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(54) Title: POLYOLEFIN RESINS FOR CONTAINERS

		Best Performer for Liquid Forming & Filling	'Beverage' Application Resin	'Home & Personal Care' Application Resin	'High Clarity' Package
Melt Flow Index (MFI) Direct Correlation to Molecular Weight]	Full Range	0.3 - 10.0 g/10 min @ 190 C under 2.16 kg			
	Preferably	< 4.0 for repeatable material distribution			
	Most Preferably	< 2.0 for repeatable material distribution			
	Comments / Findings	Package ruptures decrease & material distribution consistency improves with increased polymer molecular weight (decreased MFI). EBM resins (chromium catalyzed; highest molecular weight; fractional MFI; MFI <1) showed the fewest number of package ruptures. Main issue with <1 MFI resins is that they are not amenable to injection.			
Polydispersity index (PDI) [Direct Correlation to Molecular Weight Distribution]	Full Range	4 - 25	4 - 25		4 - 25
	Preferably	>7	>7	>8	>7
	Most Preferably	>9	>9	>9	>9
	Comments / Findings	Specifying molecular weight distribution by PDI: Grades with a PDI < 7 showed a failure rate of >25% Grades with a PDI of 7 - 9 showed a failure rate of <10% Grades with a PDI of > 9 showed a failure rate of 0% (30 for 30) ESCR increases with increasing molecular weight distribution (increasing PDI).			

To FIG-4B

FIG - 4A

(57) Abstract: A high-density polyethylene (HDPE) resin configured to be molded into a preform that can be biaxially expanded within a cavity of a container mold by introducing an incompressible fluid under pressure into the preform to stretch the preform to assume a shape of a surrounding mold cavity of the container mold. The HDPE resin has: a melt flow index of between 0.3 and 10.0 grams per 10 minutes at a temperature of 190°C under 2.16 kilograms of load; a polydispersity index of 4 - 24; and a density of 0.943 - 0.965 grams per cubic centimeter.

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[Continued on next page]

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POLYOLEFIN RESINS FOR CONTAINERS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 62/720,576, filed on August 21, 2018. The entire disclosure of the above application is incorporated herein by reference.

FIELD

[0001] The present disclosure relates to containers formed of polyolefin resin.

BACKGROUND

[0002] This section provides background information related to the present disclosure, which is not necessarily prior art.

[0003] Biaxial stretching is usually used to stretch and form polymers into plastic packages, using processes such as injection stretch bow molding (ISBM). Typically, the polymers used during such biaxial stretching operations orient and strengthen locally, providing measurable properties such as “strain hardening” or “crystallization” that minimize package ruptures. The most useful and widely used polymer having good orientation and localized strengthening properties during biaxial stretching is polyethylene terephthalate (PET). Manufacturers and fillers, as well as consumers, have recognized that PET packages are lightweight, inexpensive, recyclable and manufacturable in large quantities. Other polyolefin materials, such as high density polyethylene, are also desirable for use in forming packages, as discussed below.

[0004] Traditionally ISBM and filling have developed as two independent processes, in many cases operated by different companies. In order to make package filling more cost effective, some fillers have moved blow molding in house, in many cases integrating ISBM machines directly into their filling lines. The equipment manufacturers have recognized this advantage and are selling “integrated” systems that are designed to ensure that the blow molder and the filler are fully synchronized. Despite the efforts in bringing the two processes closer together, blow molding and filling continue to be two independent, distinct processes. As a result, significant costs may be incurred while performing these two processes separately.

[0005] Known methods of simultaneously forming and filling a package are disclosed in commonly-owned U.S. Pat. Nos. 8573964, 8714963, and 8858214, hereby incorporated herein by reference in their entireties. The methods disclosed therein require numerous pieces of equipment including a mold station comprising a pressure source, blow nozzle, stretch rod, and a mold cavity.

[0006] The technology for simultaneously forming and filling a package presents processing parameters which are not readily available when forming rigid plastic packages, such as bottles, using air. Unlike air, liquid, when used as a pressure source, does not significantly contract or expand with changes in temperature and pressure (incompressible). Additionally, the heat capacity for liquid is much higher than for air and fluctuations in liquid temperature during forming are not significant. Further, the incoming liquid temperature is settable (can be controlled to a specific set point) and can be used to manipulate material distribution of the plastic in the formed package. Finally, the volumetric flow rate of the injected fluid may be precisely controlled, to thereby control a rate of polymeric stretching during the injection process.

[0007] Currently, it is not practical to form packages from high density polyethylene (HDPE) using air. HDPE exhibits poor polymer orientation and localized strengthening during biaxial stretching processes when air is used as the pressure source. However, when using liquid as the pressure source, additional process controls are available to aid in repeatable control of material distribution for the minimization of package ruptures, including: (1) forming with and incompressible fluid, (2) controlling the fluid temperature, and (3) precision control of the volumetric flowrate for forming. It is desirable to identify and to optimize the HDPE resin properties that lend themselves to the simultaneous formation and filling of packages. It is further desirable to identify the forming conditions (e.g. liquid temperature; forming speed) that optimize package to package consistency. Finally, it is desirable to identify how changes to forming conditions impact end package properties.

[0008] The present disclosure advantageously provides for a preform configured to form a container when the preform is seated in a cavity of a mold and the preform is expanded within a cavity of a mold by introducing an incompressible fluid under a blow pressure into the preform to stretch the preform to assume a shape of the surrounding cavity, the preform comprising. The present disclosure provides numerous additional advantages and unexpected results as set forth herein, and as one skilled in the art will appreciate.

SUMMARY

[0009] This section provides a general summary of the disclosure, and is not a comprehensive disclosure of its full scope or all of its features.

[0010] The present disclosure includes a preform configured to form a container when the preform is seated in a cavity of the mold and the preform is expanded within the cavity of a mold by introducing an incompressible fluid under a blow pressure into the preform to stretch the preform to assume a shape of the surrounding cavity. The preform includes a high-density polyethylene (HDPE) resin having: a melt flow index of between 0.3 and 10.0 grams per 10 minutes at a temperature of 190ºC under 2.16 kilograms of load through a test fixture of ASTM D1238 [5]; a polydispersity index of 4 - 24; and a density of between 0.943 and 0.965 grams per cubic centimeter.

[0011] Further areas of applicability will become apparent from the description provided herein. The description and specific examples in this summary are intended for purposes of illustration only and are not intended to limit the scope of the present disclosure.

DRAWINGS

[0012] The drawings described herein are for illustrative purposes only of selected embodiments and not all possible implementations, and are not intended to limit the scope of the present disclosure.

[0013] Figure 1 is a cross-sectional view of a system for simultaneously forming and filling a container from a preform, the preform made from high-density polyethylene in accordance with the present disclosure;

[0014] Figure 2 illustrates area 2 of Figure 1 as a close-up view;

[0015] Figure 3 illustrates an exemplary container formed from a preform in accordance with the present teachings;

[0016] Figure 4A illustrates exemplary properties of preforms according to the present teachings;

[0017] Figure 4B illustrates additional exemplary properties of preforms according to the present teachings; and

[0018] Figure 4C illustrates further exemplary properties of preforms according to the present teachings.

[0019] Corresponding reference numerals indicate corresponding parts throughout the several views of the drawings.

DETAILED DESCRIPTION

[0020] Example embodiments will now be described more fully with reference to the accompanying drawings.

[0021] Figure 1 is a cross-sectional view of a container forming and filling system 10. The system 10 can be connected to any suitable fluid source 12 for simultaneously forming and filling any suitable polymeric container (such as container 110 of Figure 3) from a preform 14. Any suitable fluid can be used. For example, water, juice, flavored drinks, carbonated soda, detergents, oils, chemicals, and the like. The fluid expands the preform 14 within any suitable mold 16, which has an inner mold surface 18 defining any suitable container shape.

[0022] Specifically, fluid from the fluid source 12 passes through fluid inlet 20 into a fluid/filing cylinder 22. Excess fluid exits the system 10 through a fluid outlet 24. The fluid cylinder 22 controls the fill velocity at which fluid flows into the preform 14. The fluid cylinder 22 is controlled by a control module 30. In this application, the term "control module" may be replaced with the term "circuit." The term "control module" may refer to, be part of, or include processor hardware (shared, dedicated, or group) that executes code and memory hardware (shared, dedicated, or group) that stores code executed by the processor hardware. The code is configured to provide the features of the system 10, and the control module 30 thereof, described herein.

[0023] With continued reference to Figure 1, and additional reference to Figure 2, the fluid cylinder 22 injects the fluid to a nozzle 40, and specifically to a fluid path 44 defined by a nozzle receptacle 42 of the nozzle 40. Connected to the nozzle 40 is a finish 50 of the preform 14 and the container 110 formed therefrom. The finish 50 defines an opening 52 through which the fluid is injected.

[0024] Seated within the nozzle receptacle 42 is a seal pin 60. The seal pin 60 includes a sealing surface 62, which is arranged opposite to a nozzle sealing surface 46 of the nozzle 40. In a closed position, the seal pin 60 is arranged such that the sealing surface 62 abuts the nozzle sealing surface 46 in order to prevent fluid from flowing through the nozzle 40 and into the preform 14. From the closed position, the seal pin 60 is movable to an open position, such as illustrated in Figure 2. When the seal pin 60 is open, the sealing surface 62 is spaced apart from the nozzle sealing surface 46 to define a nozzle passage 70 therebetween. Fluid flowing from the fluid cylinder 22 and through the fluid path 44 can thus flow through the nozzle passage 70 to the finish 50, and specifically through the opening 52 of the finish 50 in order to form and fill the container

from the preform 14. The position of the seal pin 60, such as in a closed position or any degree of an open position, is detected with any suitable seal pin position detector or sensor 64 (see Figure 1). Any suitable seal pin position detector 64 can be used, such as any suitable laser sensor or linear variable differential transducer (LVDT). The control module 30 receives inputs from the seal pin position detector or sensor 64 so that the control module 30 knows the position of the seal pin 60.

[0025] A stretch rod 80 is included to facilitate stretching of the preform 14 into the mold 16. The stretch rod 80 extends within and beyond the seal pin 60, and is movable independent of the seal pin 60. As fluid is injected into the preform 14, the stretch rod 80 is positioned so as to extend through the finish 50 to a bottom surface of the preform 14, such as is illustrated in Figure 1. Thus the presence of the stretch rod 80 within the finish 50 reduces the area of the opening 52 through which fluid can flow into the preform 14.

[0026] The preform 14 is made of high-density polyethylene (HDPE) resin. Material distribution during simultaneous forming and filling of a container (such as the container 110) from the preform 14 made of HDPE resin is highly dependent on the resin microstructure. HDPE commercial resin grades vary in several characteristics that potentially impact the extent to which the polymer will distribute when biaxially oriented. Exemplary HDPE resin parameters for the preform 14 and exemplary resulting container 110 are described herein, and set forth in Figures 4A, 4B, and 4C.

(1) Molecular Weight [Indirectly measured as inversely proportional to MFI]

[0027] HDPE resin grades for extrusion blow molding (EBM) applications are higher in molecular weight than HDPE resin grades chosen for injection applications. The longer the polymer chain, the higher the molecular weight. Melt strength in the extruded EBM parison increases with increasing polymer chain length. It is expected that the increase in the melt strength in EBM translates to increased polymer entanglement for even stress distribution during biaxial orientation. A balance must be sought for the injectability to preforms (shear thinning nature) and the chain length needed to maintain integrity during biaxial orientation.

(2) Molecular Weight Distribution [Directly reported as the polydispersity index (PDI)]

[0028] Polymer weight dispersity may impact material distribution consistency. Molecular weights in HDPE resins range from highly uniform to widely dispersed (see "A Guide to Polyolefin Blow Molding," LyondellBasell Industries, pp. 1 – 57, which is incorporated herein by reference in its entirety). The molecular weight distribution is highly dependent on the catalyst system used, the use of a single reactor or multiple

reactors in series, and the comonomers. Resins selected for this commercial screening span the commercially available densities, catalyst systems and modalities.

[0029] HDPE can be generated with reactors in series. Interlacing longer polymer chains with shorter chains of HDPE yield the following benefits, which may increase material distribution consistency in ISBM:

[0030] (a) Low molecular weight polymer chains have a fast initial rate of shear thinning within the melt (see "B5845 Bimodal Molecular Weight Polyethylene for Blow Molding," Total Petrochemicals USA, Inc., which is incorporated herein by reference in its entirety). Low shear mobility of polymer within the resin matrix eases processability (see *Id.*). Low shear mobility of polymer may aid in material distribution consistency.

[0031] (b) The high molecular weight 'tie molecules' act to generate a physical network between the crystal regions of lower molecular weight polymers (see Cazenave, J. et al. "Structural Approaches of Polyethylene Environmental Stress-Crack Resistance," Oil & Gas Science and Technology Vol. 61, No. 6, pp. 735-742 (2006), which is incorporated herein by reference in its entirety; see Chen, Y. et al., "Structure and Rheological Property Relationship of Bimodal Polyethylene with Improved Environmental Stress Cracking Resistance," Polymer Science, Ser. A, Vol 56 No 5, pp. 671-680 (2014), which is incorporated herein by reference in its entirety). As the lower molecular weight polymers begin the initial deformation, the higher molecular weight polymers will act to branch between these more mobile regions.

[0032] (c) Rheological profiling of bimodal ethylene (BE) HDPE grades show that an increase in the fraction of the higher molecular weight polymer in the HDPE melt increases the elasticity of the melt (ability to recover from applied deformation force) (see Chen, Y. et al., "Structure and Rheological Property Relationship of Bimodal Polyethylene with Improved Environmental Stress Cracking Resistance," Polymer Science, Ser. A, Vol 56 No 5, pp. 671-680 (2014)). The attributes of early chain mobility, elastic recovery and a linked physical network between crystalline sections make multimodal HDPE resin grades appealing to an ISBM process.

(3) Co-Polymer Content [Indirectly measured by the density of the resin]

[0033] Density of HDPE is a result of (1) ethylene / comonomer molar ratio; (2) temperatures within the reactors; (3) catalyst type. Homopolymer HDPE resin grades are expected to have highest density and stiffness, but the poorest ESCR and no entanglement due to side chains. For an example of a homopolymer with poor ESCR and high density (see UNIVAL™ DMDA-6400 NT 7, "High Density Polyethylene Resin).

Addition of "comonomers" decreases density, crystallinity, and stiffness while increasing ESCR, toughness and clarity (see "A Guide to Polyolefin Blow Molding," LyondellBasell Industries, pp. 1 – 57, which is incorporated herein by reference in its entirety). The 'stiffness' and the 'entanglement' extent of the resin is expected to impact the material distribution consistency.

Molecular Weight

[0034] Package ruptures decrease & material distribution consistency improves with increased polymer molecular weight (decreased MFI).

[0035] (1) EBM resins (highest molecular weight; fractional MFI; MFI <1) showed the fewest number of package ruptures.

[0036] (2) Main issue with EBM resins is that HDPE resin grades with MFIs <1 are not amenable to injection.

Modality

[0037] Multimodality aids the mobility of the polymer chains during the biaxial orientation.

[0038] (1) Comparing Ziegler-Natta catalyzed HDPEs, the multimodal grades showed a decrease in rupture percentage by about 30%, when comparing between multimodal and unimodal grades of comparable MFIs and density.

[0039] (2) Comparing Chromium catalyzed HDPEs, the unimodal resin grade was limited in its hoop and axial stretch ratios. The multimodal chromium catalyzed HDPE was a higher molecular weight HDPE, but its polymer chains had greater mobility than the unimodal.

Copolymer Content

[0040] Copolymer content increases lead to an increase in the rupture frequency. Higher copolymer content decreases the energy needed to deform the material.

[0041] (1) Unimodal HDPEs with densities < 0.955 all had rupture percentages of >28%. Whereas unimodal HDPEs with densities > 0.955 & MFIs < 6 all had rupture percentages of < 10%. Therefore, package failures decrease with decreasing copolymer content.

[0042] (2) Homopolymer resins have an unacceptable ESCR for the HPC market.

Liquid Flow Rate Analysis

[0043] Simultaneous forming and filling of HDPE packages is possible using liquid flowrates in excess of 6.0 L/sec down to 0.5 L/sec. Using any of the resins described

herein, optimal package formation is obtained when the liquid flowrates is less than 3.0 L/sec. A preferred liquid flowrate should be in the range of 0.5 to 3.0 L/sec.

[0044] Simultaneous forming and filling of HDPE packages is additionally possible using injection liquid temperature in the range of 85°C down to 9°C. Using any of the resins described herein, optimal package formation is obtained when the liquid temperature is less than 45°C. A preferred incoming fluid temperature is between 9°C to 30°C.

[0045] In the cases where a stretch rod is used to aid in axially stretching the preform during simultaneous forming and filling of an HDPE package using any of the resins described herein, optimal package formation is obtained when the stretch rod reaches the base of the mold by the time the package is 0-50% formed. Preferably, the stretch rod should reach the base of the mold with less than 20% of the end volume of fluid introduced to the package.

Package from Process

[0046] Evaluating containers simultaneously formed and filled using the preform 14 formed of any of the resins described herein, liquid temperature can be used as a driver to impact end package crystallinity. Optimal package formation is obtained when forming packages with an injection liquid temperature less than 45°C. When formed using an injection liquid temperature less than 45°C, a lower crystallinity is obtained than in the packages formed at 63°C. The lower the liquid temperature for forming, the lower the percent crystallinity in the upper panel of the end container. Lower crystallinity is desirable as this results in greater clarity, and higher ESCR. Accordingly, during simultaneous forming and filling of an HDPE package using any of the resins described herein, optimal package formation is obtained when the injection fluid temperature is less than 45°C to minimize end package crystallinity.

Exemplary Compositions for HDPE Preforms 14 In Accordance with the Present Disclosure

[0047] The present disclosure provides for various HDPE resins, any of which the preform 14 may be molded from. In general, HDPE resins in accordance with the present disclosure vary in three major physical property descriptors: (1) Molecular Weight [Interpreted from Melt Flow Index (MFI)]; (2) Molecular Weight Distribution [Measured by polydispersity index (PDI)]; and (3) Comonomer content [Interpreted from Density]. Properties of various exemplary HDPE resins from which the preform 14 may be molded are described below and set forth in Figures 4A, 4B, and 4C.

[0048] In one embodiment, an HDPE resin for use in a simultaneous blowing and filling operation includes the following physical properties:

1) Molecular weight - MFI ranging from 0.3 – 10.0 g/10 min @ 190 C under 2.16 kg.
    a. Preferably, MFI should be ≤ 4.0 for repeatable material distribution.
    b. Most preferably, MFI should be < 2.0 for repeatable material distribution.
2) Molecular Weight Distribution - PDI of 4 – 25.
3) For resins generated with a Ziegler-Natta catalyst system or resins that are chromium catalyzed, where the resin has a MFI > 1 g/10min @ 190 C under 2.16 kg, a multimodal resin is preferred.
4) Density of 0.943 – 0.965 g/cm^3.

[0049] In another embodiment, the present disclosure describes an HDPE resin for use in a simultaneous blowing and filling operation suitable for manufacturing packages for the 'beverage' market. The resin includes the following physical properties:

1) Molecular weight - MFI ranging from 0.3 – 10.0 g/10 min @ 190 C under 2.16 kg.
    a. Preferably, MFI should be ≤ 4.0 for repeatable material distribution.
    b. Most preferably, MFI should be < 2.0 for repeatable material distribution.
2) Molecular Weight Distribution - PDI of 4 – 25.
3) For resins generated with a Ziegler-Natta catalyst system or resins that are chromium catalyzed, where the resin has a MFI > 1 g/10min @ 190 C under 2.16 kg, a multimodal resin is preferred.
4) Density > 0.96 g/cm^3.

[0050] In another embodiment, the present disclosure describes an HDPE resin for use in a simultaneous blowing and filling operation suitable for manufacturing packages suited to environments requiring chemical resistance. The resin includes the following physical properties:

1) Molecular weight - MFI ranging from 0.3 – 10.0 g/10 min @ 190 C under 2.16 kg.
    a. Preferably, MFI should be ≤ 4.0 for repeatable material distribution.
    b. Most preferably, MFI should be < 2.0 for repeatable material distribution.
2) Molecular Weight Distribution - PDI > 9.
3) For resins generated with a Ziegler-Natta catalyst system or resins that are chromium catalyzed, where the resin has a MFI > 1 g/10min @ 190 C under 2.16 kg, a multimodal resin is preferred.
4) Density <0.962 g/cm^3.

[0051] In another embodiment, the present disclosure describes an HDPE resin for use in a simultaneous blowing and filling operation suitable for manufacturing packages having a high opacity. The resin includes the following physical properties:

1) Molecular weight - MFI ranging from 0.3 – 10.0 g/10 min @ 190 C under 2.16 kg.
    a. Preferably, MFI should be $\leq$ 4.0 for repeatable material distribution.
    b. Most preferably, MFI should be < 2.0 for repeatable material distribution.
2) Molecular Weight Distribution - PDI of 4 – 25.
3) For resins generated with a Ziegler-Natta catalyst system or resins that are chromium catalyzed, where the resin has a MFI > 1 g/10min @ 190 C under 2.16 kg, a multimodal resin is preferred.
4) Density <0.95 g/cm^3.

[0052] Process conditions were also discovered to optimize package forming consistency using any of the above described HDPE resins. In one embodiment, an HDPE resin having one or more of the above properties was simultaneously formed into a package and was filled, where the liquid flowrate is within a range of 0.5 to 3.0 L/sec.

[0053] In another embodiment, an HDPE resin having one or more of the above properties was simultaneously formed into a package and was filled, where the fluid temperature is within a range of 9 to 30 °C.

[0054] In another embodiment, an HDPE resin having one or more of the above properties was simultaneously formed into a package and was filled, where a stretch rod is used to aid in axially stretching the preform. The stretch rod optimally reaches the base of the mold with less than 20% of the end volume is introduced during the forming process, with the rest of the volume introduced after the stretch rod reaches the base of the mold.

[0055] Finally, a temperature of the injection fluid was modified to optimize the crystallinity of a package formed using any of the above described HDPE resins. In one embodiment, an HDPE resin having one or more of the above properties was simultaneously formed into a package and was filled, where the injection fluid temperature is less than 45°C. Forming at this temperature results in lower crystallinity, leading to greater clarity and higher Environmental Stress Crack Resistance ("ESCR").

[0056] The present disclosure provides numerous advantages. For example, polyethylene comes in many different forms, including: very low density, low density, linear low density, medium density, cross-linked, high density, and ultra-high molecular weight. Compared to lower density variations, high density polyethylene is very linear

and has much fewer branches; the lack of branching allows the molecules to pack closer together making the polyethylene denser than those with many branches. The ability of the system 10 to form containers out of polyolefin resins greatly increases the value of the system 10. Polyethylene terephthalate (PET) containers can advantageously be produced on the same system as olefins (specifically HDPE), reducing the number of different machines in a single plant.

Glossary of Terms

[0057] Adjusted Sum of Squares – Quantifies the variation between sets. The greater the Adj SS, the more significant the factor impacts the outcome.

[0058] ANOVA (Analysis of Variance) – Analysis of the difference between 3 or more group means to determine if the populations statistically significantly different from each other.

[0059] Axial – Extending in the direction perpendicular to the cyclic plane of the preform cross section. In the plane parallel to the extending stretch rod.

[0060] Biaxial – Relating to two axes. In the case of the stretch formation of packages, the axes referenced are the hoop and the axial.

[0061] Bimodal - In reference to multiple modes of molecular weights, please see 'multimodal'

[0062] Blow out – A rupture or a failure in the integrity of the packaging.

[0063] BOR (Blow out ratio) or BUR (Blow-up ratio) - The product of the axial stretch ratio and the hoop stretch ratio.

[0064] Comonomer – Monomer included in the generation of a polymer, aside from the primary monomer. In the case of HDPE, the alpha olefin comonomers include butene, hexene and octene.

[0065] Copolymer – A polymer resulting from the polymerization of the primary monomer with a comonomer.

[0066] Crystallization – The parallel alignment of polymers.

[0067] DOE (Design of Experiments) – The design of a statistical analysis in order to describe the source of the variation.

[0068] DSC (Differential scanning calorimetry) – A thermoanalytical technique for the determination of the amount of energy required to increase the temperature of the sample.

[0069] EBM (Extrusion Blow Molding) – A process for package formation involving the extrusion of a melted parison into a mold. Air is then blown into the parison, inflating into the mold.

[0070] Enthalpy – Energy per unit mass needed to change the temperature of the material.

[0071] ESCR (Environmental Stress Crack Resistance) – The resistance of material to failure due to chemical attack.

[0072] Factors – In DOE, the independent variables that can be altered in order to explore the sources of variation.

[0073] Free Blow – Blowing of a preform without the restriction of a mold.

[0074] HDPE (High Density Polyethylene) – Polymer composed primarily from the polymerization of ethylene monomers. Density range for HDPE is defined as 0.941 to 0.965 g/cm3

[0075] HMFI (High Melt Flow Index) – Referring to the g/10 min flow rate of the polymer through a ASTM D1238 die under the conditions of 190 C and under 21.6 kg. of load through an extrusion plastometer test fixture with die orifice diameter of 2.0955 mm and length of 8.000 mm (see ASTM D 1238, “Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer,” which is incorporated herein by reference in its entirety).

[0076] Homopolymer – Polymer formed from one type of monomer.

[0077] Hoop – Extending in the cylindrically symmetrical direction (perpendicular to the stretch rod / axial plane).

[0078] HPC (Home and Personal Care) – Products related to home and to personal cleanliness.

[0079] Incompressible – Density (mass per volume) does not change under the application of force.

[0080] ISBM (Injection Stretch Blow Molding) – A process for package formation involving the inflating of a re-heated preform into a mold.

[0081] Lenth’s PSE (Pseudo standard error) – Measure determining if effects observed are sparse or significant via comparison to a calculated pseudo standard error.

[0082] Levels – In DOE, the different settings / values for the factors (independent variables).

[0083] Main effector – A factor which has a significant effect on the output from the process.

[0084] MFI (Melt Flow Index) – Referring to the g/10 min flow rate of the polymer through a ASTM D1238 die under the conditions of 190 C and under 2.16 kg. of load through an extrusion plastometer test fixture with die orifice diameter of 2.0955 mm and length of 8.000 mm (see ASTM D 1238, "Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer," which is incorporated herein by reference in its entirety).

[0085] Multimodal - *Referring to several distributions having separate maxima.

[0086] MW (Molecular Weight) – For the individual polymer, this is the mass of the polymer calculated as the sum of the atomic weights of the individual constituents. For a polymer melt, this is the average of the molecular weights for all of the polymers in the melt.

[0087] Opacity – The measure for the transparency of the analyte.

[0088] p-value – If $p < 0.05$, we can reject the null hypothesis that the individual sets will be equal.

[0089] Pareto – A bar chart organized in order of decreasing frequency.

[0090] PDI (Polydispersity Index) – A measure for the distribution of the molecular mass as MW / MN

[0091] Self Leveling – In crystalline materials, the observation of wall thickness naturally leveling during stretching. As the material deforms, sections which begin to thin 'strain harden.' The parts which initially thin are the areas of least resistance to deformation. As these low resistance areas thin, they become the areas of greatest resistance due to the strain induced crystallization. The thicker areas then move until they reach equivalent strength. Without strain hardening, the point of least resistance would continually deform until failure is observed.

[0092] Standardized Effects – T-statistics that test the null hypothesis that the effect is 0. The absolute value of the standardized effect is compared to Lenth's PSE to determine if the effect is statistically significant.

[0093] Stiffness - Specific energy (energy per unit volume) required to deform the material

[0094] Strain – Deformation of the material relative to the reference length.

[0095] Strain Hardening – In crystalline materials, the observation of material hardening due to the forced alignment of polymers (generation of crystals) during material deformation.

[0096] Strength – The force per unit area required to deform a material. If the point that strength is referenced on the stress/strain curve is the maximum resistance to deformation, it is called the ultimate strength.

[0097] Stress – Force per unit area exerted on an object.

[0098] Unimodal – Referring to one distribution having one maxima.

[0099] Variance – The expectation of the squared deviation of a random variable from the mean.

[0100] The foregoing description of the embodiments has been provided for purposes of illustration and description. It is not intended to be exhaustive or to limit the disclosure. Individual elements or features of a particular embodiment are generally not limited to that particular embodiment, but, where applicable, are interchangeable and can be used in a selected embodiment, even if not specifically shown or described. The same may also be varied in many ways. Such variations are not to be regarded as a departure from the disclosure, and all such modifications are intended to be included within the scope of the disclosure.

[0101] Example embodiments are provided so that this disclosure will be thorough, and will fully convey the scope to those who are skilled in the art. Numerous specific details are set forth such as examples of specific components, devices, and methods, to provide a thorough understanding of embodiments of the present disclosure. It will be apparent to those skilled in the art that specific details need not be employed, that example embodiments may be embodied in many different forms and that neither should be construed to limit the scope of the disclosure. In some example embodiments, well-known processes, well-known device structures, and well-known technologies are not described in detail.

[0102] The terminology used herein is for the purpose of describing particular example embodiments only and is not intended to be limiting. As used herein, the singular forms "a," "an," and "the" may be intended to include the plural forms as well, unless the context clearly indicates otherwise. The terms "comprises," "comprising," "including," and "having," are inclusive and therefore specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof. The method steps, processes, and operations described herein are not to be construed as necessarily requiring their performance in the particular order discussed or illustrated, unless specifically identified as an order of

performance. It is also to be understood that additional or alternative steps may be employed.

[0103] When an element or layer is referred to as being "on," “engaged to,” "connected to," or "coupled to" another element or layer, it may be directly on, engaged, connected or coupled to the other element or layer, or intervening elements or layers may be present. In contrast, when an element is referred to as being "directly on," “directly engaged to,” "directly connected to," or "directly coupled to" another element or layer, there may be no intervening elements or layers present. Other words used to describe the relationship between elements should be interpreted in a like fashion (e.g., “between” versus “directly between,” “adjacent” versus “directly adjacent,” etc.). As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

[0104] Although the terms first, second, third, etc. may be used herein to describe various elements, components, regions, layers and/or sections, these elements, components, regions, layers and/or sections should not be limited by these terms. These terms may be only used to distinguish one element, component, region, layer or section from another region, layer or section. Terms such as “first,” “second,” and other numerical terms when used herein do not imply a sequence or order unless clearly indicated by the context. Thus, a first element, component, region, layer or section discussed below could be termed a second element, component, region, layer or section without departing from the teachings of the example embodiments.

[0105] Spatially relative terms, such as “inner,” “outer,” "beneath," "below," "lower," "above," "upper," and the like, may be used herein for ease of description to describe one element or feature's relationship to another element(s) or feature(s) as illustrated in the figures. Spatially relative terms may be intended to encompass different orientations of the device in use or operation in addition to the orientation depicted in the figures. For example, if the device in the figures is turned over, elements described as "below" or "beneath" other elements or features would then be oriented "above" the other elements or features. Thus, the example term "below" can encompass both an orientation of above and below. The device may be otherwise oriented (rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein interpreted accordingly.

CLAIMS

What is claimed is:

1. A high-density polyethylene (HDPE) resin configured to be molded into a preform that can be biaxially expanded within a cavity of a container mold by introducing an incompressible fluid under pressure into the preform to stretch the preform into a container having a shape of a surrounding mold cavity of the container mold, the HDPE resin comprising:

a melt flow index of 0.3 - 10.0 grams per 10 minutes at a temperature of 190ºC under 2.16 kilograms of load through an extrusion plastometer test fixture with die orifice diameter of 2.0955 mm and length of 8.000 mm;

a polydispersity index of 4 - 24; and

a density of 0.943 - 0.965 grams per cubic centimeter.

2. The HDPE resin of Claim 1, wherein:

the HDPE resin is from a chromium catalyst system; and

the HDPE resin has a melt flow index of less than 1 gram per 10 minutes at a temperature of 190ºC under 2.16 kilograms of load through an extrusion plastometer test fixture with a die orifice diameter of 2.0955 mm and a length of 8.000 mm.

3. A container formed from the preform molded from the HDPE resin of Claim 1, wherein a ratio of a volume of the incompressible fluid encapsulated to a mass of the container formed from the HDPE resin is up to 60ml per gram.

4. The HDPE resin of Claim 2, wherein a ratio of a volume of the incompressible fluid encapsulated in the preform to a mass of a container formed from the HDPE resin is up to 60ml per gram.

5. The HDPE resin of Claim 2, wherein a ratio of a volume of the incompressible fluid encapsulated in the preform to a mass of a container formed from the HDPE resin for the fractional melt flow index HDPE resin is as high as 98ml per gram;

wherein the fractional melt flow index of the HDPE resin is multimodal.

6. The HDPE resin of Claim 1, wherein the HDPE resin is from a Ziegler-Natta catalyst system.

7. The HDPE resin of Claim 6, wherein the Ziegler-Natta catalyst system is multimodal.

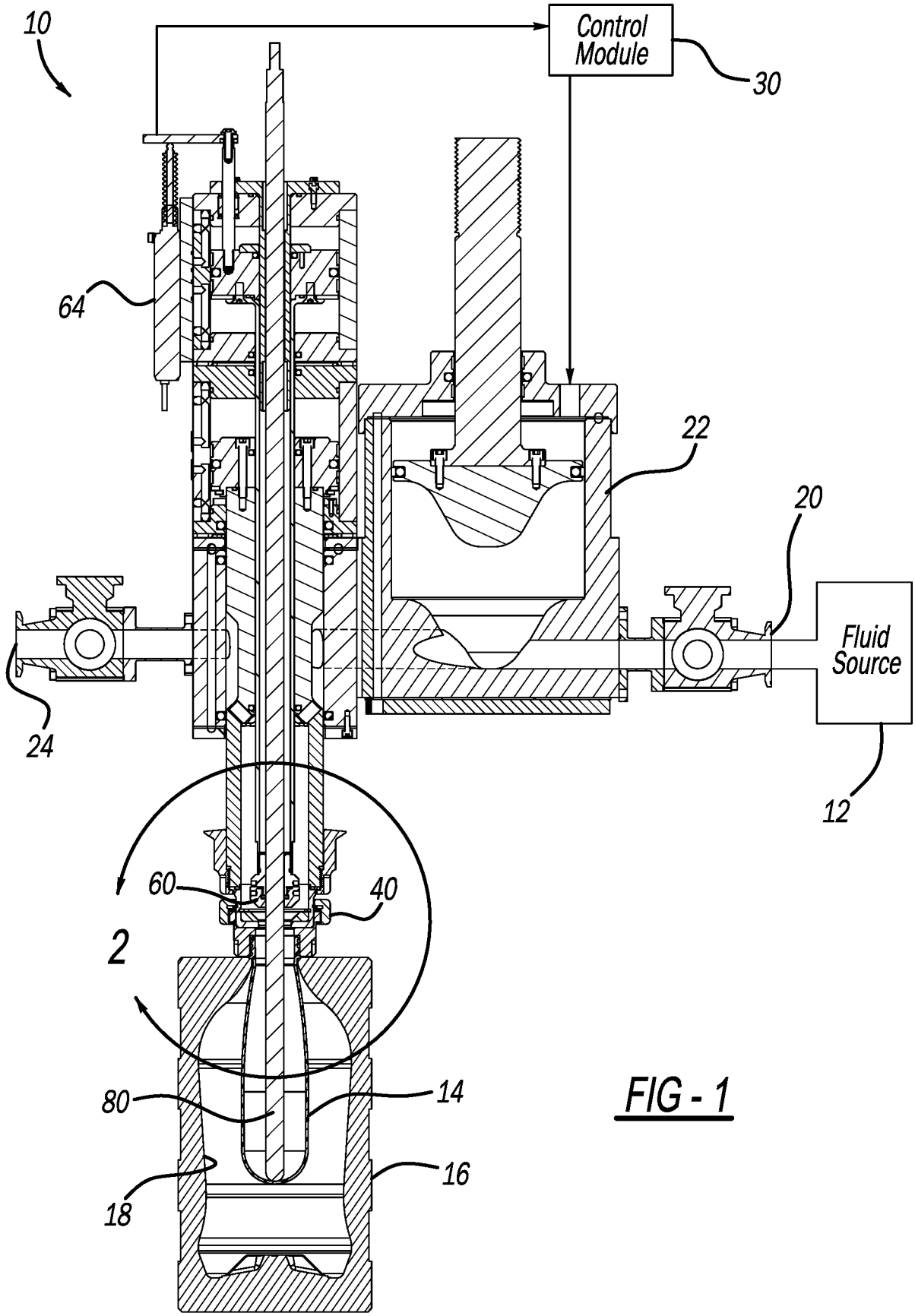
8. The HDPE resin of Claim 1, wherein the melt flow index is 0.3 - 4.0 grams per 10 minutes at a temperature of 190ºC under 2.16 kilograms of load through an extrusion plastometer test fixture with a die orifice diameter of 2.0955 mm and a length of 8.000 mm.

9. The HDPE resin of Claim 1, wherein the melt flow index is 0.3 - 2.0 grams per 10 minutes at a temperature of 190ºC under 2.16 kilograms of load through an extrusion plastometer test fixture with a die orifice diameter of 2.0955 mm and a length of 8.000 mm.

10. The HDPE resin of Claim 1, wherein the HDPE resin has a polydispersity index of 7 - 24.

11. The HDPE resin of Claim 1, wherein the HDPE resin has a polydispersity index of 9 - 24.

12. The polyolefin resin of Claim 1, wherein the resin is a multimodal resin having a polydispersity index greater than 7.


10
Control Module
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64
22
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Fluid Source
24
12
60
40
2
80
14
16
18

FIG - 1

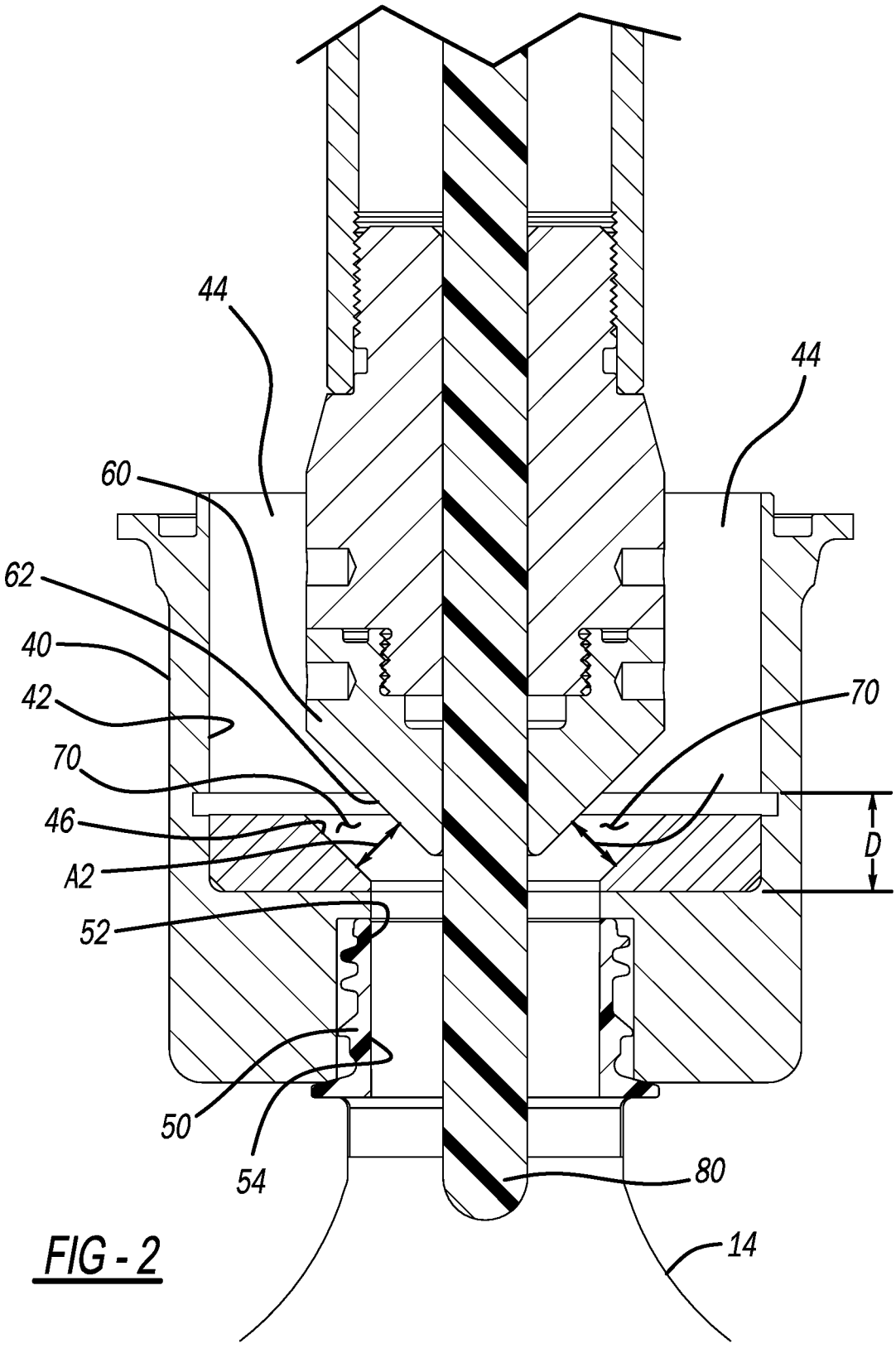

FIG - 2

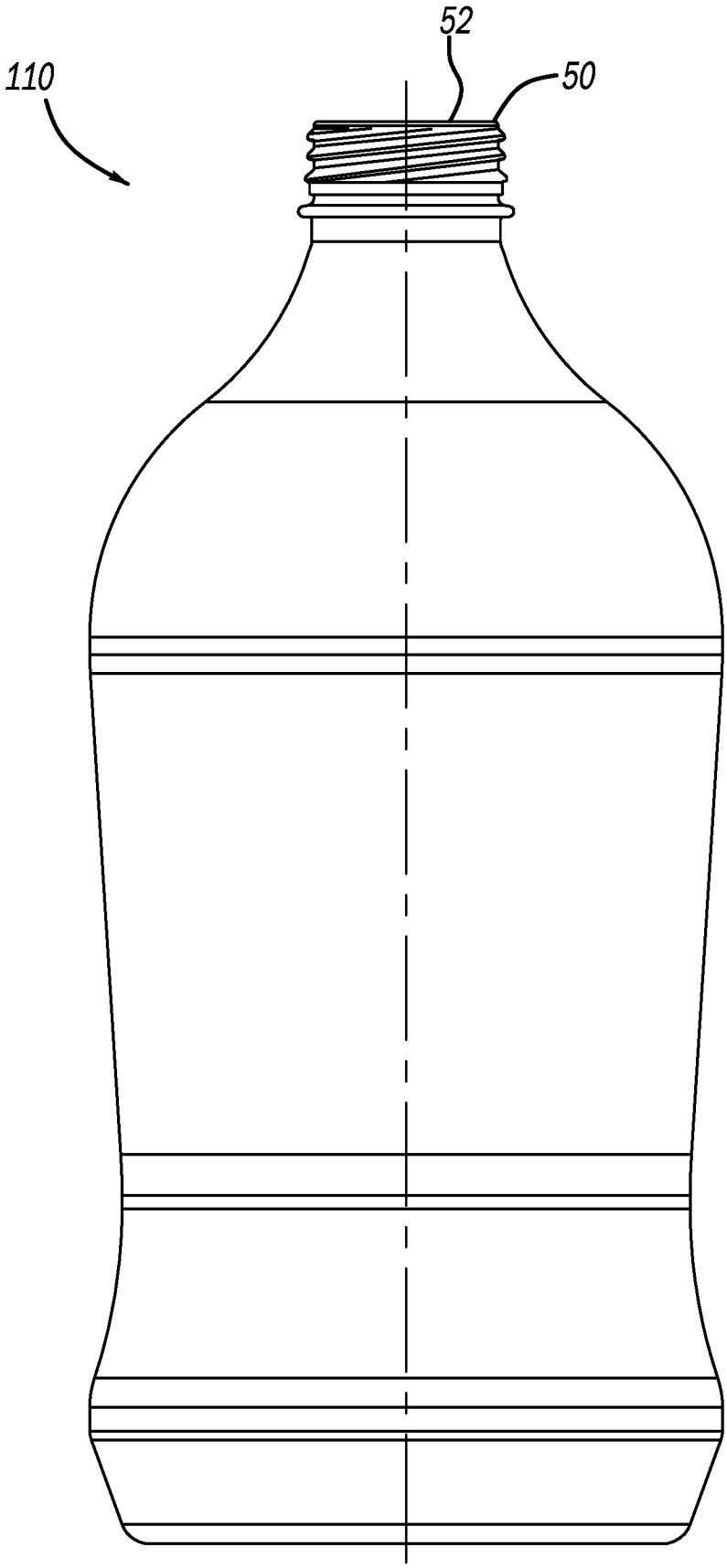

FIG - 3

		Best Performer for Liquid Forming & Filling	'Beverage' Application Resin	'Home & Personal Care' Application Resin	'High Clarity' Package
Melt Flow Index (MFI) Direct Correlation to Molecular Weight]	Full Range	0.3 – 10.0 g/10 min @ 190 C under 2.16 kg			
	Preferably	< 4.0 for repeatable material distribution			
	Most Preferably	< 2.0 for repeatable material distribution			
	Comments / Findings	Package ruptures decrease & material distribution consistency improves with increased polymer molecular weight (decreased MFI). EBM resins (chromium catalyzed; highest molecular weight; fractional MFI; MFI <1) showed the fewest number of package ruptures. Main issue with <1 MFI resins is that they are not amenable to injection.			
Polydispersity index (PDI) [Direct Correlation to Molecular Weight Distribution]	Full Range	4 – 25	4 – 25		4 – 25
	Preferably	>7	>7	>8	>7
	Most Preferably	>9	>9	>9	>9
	Comments / Findings	Specifying molecular weight distribution by PDI: Grades with a PDI < 7 showed a failure rate of >25% Grades with a PDI of 7 – 9 showed a failure rate of <10% Grades with a PDI of > 9 showed a failure rate of 0% (30 for 30) ESCR increases with increasing molecular weight distribution (increasing PDI).			

To FIG-4B

FIG - 4A

To FIG-4A

		Best Performer for Liquid Forming & Filling	'Beverage' Application Resin	'Home & Personal Care' Application Resin	'High Clarity' Package
Modality	Full Range (Chromium Catalyst)	Resin from a Chromium catalyst system with a PDI >7			
	Preferably (Chromium Catalyst)	Multimodal resin from a Chromium catalyst system			
	Comments / Findings	Chromium catalyzed resins have PDIs >9 and showed no ruptures in blowing the target test package. *** Comparing Chromium catalyzed HDPEs, the unimodal resin grade was limited in its free blow hoop and axial stretch ratios . The bimodal chromium catalyzed HDPE was a higher molecular weight HDPE, but its polymer chains had greater mobility than the unimodal.			
	Full Range (Ziegler-Natta Catalyst)	Resin from a Ziegler-Natta catalyst system with a PDI >7			
	Preferably (Ziegler-Natta Catalyst)	Multimodal resin from a Ziegler-Natta catalyst system.			
	Comments / Findings	Comparing Ziegler-Natta catalyzed HDPEs, the bimodal grades showed a decrease in rupture % by about 30%, when comparing between bimodal and unimodal grades of comparable MFIs and polydispersity indexes [indirect measure for MW & direct measure for MW distribution].			

To FIG-4C

FIG - 4B

To FIG-4B

		Best Performer for Liquid Forming & Filling	'Beverage' Application Resin	'Home & Personal Care' Application Resin	'High Clarity' Package
Density [Direct Correlation to Comonomer content]	Full Range	0.943 – 0.965 g/cm^3	>0.96 g/cm^3	<0.962 g/cm^3	<0.95 g/cm^3
	Most Preferably		>0.963 g/cm^3	0.95 - 0.96 g/cm^3	
	Comments / Findings	Homopolymers are typically used in 'beverage' applications for organoleptics. Homopolymers have density >0.96 g/cm^3		ESCR increases with increasing copolymer content (decreasing density). Best packages balance strength with ESCR. Preferred range balances ESCR with strength for HPC.	Clarity increase was statistically significant for HDPE packages with density <0.95 g/cm^3 from packages with density ≥ 0.95 g/cm^3

FIG - 4C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/033280

A. CLASSIFICATION OF SUBJECT MATTER

B29C 49/00(2006.01)i, B29B 11/14(2006.01)i, C08L 23/06(2006.01)i, C08F 110/02(2006.01)i, C08F 2/38(2006.01)i, B29L 31/00(2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B29C 49/00; B29B 7/00; B29C 49/06; B29C 49/08; B29C 49/46; B32B 27/32; B65D 1/02; B29B 11/14; C08L 23/06; C08F 110/02; C08F 2/38; B29L 31/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: polyethylene, HDPE, preform, container, melt flow index, polydispersity index, density, catalyst

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013-0213982 A1 (RADERMACHER, F.) 22 August 2013 see abstract; claim 28; and paragraphs [0036]-[0038].	1-12
A	US 2007-0087214 A1 (PORTNOY, R. C. et al.) 19 April 2007 See abstract; and paragraphs [0028], [0038], [0042].	1-12
A	EP 1495861 A1 (TOTAL PETROCHEMICALS RESEARCH FELUY) 12 January 2005 See abstract; paragraph [0044]; and claims 1, 7.	1-12
A	US 2017-0326779 A1 (DISCMA AG) 16 November 2017 See abstract; and claims 1, 5.	1-12
A	US 2017-0312972 A1 (DISCMA AG) 02 November 2017 See abstract.	1-12

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 September 2019 (09.09.2019)	**10 September 2019 (10.09.2019)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2019/033280

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