TREF column was then equilibrated at 30°C for 30 minutes. The crystallized ethylene interpolymer product was then eluted from the TREF column by passing pure TCB solvent through the column at a flow rate of 0.75 mL/minute as the temperature of the column was slowly increased from 30°C to 120°C using a heating rate of 0.25°C per minute. Using Polymer ChAR software a TREF distribution curve was generated as the ethylene interpolymer product was eluted from the TREF column, i.e. a TREF distribution curve is a plot of the quantity (or intensity) of ethylene interpolymer eluting from the column as a function of TREF elution temperature. A $CDBI_{50}$ was calculated from the TREF distribution curve for each ethylene interpolymer product analyzed. The "$CDBI_{50}$" is defined as the percent of ethylene interpolymer whose composition is within 50% of the median comonomer composition (25% on each side of the median comonomer composition); it is calculated from the TREF composition distribution curve and the normalized cumulative integral of the TREF composition distribution curve. Those skilled in the art will understand that a calibration curve is required to convert a TREF elution temperature to comonomer content, i.e. the amount of comonomer in the ethylene interpolymer fraction that elutes at a specific temperature. The generation of such calibration curves are described in the prior art, e.g. Wild et al., J. Polym. Sci., Part B, Polym. Phys., Vol. 20 (3), pages 441-455: hereby fully incorporated by reference.

Heat Deflection Temperature

The heat deflection temperature of an ethylene interpolymer product was determined using ASTM D648-07 (approved March 1, 2007). The heat deflection temperature is the temperature at which a deflection tool applying 0.455 MPa (66

PSI) stress on the center of a molded ethylene interpolymer plaque (3.175 mm (0.125 in) thick) causes it to deflect 0.25 mm (0.010 in) as the plaque is heated in a medium at a constant rate.

Vicat Softening Point (Temperature)

The Vicat softening point of an ethylene interpolymer product was determined according to ASTM D1525-07 (published December 2009). This test determines the temperature at which a specified needle penetration occurs when samples are subjected to ASTM D1525-07 test conditions, i.e. heating Rate B (120 ±10°C/hr and 938 gram load (10 ±0.2N load).

Neutron Activation Analysis (NAA)

Neutron Activation Analysis, hereafter NAA, was used to determine catalyst residues in ethylene interpolymers and was performed as follows. A radiation vial (composed of ultrapure polyethylene, 7 mL internal volume) was filled with an ethylene interpolymer product sample and the sample weight was recorded. Using a pneumatic transfer system the sample was placed inside a SLOWPOKE™ nuclear reactor (Atomic Energy of Canada Limited, Ottawa, Ontario, Canada) and irradiated for 30 to 600 seconds for short half-life elements (e.g., Ti, V, Al, Mg, and Cl) or 3 to 5 hours for long half-life elements (e.g. Zr, Hf, Cr, Fe and Ni). The average thermal neutron flux within the reactor was $5x10^{11}/cm^2/s$. After irradiation, samples were withdrawn from the reactor and aged, allowing the radioactivity to decay; short half-life elements were aged for 300 seconds or long half-life elements were aged for several days. After aging, the gamma-ray spectrum of the sample was recorded using a germanium semiconductor gamma-ray detector (Ortec model GEM55185, Advanced Measurement Technology Inc., Oak Ridge, TN, USA) and a multichannel analyzer (Ortec model DSPEC Pro). The amount of each element in

the sample was calculated from the gamma-ray spectrum and recorded in parts per million relative to the total weight of the ethylene interpolymer sample. The N.A.A. system was calibrated with Specpure standards (1000 ppm solutions of the desired element (greater than 99% pure)). One mL of solutions (elements of interest) were pipetted onto a 15 mm x 800 mm rectangular paper filter and air dried. The filter paper was then placed in a 1.4 mL polyethylene irradiation vial and analyzed by the N.A.A. system. Standards are used to determine the sensitivity of the N.A.A. procedure (in counts/µg).

Dilution Index (Y_d) Measurements

A series of small amplitude frequency sweep tests were run on each sample using an Anton Paar MCR501 Rotational Rheometer equipped with the "TruGap™ Parallel Plate measuring system". A gap of 1.5 mm and a strain amplitude of 10% were used throughout the tests. The frequency sweeps were from 0.05 to 100 rad/s at the intervals of seven points per decade. The test temperatures were 170°, 190°, 210° and 230°C. Master curves at 190°C were constructed for each sample using the Rheoplus/32 V3.40 software through the Standard TTS (time-temperature superposition) procedure, with both horizontal and vertical shift enabled.

The Y_d and X_d data generated are summarized in Table 10. The flow properties of the ethylene interpolymer products, e.g., the melt strength and melt flow ratio (MFR) are well characterized by the Dilution Index (Y_d) and the Dimensionless Modulus (X_d) as detailed below. In both cases, the flow property is a strong function of Y_d and X_d in addition a dependence on the zero-shear viscosity. For example, the melt strength (hereafter MS) values of the disclosed Examples and the Comparative Examples were found to follow the same equation, confirming

that the characteristic VGP point $((\sqrt{2})G_c^*/G_x^*,\ \delta_c)$ and the derived regrouped coordinates (X_d, Y_d) represent the structure well:

$$\text{MS} = a_{00} + a_{10}log\eta_0 - a_{20}(90 - \delta_c) - a_{30}((\sqrt{2})G_c^*/G_x^*)$$

$$-a_{40}(90 - \delta_c)((\sqrt{2})G_c^*/G_x^*)$$

where

a_{00} = -33.33; a_{10} = 9.529; a_{20} = 0.03517; a_{30} = 0.894; a_{40} = 0.02969

and r^2 = 0.984 and the average relative standard deviation was 0.85%. Further, this relation can be expressed in terms of the Dilution Index (Y_d) and the Dimensionless Modulus (X_d):

$$\text{MS} = a_0 + a_1 log\eta_0 + a_2 Y_\text{d} + a_3 X_\text{d} + a_4 Y_\text{d} X_\text{d}$$

where

a_0 = 33.34; a_1 = 9.794; a_2 = 0.02589; a_3 = 0.1126; a_4 = 0.03307

and r^2 = 0.989 and the average relative standard deviation was 0.89%.

The MFR of the disclosed Examples and the Comparative samples were found to follow a similar equation, further confirming that the dilution parameters Y_d and X_d show that the flow properties of the disclosed Examples differ from the reference and Comparative Examples:

$$\text{MFR} = b_0 - b_1 log\eta_0 - b_2 Y_d - b_3 X_d$$

where

b_0 = 53.27; b_1 = 6.107; b_2 = 1.384; b_3 = 20.34

and r^2 = 0.889 and the average relative standard deviation and 3.3%.

Further, the polymerization process and catalyst formulations disclosed herein allow the production of ethylene interpolymer products that can be converted into flexible manufactured articles that have a desired balance of physical properties (i.e. several end-use properties can be balanced (as desired) through

multidimensional optimization); relative to comparative polyethylenes of comparable density and melt index.

Dart Impact

Film dart impact strength was determined using ASTM D1709-09 Method A (May 1, 2009). In this disclosure the dart impact test employed a 1.5 inch (38 mm) diameter hemispherical headed dart.

Puncture

Film "puncture", the energy (J/mm) required to break the film was determined using ASTM D5748-95 (originally adopted in 1995, reapproved in 2012).

Lubricated Puncture

The "lubricated puncture" test was performed as follows: the energy (J/mm) to puncture a film sample was determined using a 0.75-inch (1.9-cm) diameter pear-shaped fluorocarbon coated probe travelling at 10-inch per minute (25.4-cm/minute). ASTM conditions were employed. Prior to testing the specimens, the probe head was manually lubricated with Muko Lubricating Jelly to reduce friction. Muko Lubricating Jelly is a water-soluble personal lubricant available from Cardinal Health Inc., 1000 Tesma Way, Vaughan, ON L4K 5R8 Canada. The probe was mounted in an Instron Model 5 SL Universal Testing Machine and a 1000-N load cell as used. Film samples (1.0 mil (25 μm) thick, 5.5 inch (14 cm) wide and 6 inch (15 cm) long) were mounted in the Instron and punctured.

Tensile Properties

The following film tensile properties were determined using ASTM D882-12 (August 1, 2012): tensile break strength (MPa), elongation at break (%), tensile yield strength (MPa), tensile elongation at yield (%) and film toughness or total

energy to break (ft·lb/in^3). Tensile properties were measured in the both the machine direction (MD) and the transverse direction (TD) of the blown films.

Film Modulus

The secant modulus is a measure of film stiffness. The secant modulus is the slope of a line drawn between two points on the stress-strain curve, i.e. the secant line. The first point on the stress-strain curve is the origin, i.e. the point that corresponds to the origin (the point of zero percent strain and zero stress), and; the second point on the stress-strain curve is the point that corresponds to a strain of 1%; given these two points the 1% secant modulus is calculated and is expressed in terms of force per unit area (MPa). The 2% secant modulus is calculated similarly. This method is used to calculated film modulus because the stress-strain relationship of polyethylene does not follow Hook's law; i.e. the stress-strain behavior of polyethylene is non-linear due to its viscoelastic nature. Secant moduli were measured using a conventional Instron tensile tester equipped with a 200 lbf load cell. Strips of monolayer film samples were cut for testing with following dimensions: 14 inch long, 1 inch wide and 1 mil thick; ensuring that there were no nicks or cuts on the edges of the samples. Film samples were cut in both the machine direction (MD) and the transverse direction (TD) and tested. ASTM conditions were used to condition the samples. The thickness of each film was accurately measured with a hand-held micrometer and entered along with the sample name into the Instron software. Samples were loaded in the Instron with a grip separation of 10 inch and pulled at a rate of 1 inch/min generating the strain-strain curve. The 1% and 2% secant modulus were calculated using the Instron software.

Flexural Properties

The flexural properties, i.e. flexural secant and tangent modulus and flexural strength were determined using ASTM D790-10 (published in April 2010).

Puncture-Propagation Tear

Puncture-propagation tear resistance of blown film was determined using ASTM D2582-09 (May 1, 2009). This test measures the resistance of a blown film to snagging, or more precisely, to dynamic puncture and propagation of that puncture resulting in a tear. Puncture-propagation tear resistance was measured in the machine direction (MD) and the transverse direction (TD) of the blown films.

Elmendorf Tear

Film tear performance was determined by ASTM D1922-09 (May 1, 2009); an equivalent term for tear is "Elmendorf tear". Film tear was measured in both the machine direction (MD) and the transverse direction (TD) of the blown films.

Optical Properties

Film optical properties were measured as follows: Haze, ASTM D1003-13 (November 15, 2013), and; Gloss ASTM D2457-13 (April 1, 2013).

Dynatup Impact

Instrumented impact testing was carried out on a machine called a Dynatup Impact Tester purchased from Illinois Test Works Inc., Santa Barbara, CA, USA; those skilled in the art frequently call this test the Dynatup impact test. Testing was completed according to the following procedure. Test samples are prepared by cutting about 5 inch (12.7 cm) wide and about 6 inch (15.2 cm) long strips from a roll of blown film; film was about 1 mil thick. Prior to testing, the thickness of each sample was accurately measured with a handheld micrometer and recorded. ASTM conditions were employed. Test samples were mounted in the 9250

Dynatup Impact drop tower/test machine using the pneumatic clamp. Dynatup tup #1, 0.5 inch (1.3 cm) diameter, was attached to the crosshead using the Allen bolt supplied. Prior to testing, the crosshead is raised to a height such that the film impact velocity is 10.9 ±0.1 ft/s. A weight was added to the crosshead such that: 1) the crosshead slowdown, or tup slowdown, was no more than 20% from the beginning of the test to the point of peak load and 2) the tup must penetrate through the specimen. If the tup does not penetrate through the film, additional weight is added to the crosshead to increase the striking velocity. During each test the Dynatup Impulse Data Acquisition System Software collected the experimental data (load (lb) versus time). At least 5 film samples are tested and the software reports the following average values: "Dynatup Maximum (Max) Load (lb)", the highest load measured during the impact test; "Dynatup Total Energy (ft·lb)", the area under the load curve from the start of the test to the end of the test (puncture of the sample), and; "Dynatup Total Energy at Max Load (ft·lb)", the area under the load curve from the start of the test to the maximum load point.

Hexane Extractables

Hexane extractables was determined according to the Code of Federal Registration 21 CFR §177.1520 Para (c) 3.1 and 3.2; wherein the quantity of hexane extractable material in a film is determined gravimetrically. Elaborating, 2.5 grams of 3.5 mil (89 μm) monolayer film was placed in a stainless steel basket, the film and basket were weighed (w^i), while in the basket the film was: extracted with n-hexane at 49.5°C for two hours; dried at 80°C in a vacuum oven for 2 hours; cooled in a desiccator for 30 minutes, and; weighed (w^f). The percent loss in weight is the percent hexane extractables (w^{C6}): $w^{C6} = 100 \times (w^i - w^f)/w^i$.

Preparation of Multilayer Films

Multilayer films were produced on a 9-layer line commercially available from Brampton Engineering (Brampton ON, Canada). The structure of the 9-layer films produced is shown in Table 5. The total thickness of the multilayer film was held constant at 3.5-mil. The die technology consisted of a pancake die, FLEX-STACK Co-extrusion die (SCD), with flow paths machined onto both sides of a plate, the die tooling diameter was 6.3-inches, in this disclosure a die gap of 85-mil was used consistently, film was produced at a Blow-Up-Ratio (BUR) of 2.5 and the output rate of the line was held constant at 250 lb/hr. The specifications of the nine extruders follow: screws 1.5-in diameter, 30/1 length to diameter ratio, 8-polyethylene screws with single flights and Madddox mixers, 1-Nylon screw, extruders were air cooled, equipped with 20-H.P. motors and all extruders were equipped with gravimetric blenders. The nip and collapsing frame included a Decatex horizontal oscillating haul-off and pearl cooling slats just below the nips. The line was equipped with a turret winder and oscillating slitter knives. The table below summarizes the temperature settings used. All die temperatures were maintained at a constant 480°F, i.e. layer sections, mandrel bottom, mandrel, inner lip and outer lip.

Extruder/Layer	All Temperatures in °F						
	Feed Throat	Barrel zone 1	Barrel zone 2	Barrel zone 3	Barrel zone 4	Screen	Adaptor
Layer I (outside of bubble)	100	455	480	480	480	480	480
Layer H	75	360	420	410	410	410	410
Layer G	75	360	420	410	410	410	410
Layer F	75	360	420	410	410	410	410
Layer E	100	455	480	480	480	480	480
Layer D	75	360	420	410	410	410	410
Layer C	75	360	420	410	410	410	410
Layer B	75	360	420	410	410	410	410
Layer A (inside of Bubble)	75	360	420	410	410	410	410

Caulkability Test

This test is an integrated package test system that measures the seal strength and integrity of flexible, rigid, and semi-rigid packages. The seal strength and integrity of the package is measure by inflating the package using compressed air. The system includes a restraining plate fixture to perform restrained tests on closed packages and is compliant with ASTM F2054.

This test allows one to evaluate the caulkability, or seal through contamination performance, of a sealant layer in a multilayer film. Definitions and a description of the caulkability test follow. "Burst Test": also called the seal strength test, the package is connected to the instrument via a needle and the package seal strength is determined by increasing the air pressure in the package until it bursts, if the package seals are strong, typically the film structure will expand and burst instead of a failure by seal leakage, the Burst Test is compliant with ASTM F2054-13 (published June 2013). "Leak Test": also called the pressure loss test is used to evaluate the integrity of a package, the Leak Test is compliant with ASTM F2095-07 (published September 2013); the package is connected to the instrument with the needle and the pressure inside the package is set to 50% of the burst pressure; the test pressure and the pressure loss during the test can be used as a measure of the package integrity; these results also provide a theoretical "hole size" of the leak; this information can be used to calculate a leak rate and average hole size, this calculation is compliant to ASTM F2095; "Hole Length" is the seal width measured in millimeters used to calculate the hole size; "Volume" is the inflated volume of the packages minus the volume of the product within the package; "Caulkability" a term related to a sealant's ability to encapsulate contamination in

the seal area or to flow into a void within the seal area completely so the package does not leak.

The experimental apparatus consists of the following items:

1. Mocon Lippke Package Test System 4500, 1bar
2. Needle (Sharp 1B or Blunt 2B)
3. Septa Black 4mm
4. ASTM Compliant Restraining Plate Fixture
5. PC-Software Version 1.2 with hole size calculation
6. Impulse Sealer

The following describes the preparation of a film package (or pouch) for caulkability testing, where the films consists of the 9-layer films described in Table 5. Cut 16 film specimens forming a 1-ply sheet (of the 9-layer film) 14-long and 7-in wide (the 14 inch dimension is in the transverse direction of the film, i.e. the transverse direction as defined during film production on the blown film line); fold the film sheet in half forming a 2-ply sheet 7-in square (see Step 1 in Figure 7); place 3-Styrofoam packaging peanuts inside the pouch to maintain a separation between the upper and lower film layer (not shown in Figure 7); impulse seal the top of the 2-ply sheet (see Step 2 in Figure 7); impulse seal the left edge of the 2-ply sheet (see Step 3 in Figure 7); position the contaminant (copper wire, 0.01 inches in diameter) between the 2-ply sheet (see Step 4 in Figure 7), and; heat seal the remaining open end of the pouch (bottom) using the SL5 sealer (140°C/40psi/0.5s dwell time) ensuring that the contaminant is entrapped within the heat seal. The resulting package has a volume of about 650 ml. Make 5 pouches containing the copper wire contaminant for the Leak Test, and; make 5 pouches without the copper wire contaminant for the Burst Test. Using the Burst Test,

inflate the pouches (without contaminant) and determine the average burst pressure of 5 pouches (let's assume an average burst pressure of 8 psi). Using 50% of the average burst pressure inflate the contaminated pouches (i.e. to 4 psi), conduct the Leak Test and monitor the pressure decay, time and calculate the hole size (µm).

To calculate a leak rate (volume flow) a pressure loss ΔP and time Δt are needed; these are measured in the Leak Test. The volume is specified as a test parameter. The Leak Rate according to ASTM F2095 is calculated as follows:

$$Q(sccs) = (\Delta P(atm) \times V(cm^3))/\Delta t(s)$$

For example: a package with a volume (V) of one liter (1000 cm^3) is tested for 30 seconds and loses 10 mbar (= 9.87×10^{-3} atm) in that time. A leak rate of 0.329 sccs results; to convert the leak rate from sccs to (mbar*cm^3/s) multiply by 1.01325.

The "Hole Size" is calculated using the Hagen-Poiseullie's Law; where the following is required: a leak rate (volume flow, cc/sec), path length (hole length, cm), differential pressure and dynamic viscosity. The leak rate is determined as described above (Leak Test); differential pressure is measured during the Pressure Loss test; hole length is specified as part of the Pressure Loss test parameter set and the viscosity is a constant (air is the working fluid; air = 1.827×10^{-4} Pa·s at 18°C).

The effective (average) Hole Size is calculated using the Hagen-Poiseuille's law as follows.

$$Q = \pi r^4 (P_1 - P_2)/(8NL)$$

The pressure in the package is changing during the test,

$$P_1 - P_2 = (P - \frac{\Delta P}{2})$$

which results in:

$$r = \sqrt[4]{\frac{Q8NL}{\pi(P - \left(\frac{\Delta P}{2}\right))}}$$

and the diameter of the hole is determined by the following relationship. In this disclosure the diameter of the hole, *d*, is defined as the "hole size" and is measured in microns (μm).

$$d = 2 \cdot 1000 \left(\frac{\mu m}{cm}\right) \cdot \sqrt[4]{\frac{Q8NL}{\pi(P - \left(\frac{\Delta P}{2}\right)}}$$

EXAMPLES

Polymerization

The following examples are presented for the purpose of illustrating selected embodiments of this disclosure; it being understood, that the examples presented do not limit the claims presented.

An embodiments of an ethylene interpolymer product was produced in a continuous solution polymerization pilot plant comprising reactors arranged in a series configuration. Methylpentane was used as the process solvent (a commercial blend of methylpentane isomers). The volume of the first CSTR reactor (R1) was 3.2 gallons (12 L), the volume of the second CSTR reactor (R2) was 5.8 gallons (22 L) and the volume of the tubular reactor (R3) was 4.8 gallons (18 L). Examples of ethylene interpolymer products were produced using an R1 pressure from about 14 MPa to about 18 MPa; R2 was operated at a lower pressure to facilitate continuous flow from R1 to R2. R1 and R2 were operated in series mode, wherein the first exit stream from R1 flows directly into R2. Both CSTR's were agitated to give conditions in which the reactor contents were well mixed. The process was operated continuously by feeding fresh process solvent, ethylene, 1-octene and hydrogen to the reactors.

The single site catalyst components used were: component (i), cyclopentadienyl tri(tertiary butyl)phosphinimine titanium dichloride, (Cp[(t-Bu)$_3$PN]TiCl$_2$), hereafter PIC-1; component (ii), methylaluminoxane (MAO-07); component (iii), trityl tetrakis(pentafluoro-phenyl)borate, and; component (iv), 2,6-di-tert-butyl-4-ethylphenol. The single site catalyst component solvents used were methylpentane for components (ii) and (iv) and xylene for components (i) and (iii). The quantity of PIC-1 added to R1, "R1 (i) (ppm)" is shown in Table 2A; to be clear, in Example 2 in Table 2A, the solution in R1 contained 0.12 ppm of component (i), i.e. PIC-1. The mole ratios of the single site catalyst components employed to produce Example 2 were: R1 (ii)/(i) mole ratio = 100, i.e. [(MAO-07)/(PIC-1)]; R1 (iv)/(ii) mole ratio = 0.0, i.e. [(2,6-di-tert-butyl-4-ethylphenol)/(MAO-07)], and; R1 (iii)/(i) mole ratio = 1.1, i.e. [(trityl tetrakis(pentafluoro-phenyl)borate)/(PIC-1)].

The in-line Ziegler-Natta catalyst formulation was prepared from the following components: component (v), butyl ethyl magnesium; component (vi), tertiary butyl chloride; component (vii), titanium tetrachloride; component (viii), diethyl aluminum ethoxide, and; component (ix), triethyl aluminum. Methylpentane was used as the catalyst component solvent. The in-line Ziegler-Natta catalyst formulation was prepared using the following steps. In step one, a solution of triethylaluminum and dibutylmagnesium ((triethylaluminum)/(dibutylmagnesium) molar ratio of 20) was combined with a solution of tertiary butyl chloride and allowed to react for about 30 seconds (HUT-1); in step two, a solution of titanium tetrachloride was added to the mixture formed in step one and allowed to react for about 14 seconds (HUT-2), and; in step three, the mixture formed in step two was allowed to reactor for an additional 3 seconds (HUT-3) prior to injection into R2. The in-line Ziegler-Natta procatalyst formulation was injected into R2 using process

solvent, the flow rate of the catalyst containing solvent was about 49 kg/hr. The in-line Ziegler-Natta catalyst formulation was formed in R2 by injecting a solution of diethyl aluminum ethoxide into R2. The quantity of titanium tetrachloride "R2 (vii) (ppm)" added to reactor 2 (R2) is shown in Table 2A; to be clear in Example 2 the solution in R2 contained 4.2 ppm of $TiCl_4$. The mole ratios of the in-line Ziegler-Natta catalyst components are also shown in Table 2A, specifically: R2 (vi)/(v) mole ratio, i.e. [(tertiary butyl chloride)/(butyl ethyl magnesium)]; R2 (viii)/(vii) mole ratio, i.e. [(diethyl aluminum ethoxide)/(titanium tetrachloride)], and; R2 (ix)/(vii) mole ratio, i.e. [(triethyl aluminum)/(titanium tetrachloride)]. To be clear, in Example 2, the following mole ratios were used to synthesize the in-line Ziegler-Natta catalyst: R2 (vi)/(v) mole ratio = 2.07; R2 (viii)/(vii) mole ratio = 1.35, and; R2 (ix)/(vii) mole ratio = 0.35. In all of the Examples disclosed, 100% of the diethyl aluminum ethoxide was injected directly into R2.

In Comparative Example 2, a single site catalyst formulation was employed in both reactor 1 and reactor 2.

Average residence time of the solvent in a reactor is primarily influenced by the amount of solvent flowing through each reactor and the total amount of solvent flowing through the solution process, the following are representative or typical values for the examples shown in Tables 2A-2C: average reactor residence times were: about 61 seconds in R1, about 73 seconds in R2 and about 50 seconds in R3 (the volume of R3 was about 4.8 gallons (18L)).

Polymerization in the continuous solution polymerization process was terminated by adding a catalyst deactivator to the third exit stream exiting the tubular reactor (R3). The catalyst deactivator used was octanoic acid (caprylic acid), commercially available from P&G Chemicals, Cincinnati, OH, U.S.A. The

catalyst deactivator was added such that the moles of fatty acid added were 50% of the total molar amount of titanium and aluminum added to the polymerization process; to be clear, the moles of octanoic acid added = 0.5 x (moles titanium + moles aluminum); this mole ratio was consistently used in all examples.

A two-stage devolitizing process was employed to recover the ethylene interpolymer product from the process solvent, i.e. two vapor/liquid separators were used and the second bottom stream (from the second V/L separator) was passed through a gear pump/pelletizer combination. DHT-4V (hydrotalcite), supplied by Kyowa Chemical Industry Co. LTD, Tokyo, Japan was used as a passivator, or acid scavenger, in the continuous solution process. A slurry of DHT-4V in process solvent was added prior to the first V/L separator. The molar amount of DHT-4V added was about 10-fold higher than the molar amount of chlorides added to the process; the chlorides added were titanium tetrachloride and tertiary butyl chloride.

Prior to pelletization the ethylene interpolymer product was stabilized by adding about 500 ppm of Irganox 1076 (a primary antioxidant) and about 500 ppm of Irgafos 168 (a secondary antioxidant), based on weight of the ethylene interpolymer product. Antioxidants were dissolved in process solvent and added between the first and second V/L separators.

Tables 2B and 2C disclose additional solution process parameters, e.g. ethylene and 1-octene splits between the reactors, reactor temperatures and ethylene conversions, etc. recorded during the production of Examples 2 and Comparative Example 2. In Comparative Example 2, the single-site catalyst formulation was injected into both reactor R1 and reactor R2 and ES^{R1} was 50%. In Example 2, the single site catalyst formulation was injected into R1, the in-line Ziegler-Natta catalyst formulation was injected into R2 and ES^{R1} was 40%. The

OS^{R1} (%) value of 100 shows that 100% of the 1-octene was injected in R1. The Q^{R1} (%) value of 78.2 shows that 78.2% of the ethylene was converted in R1.

TABLE 1

Computer generated Simulated Example 13: single-site catalyst formulation in R1 (PIC-1) and an in-line Ziegler-Natta catalyst formulation in R2 and R3.

Simulated Physical Property	Reactor 1 (R1)First Ethylene Interpolymer	Reactor 2 (R2) Second Ethylene Interpolymer	Reactor 3 (R3) Third Ethylene Interpolymer	Simulated Example 13
Weight Percent (%)	36.2	56.3	7.5	100
M_n	63806	25653	20520	31963
M_w	129354	84516	67281	99434
M_z	195677	198218	162400	195074
Polydispersity (M_w/M_n)	2.03	3.29	3.28	3.11
Branch Frequency (C_6 Branches per 1000C)	12.6	11.4	15.6	12.1
$CDBI_{50}$ (%) (range)	90 to 95	55 to 60	45 to 55	65 to 70
Density (g/cm^3)	0.9087	0.9206	0.9154	0.9169
Melt Index (dg/min)	0.31	1.92	4.7	1.0

TABLE 2A

Continuous solution process catalyst parameters for Example 2 and Comparative Example 2; targeting ethylene interpolymer products at 1.0 I_2 and 0.917 g/cm^3.

Process Parameter	Example 2	Comparative Example 2
R1 Catalyst	PIC-1	PIC-1
R2 Catalyst	ZN	PIC-1
R1 (i) (ppm)	0.12	0.1
R1 (ii)/(i) mole ratio	100	100
R1 (iv)/(ii) mole ratio	0	0.3
R1 (iii)/(i) mole ratio	1.1	1.2
R2 (i) (ppm)	0	0.22
R2 (ii)/(i) mole ratio	0	25
R2 (iv)/(ii) mole ratio	0	0.3
R2 (iii)/(i) mole ratio	0	1.27
R2 (vii) (ppm)	4.2	0
R2 (vi)/(v) mole ratio	2.07	0
R2 (viii)/(vii) mole ratio	1.35	0
R2 (ix)/(vii) mole ratio	0.35	0
Prod. Rate (kg/h)	94.8	80.6
Increase in Prod. Rate (%)	17.6	

TABLE 2B

Additional solution process parameters for Example 2 and Comparative Example 2.

Process Parameter	Example 2	Comparative Example 2
R3 volume (L)	18	18
ES^{R1} (%)	40	50
ES^{R2} (%)	60	50
ES^{R3} (%)	0	0
R1 ethylene concentration (wt%)	10.3	9.8
R2 ethylene concentration (wt%)	15.4	12.6
R3 ethylene concentration (wt%)	15.4	12.6
((1-octene)/ (ethylene))^{R1} (wt%)	0.67	0.71
OS^{R1} (%)	100	100
OS^{R2} (%)	0	0
OS^{R3} (%)	0	0
H_2^{R1} (ppm)	0.2	0.4
H_2^{R2} (ppm)	3.5	0.8
H_2^{R3} (ppm)	0	0
Prod. Rate (kg/h)	94.8	80.6
Increase in Prod. Rate (%)	17.6	

TABLE 2C

Additional solution process parameters for Examples 1-5 and Comparative Examples 1-2; target product 1.0 I_2 and 0.917 g/cm^3.

Process Parameter	Example 2	Comparative Example 2
R1 total solution rate (kg/h)	358.8	385.7
R2 total solution rate (kg/h)	241.2	214.3
R3 solution rate (kg/h)	0	0
Total solution rate (kg/h)	600	600
R1 inlet temp (°C)	30	30
R2 inlet temp (°C)	30	30
R3 inlet temp(°C)	130	130
R1 Mean temp (°C)	141	140
R2 Mean temp (°C)	206	188
R3 exit temp (actual) (°C)	214	195
R3 exit temp (calc) (°C)	217	193
Q^{R1} (%)	78.2	81.6
Q^{R2} (%)	80	83.9
$Q^{(R2+R3)}$ (%)	90	92.6
Q^{R3} (%)	49.8	54
Q^{T} (%)	93.1	95.6
Prod. Rate (kg/h)	94.8	80.6
Increase in Prod. Rate (%)	17.6	

TABLE 3

Physical properties of disclosed Example 2 and Comparative Example 2.

Example	Density (g/cm^3)	Melt Index I_2 (g/10 min)	Stress Exponent	M_w	M_w/M_n	$CDBI_{50}$
Example 2	0.9160	1.04	1.26	104966	3.66	71.6
Comp. Example 2	0.9147	1.06	1.29	92762	3.15	73.7

TABLE 4

Materials used to prepare the multilayer films disclosure. Ethylene interpolymer product Examples 200 and 201 (this disclosure); and Comparative samples.

Commercial Code	Material Type	Sample Code (in this disclosure)	Density (g/cm^3)	Melt Index (dg/min)	[1]S.Ex.	MFR I_{21}/I_2
	this disclosure	Example 201	0.9165	1.01	1.22	27.1
	this disclosure	Example 200	0.9250	1.04	1.24	24.2
[2]ELITE 5400G	LLDPE (SSC+ZN cat.)	Comparative C	0.9161	1.00	1.35	30.5
[3]FPs117-C	LLDPE (dual SSC cat.)	Comparative BA	0.9176	0.86	1.26	29.2
[3]FPs016-C	LLDPE (dual SSC cat.)	Comparative BC	0.9160	0.61	1.26	27.8
[3]FPs116-CX01	LLDPE (dual SSC cat.)	Comparative BD	0.9160	0.82	1.32	n/a
[4]CPC D143	LLDPE (SSC catalyst)	Comparative AE	0.9152	1.36	16.3	1.12
[2]Attane 4201G	LLDPE (ZN cat.)	Comparative BB	0.9111	0.98	1.34	31.3
[3]FP112-A	LLDPE (ZN cat.)	Comparative BE	0.9119	0.99	1.34	n/a
[3]FP120-C	LLDPE (ZN cat.)	Comparative S	0.9190	0.99	1.32	30.5
[3]PF-0118-F	LLDPE (ZN cat.)	Comparative BF	0.9180	1.00	n/a	n/a
[5]Elvax 3135X	EVA	EVA	0.9320	0.35	n/a	n/a
[5]Surlyn 1601-2	Ionomer	Ionomer	0.9420	1.30	n/a	n/a
[5]Bynel 41E710	Anhydride grafted LLDPE	Bynel	0.9120	2.70	n/a	n/a
[6]Ultramid C40 L 01	Nylon	Nylon	1.12	n/a	n/a	n/a
[3]LF-Y819-A	LDPE	LDPE-1	0.9186	0.75	n/a	n/a

[1] S.Ex. = Stress Exponent
[2] available from The Dow Chemical Company (Midland MI, USA)
[3] available from NOVA Chemicals (Calgary AB, Canada)
[4] available from Chevron Phillips Chemical Company LLC (The Woodlands TX, USA)
[5] available from DuPont Packaging & Industrial Polymers (Wilmington DE, USA)
[6] available from BASF Corporation, Florham Park NJ, USA

TABLE 5

The multilayer film structure (9-layers) used to prepare 3.5 mil blown films. The material in the sealant layer, Layer 1, was varied while keeping the other 8-layers (2 to 9) constant. Layer 1 was the insider layer, i.e. inside the bubble as the multilayer films were produced on the blown film line.

Layer Number	% of 9-layer structure	Materials and Weight% in Each Layer					
		Material A		Material B		Material C	
		Material	wt. %	Material	wt. %	Material	wt. %
Layer 9	11	Nylon	100				
Layer 8	11	[1]mLLDPE	76	Bynel	20	LDPE-1	4
Layer 7	11	mLLDPE	96	LDPE-1	4		
Layer 6	11	mLLDPE	76	Bynel	20	LDPE-1	4
Layer 5	12	Nylon	100				
Layer 4	11	mLLDPE	76	Bynel	20	LDPE-1	4
Layer 3	11	mLLDPE	96	LDPE-1	4		
Layer 2	11	mLLDPE	96	LDPE-1	4		
Layer 1	11	Test Material	91.5	[2]MB	8.5		

[1] mLLDPE = Comparative BC = FPs016-C

[2] MB = MasterBatch containing slip, antiblock and polymer processing aid in a 2 melt index LLDPE carrier. Layer 1 contained 1500 ppm of slip (Kemamide (eurcamide) available from Crompton Corporation); 6250 ppm of antiblock (SuperFloss (SiO_2) available from World Materials), and; 1500 ppm processing aid (FX5920 available from Dyneon).

TABLE 6

Summary of the "Hole Size" as measured in the caulkability test.

Sample Code	Hole Size *d* (µm)
Ionomer	91
Example 201	105
Comparative AE	117
Comparative BA	119
Comparative C	119
Comparative BB	128
Comparative S	132
Comparative BC	138
Example 200	149
Comparative BD	174
Comparative BE	183
Comparative BF	186
Comparative Blend (96% Comparative BC + 4% LDPE-1)	200
EVA	222

TABLE 7

Dilution Index (Y_d) and Dimensionless Modulus Data (X_d) for selected embodiments of ethylene interpolymers of this disclosure (Examples), relative to Comparative S, A, D and E. (MFR = melt flow rate (I_{21}/I_2); MS = melt strength)

Sample Code	Density [g/cm^3]	MI [dg/min]	MFR	MS [cN]	η_0 [kPa·s]	G^0_N [MPa]	G^*_c [kPa]	δ_c [°]	X_d	Y_d
Comp. S	0.9176	0.86	29.2	6.46	11.5	1.50	9.43	74.0	0.00	0.02
Comp. A	0.9199	0.96	29.6	5.99	10.6	1.17	5.89	80.1	-0.20	3.66
Example 6	0.9152	0.67	23.7	7.05	12.9	1.57	7.89	79.6	-0.08	4.69
Example 101	0.9173	0.95	26.3	5.73	9.67	0.84	7.64	79.0	-0.09	3.93
Example 102	0.9176	0.97	22.6	5.65	9.38	1.46	7.46	79.5	-0.10	4.29
Example 103	0.9172	0.96	25.3	5.68	9.38	1.44	7.81	79.3	-0.08	4.29
Example 110	0.9252	0.98	23.9	5.57	9.41	1.64	8.90	78.1	-0.03	3.8
Example 115	0.9171	0.75	23.4	6.83	12.4	1.48	8.18	79.2	-0.06	4.44
Example 200	0.9250	1.04	24.2	5.33	8.81	0.97	8.97	78.9	-0.02	4.65
Example 201	0.9165	1.01	27.1	5.43	8.75	0.85	6.75	79.7	-0.15	3.91
Example 120	0.9204	1.00	24.0	5.99	10.2	1.45	13.5	73.6	0.16	1.82
Example 130	0.9232	0.94	22.1	6.21	10.4	0.97	11.6	75.7	0.09	3.02
Example 131	0.9242	0.95	22.1	6.24	10.7	1.02	11.6	75.3	0.09	2.59
Comp. D	0.9204	0.82	30.6	7.61	15.4	1.58	10.8	70.4	0.06	-2.77
Comp. E	0.9161	1.00	30.5	7.06	13.8	1.42	10.4	70.5	0.04	-2.91

TABLE 8A

Unsaturation data of several embodiments of the disclosed ethylene interpolymers, as well as Comparative B, C, E, E2, G, H, H2, I and J; as determined by ASTM D3124-98 and ASTM D6248-98.

Sample Code	Density (g/cm^3)	Melt Index I_2 (dg/min)	Melt Flow Ratio (I_{21}/I_2)	Stress Exponent	Unsaturations per 100 C		
					Internal	Side Chain	Terminal
Example 11	0.9113	0.91	24.8	1.24	0.009	0.004	0.037
Example 6	0.9152	0.67	23.7	1.23	0.008	0.004	0.038
Example 4	0.9154	0.97	37.1	1.33	0.009	0.004	0.047
Example 7	0.9155	0.70	25.7	1.24	0.008	0.005	0.042
Example 2	0.9160	1.04	27.0	1.26	0.009	0.005	0.048
Example 5	0.9163	1.04	25.9	1.23	0.008	0.005	0.042
Example 3	0.9164	0.9	29.2	1.27	0.009	0.004	0.049
Example 53	0.9164	0.9	29.2	1.27	0.009	0.004	0.049
Example 51	0.9165	1.01	28.0	1.26	0.009	0.003	0.049
Example 201	0.9165	1.01	27.1	1.22	0.008	0.007	0.048
Example 1	0.9169	0.88	23.4	1.23	0.008	0.005	0.044
Example 52	0.9169	0.85	29.4	1.28	0.008	0.002	0.049
Example 55	0.9170	0.91	29.8	1.29	0.009	0.004	0.050
Example 115	0.9171	0.75	23.4	1.22	0.007	0.003	0.041
Example 43	0.9174	1.08	24.2	1.23	0.007	0.007	0.046
Comparative E2	0.9138	1.56	24.1	1.26	0.006	0.007	0.019
Comparative E	0.9144	1.49	25.6	1.29	0.004	0.005	0.024
Comparative J	0.9151	4.2	21.8	1.2	0.006	0.002	0.024
Comparative C	0.9161	1	30.5	1.35	0.004	0.004	0.030
Comparative B	0.9179	1.01	30.2	1.33	0.004	0.002	0.025
Comparative H2	0.9189	0.89	30.6	1.36	0.004	0.002	0.021
Comparative H	0.9191	0.9	29.6	1.34	0.004	0.003	0.020
Comparative I	0.9415	0.87	62	1.61	0.002	0.000	0.025
Comparative G	0.9612	0.89	49	1.58	0.000	0.000	0.023

TABLE 8B

Additional unsaturation data of several embodiments of the disclosed ethylene interpolymers; as determined by ASTM D3124-98 and ASTM D6248-98.

Sample Code	Density (g/cm^3)	Melt Index I_2 (dg/min)	Melt Flow Ratio (I_{21}/I_2)	S.Ex.	Unsaturations per 100 C		
					Internal	Side Chain	Terminal
Example 8	0.9176	4.64	27.2	1.25	0.009	0.001	0.048
Example 42	0.9176	0.99	23.9	1.23	0.007	0.006	0.046
Example 102	0.9176	0.97	22.6	1.24	0.007	0.005	0.044
Example 54	0.9176	0.94	29.9	1.29	0.009	0.002	0.049
Example 41	0.9178	0.93	23.8	1.23	0.007	0.006	0.046
Example 44	0.9179	0.93	23.4	1.23	0.007	0.007	0.045
Example 9	0.9190	0.91	40.3	1.38	0.008	0.003	0.052
Example 200	0.9250	1.04	24.2	1.24	0.006	0.005	0.050
Example 60	0.9381	4.57	22.2	1.23	0.005	0.002	0.053
Example 61	0.9396	4.82	20.2	1.23	0.002	0.002	0.053
Example 62	0.9426	3.5	25.4	1.26	0.002	0.002	0.052
Example 70	0.9468	1.9	32.3	1.34	0.001	0.002	0.042
Example 71	0.9470	1.61	34.8	1.35	0.001	0.001	0.048
Example 72	0.9471	1.51	31.4	1.34	0.001	0.002	0.043
Example 73	0.9472	1.51	31.6	1.35	0.001	0.002	0.047
Example 80	0.9528	1.53	41.1	1.38	0.002	0.000	0.035
Example 81	0.9533	1.61	50	1.43	0.002	0.000	0.044
Example 82	0.9546	1.6	59.6	1.5	0.001	0.000	0.045
Example 90	0.9588	7.51	29	1.28	0.001	0.000	0.042
Example 91	0.9589	6.72	30.4	1.29	0.002	0.000	0.041
Example 20	0.9596	1.21	31.3	1.35	0.002	0.001	0.036
Example 21	0.9618	1.31	38.3	1.39	0.002	0.001	0.037
Example 22	0.9620	1.3	51	1.49	0.002	0.001	0.041
Example 23	0.9621	0.63	78.9	1.68	0.002	0.001	0.042
Example 24	0.9646	1.98	83	1.79	0.001	0.001	0.052

TABLE 9A

Neutron Activation Analysis (NAA) catalyst residues in several embodiments of the disclosed ethylene interpolymers, as well as Comparatives G, I, J, B, C, E, E2, H and H2.

Sample Code	Density (g/cm^3)	Melt Index I_2 (dg/min)	N.A.A. Elemental Analysis (ppm)			
			Ti	Mg	Cl	Al
Example 60	0.9381	4.57	9.0	140	284	127
Example 62	0.9426	3.50	9.2	179	358	94
Example 70	0.9468	1.90	6.2	148	299	99
Example 71	0.9470	1.61	6.8	168	348	87
Example 72	0.9471	1.51	5.8	178	365	88
Example 73	0.9472	1.51	7.2	142	281	66
Example 80	0.9528	1.53	4.3	141	288	82
Example 81	0.9533	1.61	6.4	163	332	82
Example 82	0.9546	1.60	5.8	132	250	95
Example 90	0.9588	7.51	6.7	143	286	94
Example 91	0.9589	6.72	6.7	231	85	112
Example 1	0.9169	0.88	6.1	199	99	97
Example 2	0.9160	1.04	7.4	229	104	112
Example 3	0.9164	0.90	7.3	268	137	129
Comparative G	0.9612	0.89	1.6	17.2	53	11
Comparative I	0.9415	0.87	2.3	102	24	53
Comparative J	0.9151	4.20	1.4	<2	0.6	7.9
Comparative B	0.9179	1.01	0.3	13.7	47	9.3
Comparative C	0.9161	1.00	2.0	9.0	25	5.4
Comparative E2	0.9138	1.56	1.2	9.8	32.2	6.8
Comparative E	0.9144	1.49	1.3	14.6	48.8	11.3
Comparative H	0.9191	0.90	2.2	14.6	48.8	11.3
Comparative H2	0.9189	0.89	2.2	253	122	130

TABLE 9B

Additional Neutron Activation Analysis (NAA) catalyst residues in several embodiments of the disclosed ethylene interpolymers.

Sample Code	Density (g/cm^3)	Melt Index I_2 (dg/min)	N.A.A. Elemental Analysis (ppm)			
			Ti	Mg	Cl	Al
Example 4	0.9154	0.97	9.6	287	45	140
Example 5	0.9163	1.04	6.7	261	70	131
Example 6	0.9152	0.67	5.2	245	48	119
Example 7	0.9155	0.70	7.7	365	102	177
Example 8	0.9176	4.64	7.6	234	86	117
Example 9	0.9190	0.91	6.4	199	78	99
Example 51	0.9165	1.01	5.9	207	73	106
Example 52	0.9169	0.85	5.2	229	104	112
Example 53	0.9164	0.90	7.3	347	101	167
Example 54	0.9176	0.94	7.5	295	100	146
Example 55	0.9170	0.91	7.1	189	101	90
Example 41	0.9178	0.93	7.2	199	103	92
Example 42	0.9176	0.99	7.5	188	104	86
Example 43	0.9174	1.08	7.4	192	101	91
Example 44	0.9179	0.93	7.2	230	121	110
Example 102	0.9176	0.97	9.5	239	60	117
Example 115	0.9171	0.75	5.1	258	115	130
Example 61	0.9396	4.82	8.3	352	96	179
Example 10	0.9168	0.94	7.8	333	91	170
Example 120	0.9204	1.00	7.3	284	75	149
Example 130	0.9232	0.94	5.8	292	114	147
Example 131	0.9242	0.95	8.6	81.4	173	94
Example 200	0.9250	1.04	6.3	90.1	190	104

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A film comprising at least one layer, wherein said layer comprises an ethylene interpolymer product comprising:

(i) a first ethylene interpolymer;

(ii) a second ethylene interpolymer, and;

(iii) optionally a third ethylene interpolymer;

wherein said ethylene interpolymer product has a Dilution Index, Y_d, greater than 0.

2. A film comprising at least one layer, wherein said layer comprises an ethylene interpolymer product comprising:

(i) a first ethylene interpolymer;

(ii) a second ethylene interpolymer, and;

(iii) optionally a third ethylene interpolymer;

wherein said ethylene interpolymer product has ≥ 0.03 terminal vinyl unsaturations per 100 carbon atoms.

3. A film comprising at least one layer, wherein said layer comprises an ethylene interpolymer product comprising:

(i) a first ethylene interpolymer;

(ii) a second ethylene interpolymer, and;

(iii) optionally a third ethylene interpolymer;

wherein said ethylene interpolymer product has ≥ 3 parts per million (ppm) of a total catalytic metal.

4. The manufactured article of any one of claims 1-3, further characterized as having a Dimensionless Modulus, X_d, greater than 0.

5. The manufactured article of any one of claims 1 or 2, further characterized as having ≥ 3 parts per million (ppm) of a total catalytic metal.

6. The manufactured article of claim 1, further characterized as having ≥ 0.03 terminal vinyl unsaturations per 100 carbon atoms.

7. The manufactured article of claim 5, further characterized as having a Dimensionless Modulus, X_d, greater than 0.

8. The manufactured article of claim 6, further characterized as having a Dimensionless Modulus, X_d, greater than 0.

9. The manufactured article of claim 1, further characterized as having ≥ 3 parts per million (ppm) of a total catalytic metal and ≥ 0.03 terminal vinyl unsaturations per 100 carbon atoms.

10. The manufactured article of claim 9, further characterized as a Dimensionless Modulus, X_d, greater than 0.

11. The film of any one of claims 1-10 having a melt index from 0.4 to 12 dg/minute; wherein melt index is measured according to ASTM D1238 (2.16 kg load and 190°C).

12. The film of any one of claims 1-10 having a density from 0.900 to 0.935 g/cc; wherein density is measured according to ASTM D792.

13. The film of any one of claims 1-10 having a M_w/M_n from 2 to 25.

14. The film of any one of claims 1-10 having a $CDBI_{50}$ from 20% to 98%.

15. The film of any one of claims 1-10; wherein

(i) said first ethylene interpolymer is from 15 to 60 weight percent of said ethylene interpolymer product;

(ii) said second ethylene interpolymer is from 30 to 85 weight percent of said ethylene interpolymer product, and;

(iii) optionally said third ethylene interpolymer is from 0 to 30 weight percent of said ethylene interpolymer product;

wherein weight percent is the weight of said first, said second or said optional third ethylene interpolymer divided by the weight of said ethylene interpolymer product.

16. The film of any one of claims 1-10; wherein

(i) said first ethylene interpolymer has a melt index from 0.01 to 200 dg/minute;

(ii) said second ethylene interpolymer has melt index from 0.3 to 1000 dg/minute, and;

(iii) optionally said third ethylene interpolymer has a melt index from 0.5 to about dg/minute;

wherein melt index is measured according to ASTM D1238 (2.16 kg load and 190°C).

17. The film of any one of claims 1-10; wherein

(i) said first ethylene interpolymer has a density from 0.855 g/cm^3 to 0.975 g/cc;

(ii) said second ethylene interpolymer has a density from 0.89 g/cm^3 to 0.975 g/cc, and;

(iii) optionally said third ethylene interpolymer has density from 0.89 to 0.975 g/cc;

wherein density is measured according to ASTM D792.

18. The film of any one of claims 1-10; wherein said ethylene interpolymer product is synthesized using a solution polymerization process.

19. The film of any one of claims 1-10 further comprising from 0.1 to 10 mole percent of one or more α-olefin.

20. The film of claim 19; wherein said one or more α-olefin are C_3 to C_{10} α-olefins.

21. The film of claim 19; wherein said one or more α-olefin is 1-hexene, 1-octene or a mixture of 1-hexene and 1-octene.

22. The film of any one of claims 1-10; wherein said first ethylene interpolymer is synthesized using a single-site catalyst formulation.

23. The film of any one of claims 1-10; wherein said second ethylene interpolymer is synthesized using a first heterogeneous catalyst formulation.

24. The film of any one of claims 1-10; wherein said third ethylene interpolymer is synthesized using a first heterogeneous catalyst formulation or a second heterogeneous catalyst formulation.

25. The film of any one of claims 1-10 wherein said second ethylene interpolymer is synthesized using a first in-line Ziegler Natta catalyst formulation or a first batch Ziegler-Natta catalyst formulation; optionally, said third ethylene interpolymer is synthesized using said first in-line Ziegler Natta catalyst formulation or said first batch Ziegler-Natta catalyst formulation.

26. The film of any one of claims 1-10 wherein said third ethylene interpolymer is synthesized using a second in-line Ziegler Natta catalyst formulation or a second batch Ziegler-Natta catalyst formulation.

27. The film of any one of claims 1-10, having ≤ 1 part per million (ppm) of a metal A; wherein said metal A originates from a single site catalyst formulation used to synthesize said first ethylene interpolymer.

28. The film of claim 27; wherein said metal A is titanium, zirconium or hafnium.

29. The film of any one of claims 1-10 having a metal B and optionally a metal C and the total amount of said metal B plus said metal C is from 3 to 11 parts per million; wherein said metal B originates from a first heterogeneous catalyst formulation used to synthesize said second ethylene interpolymer and optionally said metal C originates from a second heterogeneous catalyst formulation used to synthesize said third ethylene interpolymer; optionally said metal B and said metal C are the same metal.

30. The film of claim 29; wherein said metal B and said metal C, are independently selected from titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, technetium, rhenium, iron, ruthenium or osmium.

31. The film of claim 29; wherein said metal B and said metal C, are independently selected from titanium, zirconium, hafnium, vanadium or chromium.

32. The film of any one of claims 1-10 wherein said first ethylene interpolymer has a first M_w/M_n, said second ethylene interpolymer has a second M_w/M_n and said optional third ethylene interpolymer has a third M_w/M_n; wherein said first M_w/M_n is lower than said second M_w/M_n and said optional third M_w/M_n.

33. The film of any one of claims 1-10 wherein the blending of said second ethylene interpolymer and said third ethylene interpolymer forms a heterogeneous ethylene interpolymer blend having a fourth M_w/M_n; wherein said fourth M_w/M_n is not broader than said second M_w/M_n.

34. The film of any one of claims 1-10 wherein said second M_w/M_n and said optional third M_w/M_n are ≤ 4.0.

35. The film of any one of claims 1-10; wherein said first ethylene interpolymer has a first $CDBI_{50}$ from 70 to 98%, said second ethylene interpolymer has a second $CDBI_{50}$ from 45 to 98% and said optional third ethylene interpolymer has a third $CDBI_{50}$ from 35 to 98%.

36. The film of claim 35; wherein said first $CDBI_{50}$ is higher than said second $CDBI_{50}$; optionally said first $CDBI_{50}$ is higher than said third $CDBI_{50}$.

37. The film of any one of claims 1-10; wherein said film is a multilayer film, wherein said multilayer film has a sealant layer, wherein said sealant layer comprises said ethylene interpolymer product and said multilayer film has a hole size ≥ 95 μm and ≤ 115 μm; wherein hole size is determined in a caulkability test.

38. The film of claim 37; wherein said multilayer film has from 2 to 11 layers.

FIGURE 1

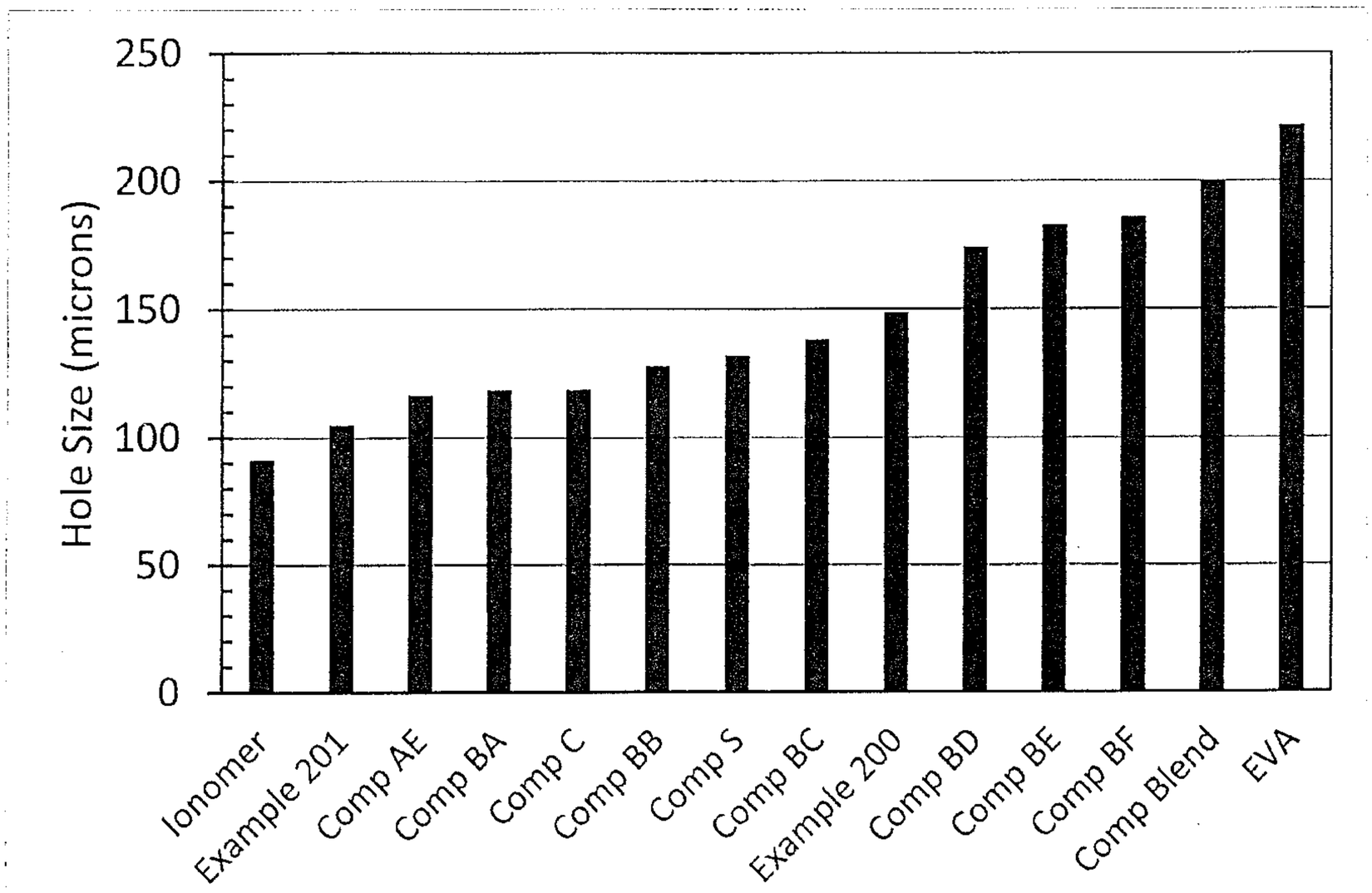


FIGURE 2

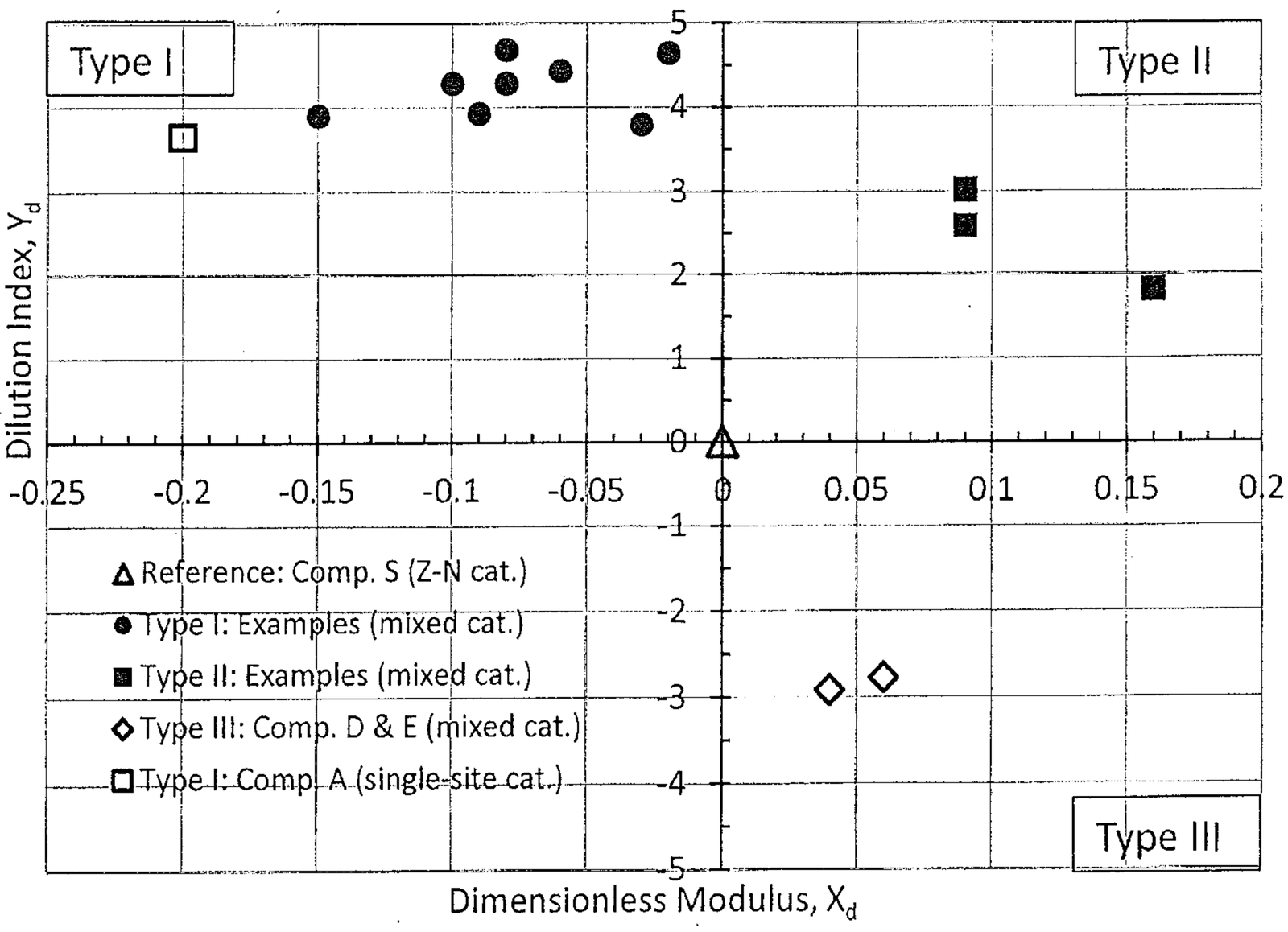


FIGURE 3

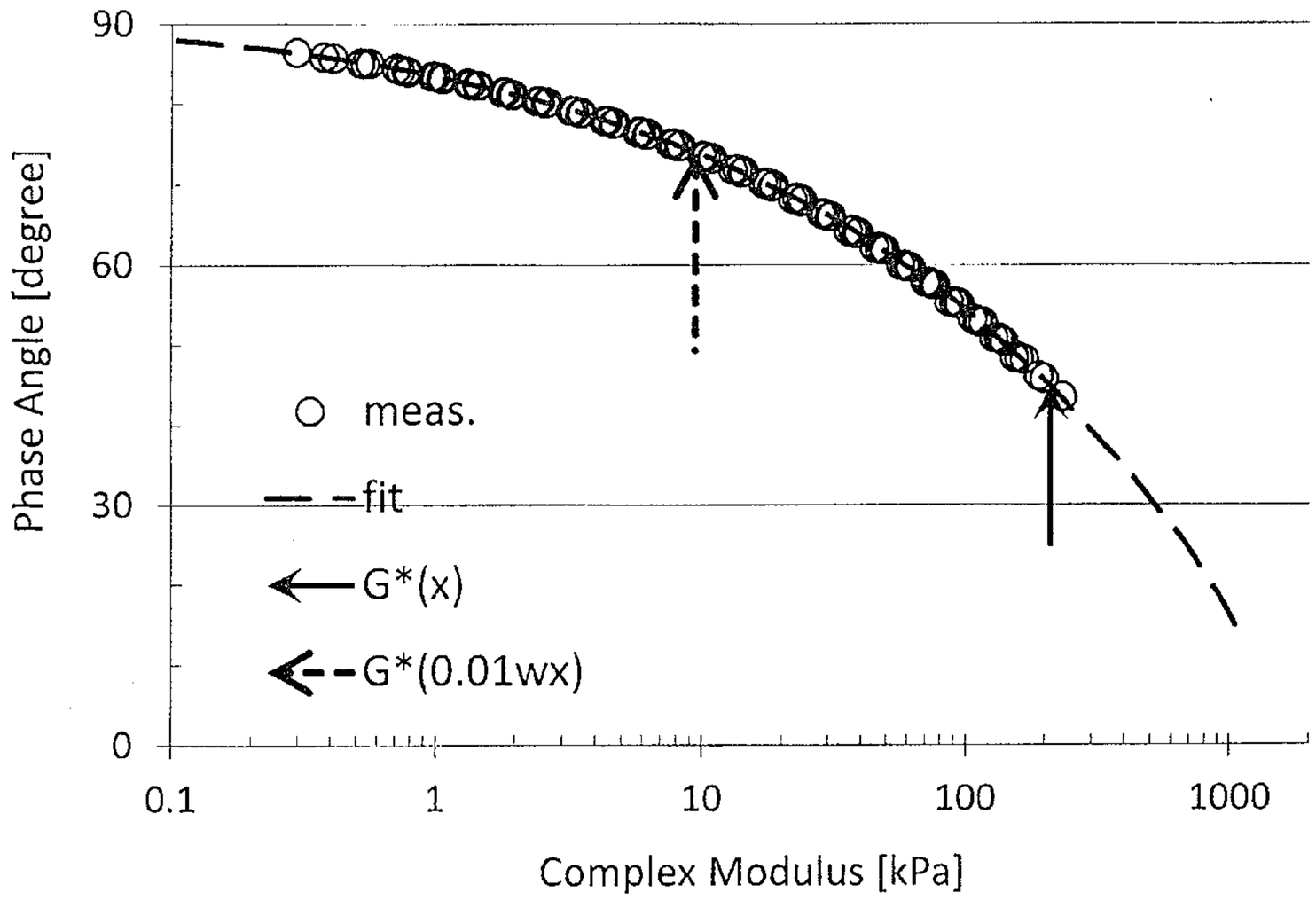


FIGURE 4

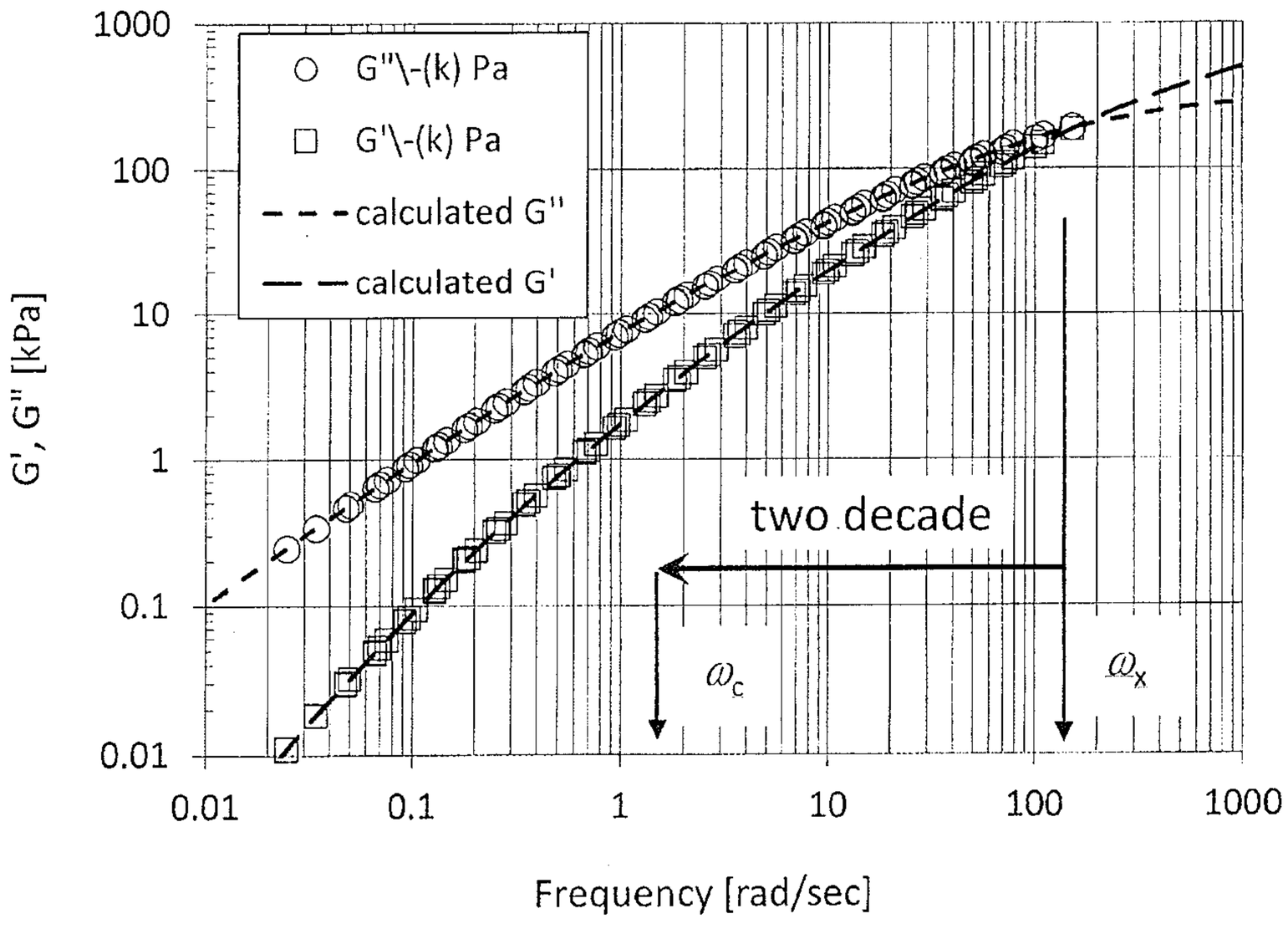


FIGURE 5

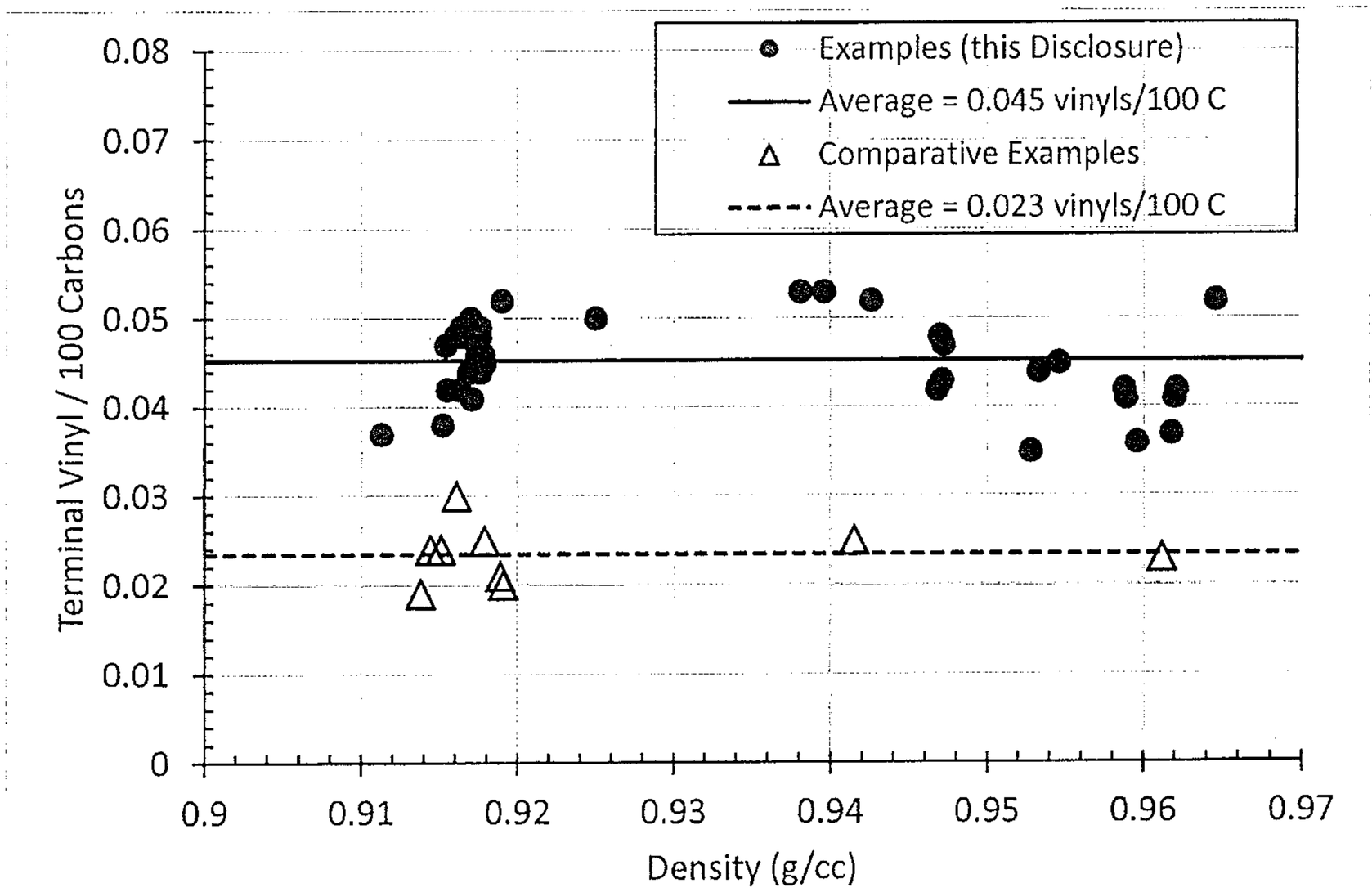


FIGURE 6

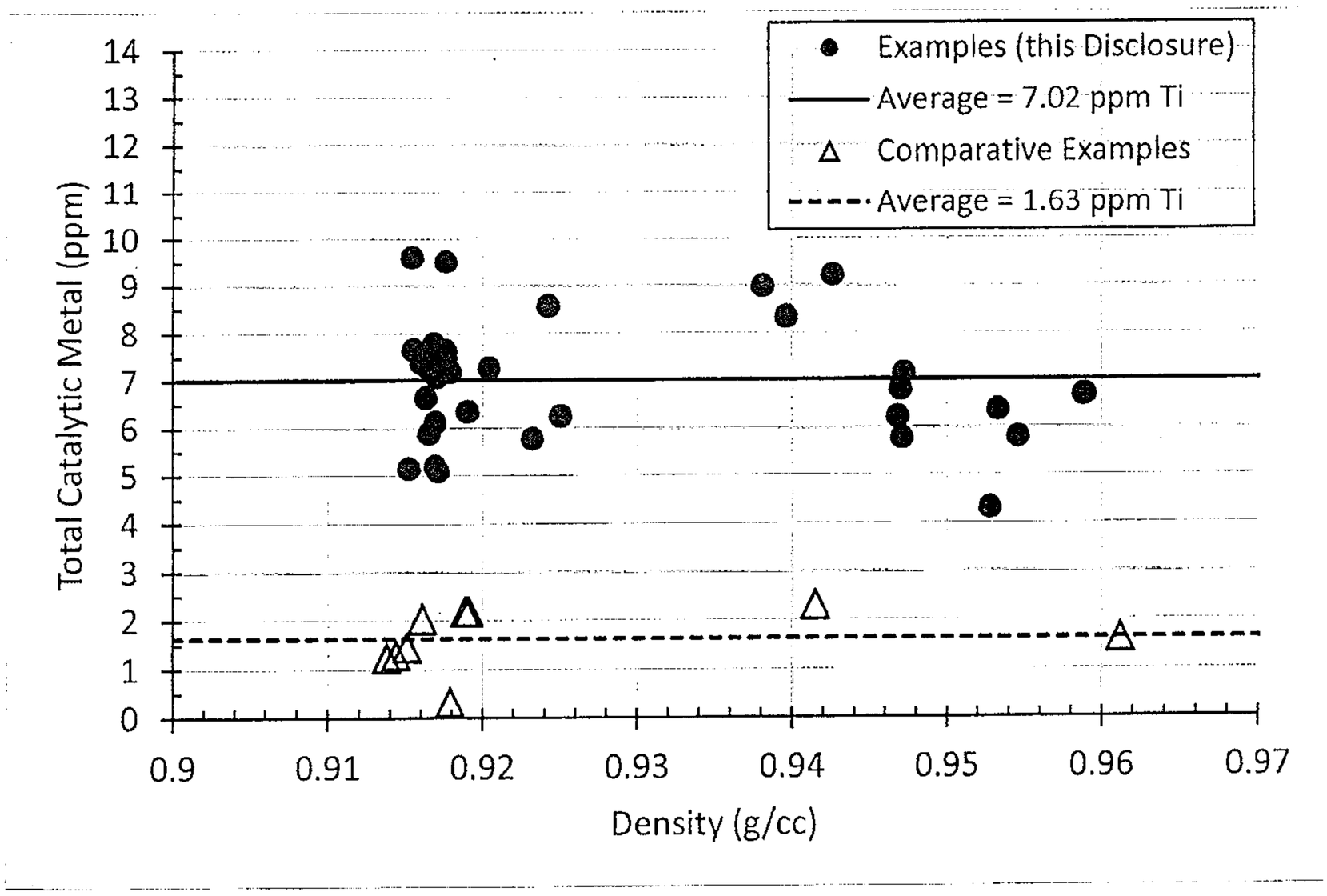
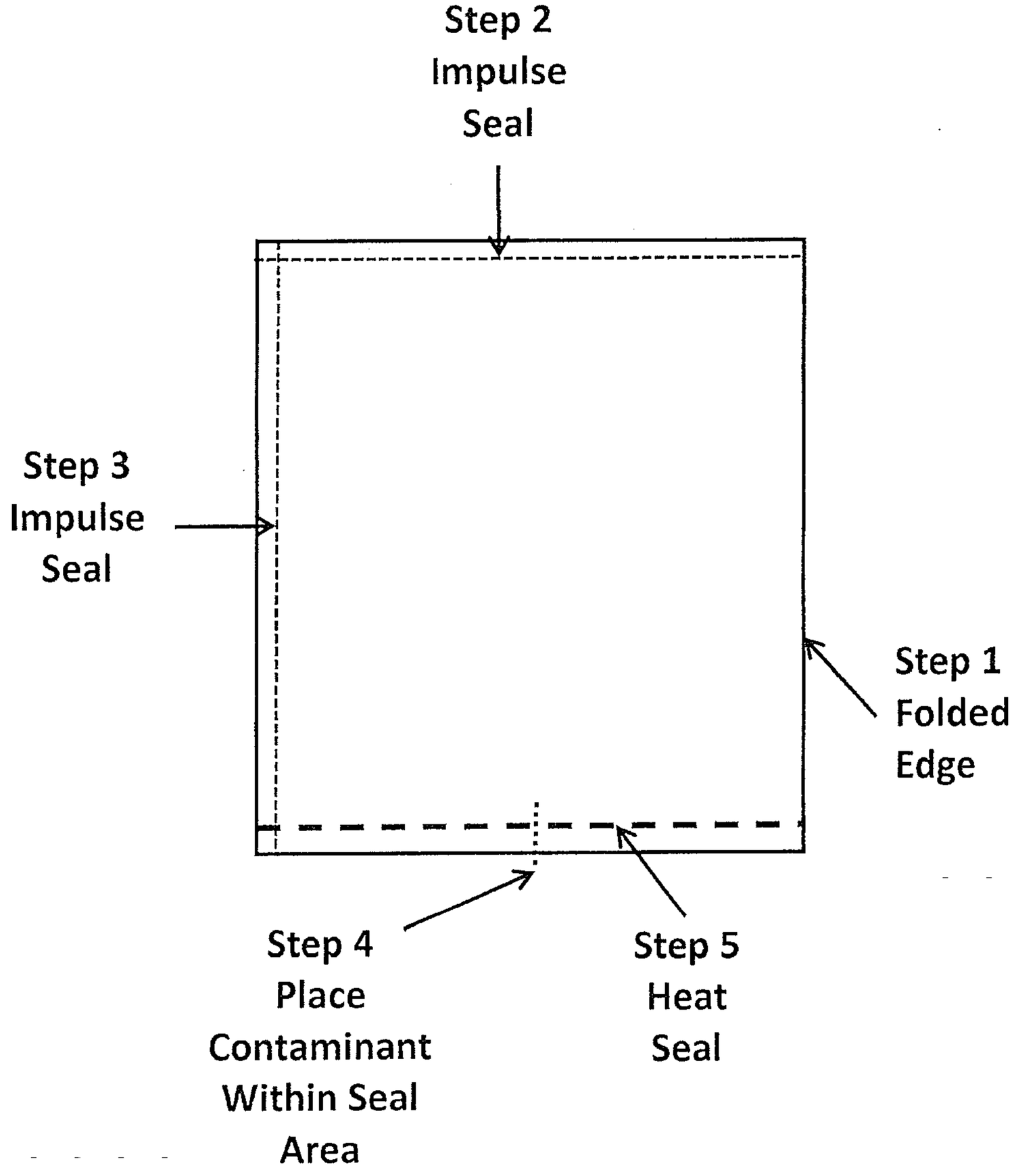


FIGURE 7


Step 2
Impulse
Seal
Step 3
Impulse
Seal
Step 1
Folded
Edge
Step 4
Place
Contaminant
Within Seal
Area
Step 5
Heat
Seal