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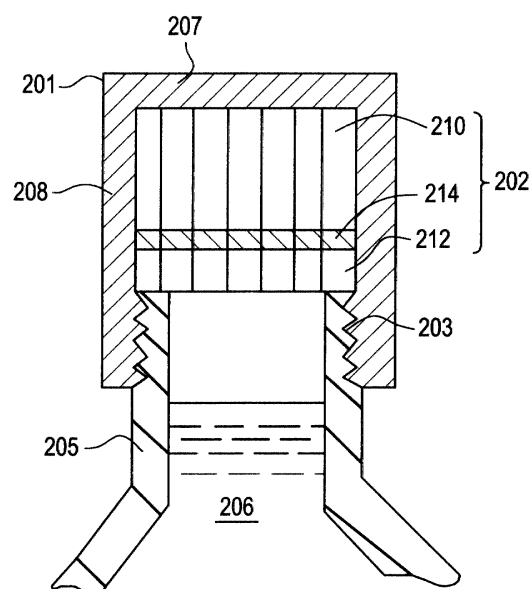
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(54) **High gas barrier asymmetric liner and closure**

(57) The present invention relates to a container closure (201) with an asymmetric liner (202). The liner (202) comprises a first layer (210) and a second layer (212) where the said second layer (212) is the layer closest to the container (205). The liner (202) also contains a gas barrier layer (214), preferably a liquid crystal polymer, between the first (210) and second layer (212). The thickness of the second layer (212) is less than the thickness of the first layer (210) to reduce the gas leakage path between the container (205) and the outside environment.

**FIG. 4**



**Description****Field of the Invention**

**[0001]** The present invention relates to liners for use in container closures and more particularly to closures with an asymmetric gas barrier liner that reduces the gas transmission rate of food or beverage containers.

**Background of the Invention**

**[0002]** Plastic liners for closures have become widely used and are commercially successful products in the food and beverage packaging industry. Plastic liners are typically a series of polymeric layers containing an outer layer, which provides good slip and torque characteristics to adequately seal and remove the closure from the container, and a gas barrier layer which reduces the transmission of gases. The liner is inserted into the interior of the closure such that the liner contacts the container lip to reduce the transmission of gas into or out of the container. Reduction of gas transmission increases the storage life of food or beverage in the container.

**[0003]** However, the problem with prior art liners is that they do not adequately retard the transmission of gases, either resulting in a loss of carbon dioxide (from soft drinks) and/or the infusion of oxygen into the container resulting in food spoilage. For example, typical barrier liners use ethylene-vinyl alcohol copolymers (EVOH) as the gas barrier layer. However, EVOH is sensitive to moisture and loses its gas barrier transmission properties when exposed to humidity over a long period of time. In order to remedy this problem, closures containing EVOH liners have either moved the EVOH layer away from the side facing the container and/or have added moisture barrier layers to protect the EVOH gas barrier layer. The problem with adding moisture barrier layers is that it increases the complexity and cost of the closure. Moving the EVOH layer away from the contents of the container enlarges the gas leakage path, illustrated in Fig. 1, which results in increased gas transmission rates.

**[0004]** Fig. 1 is a cross-sectional view of a prior art closure disclosing a closure **101** with screw threads **103** and liner **102** situated on container **105**. Container **105** contains contents **106** (e.g., a carbonated beverage). Liner **102** comprises a first outside layer **110**, gas barrier layer **114** and second outside layer **112**. Second outside layer **112** is the layer closest to contents **106** of container **105**. It is believed that the problem with prior art closure **101** is that there are leakage paths (e.g., leakage paths **120** and **122**) where gas from container **105** can escape or oxygen from outside environment **130** can enter container **105**.

**[0005]** Leakage paths **120** and **122** are for illustrative purposes only, but shows how gas can be transmitted between container **105** and outside environment **130**. For example, due to cost reasons, closure **101** is typically made from materials that are permeable to gas such as polyethylene or polypropylene which typically exhibit 3-4 orders of magnitude more gas permeability than gas barrier layers. Thus, leakage path **120** illustrates how gas from container **105** permeates through permeable second outside layer **112** of liner **102** and through the wall of closure **101** to outside environment **130**.

**[0006]** Leakage path **122** illustrates how gas can be transmitted to outside environment **130** through permeable second outside layer **112** and threads **103**. Thus, even if closure **101** is made of a high gas barrier layer material, such as aluminum, gas can still leak through threads **103** of closure **101**.

**[0007]** Accordingly, leakage paths **120** and **122** reduce the shelf life of contents **106** in container **105** because of high gas transmission rates.

**[0008]** Thus, an object of the present invention is to provide a plastic liner that reduces the gas transmission rate between the container and the outside environment as compared to prior art liners.

**[0009]** It is another object of the present invention to provide a gas barrier layer, suitable to be used in plastic liners, which is able to retain its gas barrier properties under high humidity conditions.

**[0010]** It is a further object of the present invention to provide a closure containing a small gas leakage path to reduce the amount of gas transmission between the container and outside environment.

**[0011]** It is yet another object of the present invention to provide a liner and closure which is simple, inexpensive to manufacture and reliable in operation.

**Summary of the Invention**

**[0012]** The objects of the present invention are achieved by providing an asymmetric liner suitable for use in a container closure. The liner comprises a first layer and a second layer where the said second layer is the layer closest to the container. The liner also contains a gas barrier layer between the first and second layer. The thickness of the second layer is less than the thickness of the first layer to reduce the gas leakage path between the container and the outside environment.

**[0013]** In another embodiment of the present invention, a closure for a container is provided such that the closure

comprises a base wall and a peripheral skirt. The skirt is affixed to the base wall defining a closure interior and is adapted to attach to the container. A liner is positioned inside the closure interior. The liner comprises a first layer, a second layer, and a gas barrier layer between the first and second layer where the gas barrier layer is a liquid crystal polymer (LCP).

## Brief Description of the Drawings

[0014] Reference now is made to the accompanying drawings of illustrative embodiments of the invention in which:

FIG. 1 is a cross-sectional view of a prior art closure illustrating gas leakage paths between the container and the closure.

FIG. 2 is a cross sectional view of one embodiment of the liner according to the present invention;

FIG. 3 is a cross sectional view of another embodiment of the liner according to the present invention; and

FIG. 4 is cross sectional view of one embodiment of the closure according to the present invention.

## Detailed Description of the Invention

[0015] The present invention relates to an asymmetric liner designed to reduce the gas transmission rate between the contents of a container and the outside environment. Reducing the gas leakage path between the closure and the outside environment reduces the gas transmission rate. In this application, asymmetrical means that the gas barrier layer is not situated at the midpoint of the liner.

[0016] The asymmetric liner comprises a first layer and a second layer where the second layer is the layer closest to the container. The liner also contains a gas barrier layer between the first and second layer. The thickness of the second layer is less than the thickness of the first layer to reduce the gas leakage path.

[0017] FIG. 2 is a cross sectional view of one embodiment of the liner according to the present invention. Liner 202 comprises first outside layer 210, second outside layer 212 and gas barrier layer 214 positioned between first outside layer 210 and second outside layer 212. Second outside layer 212 is the layer closest to the container and is thinner than first outside layer 210.

[0018] Generally, the total thickness of liner 202 is between about 500 to about 2000 microns ( $\mu\text{m}$ ). Preferably, the thickness of first outside layer 210 is about 375 to about 1250  $\mu\text{m}$  and more preferably about 625 to about 875  $\mu\text{m}$ . The thickness of second outside layer 212 is generally less than about 250  $\mu\text{m}$ , preferably less than about 150  $\mu\text{m}$ , more preferably less than about 75  $\mu\text{m}$  and even more preferably ranges between about 25  $\mu\text{m}$  to about 75  $\mu\text{m}$  or about 40  $\mu\text{m}$  to about 60  $\mu\text{m}$ .

[0019] The thickness of gas barrier layer 214 is typically less than about 50  $\mu\text{m}$ , preferably less than about 25  $\mu\text{m}$ , and more preferably ranges between about 2  $\mu\text{m}$  to about 15  $\mu\text{m}$ , and about 5  $\mu\text{m}$  to about 10  $\mu\text{m}$ . The exact thickness of gas barrier layer 214 is a trade-off between gas transmission rate and cost. A thicker gas barrier layer reduces gas transmission rates, but increases cost.

[0020] In addition, it should be noted that multiple gas barrier layers may also be used in this invention. The multiple gas barrier layers may be positioned between the same materials that are used to make the outer layers, or positioned between other gas barrier layer materials.

[0021] The gas barrier layer is preferably prepared from materials that provide a barrier to gas transmission and are insensitive to moisture since the gas barrier layer is positioned close to the contents of the container. EVOH may be used as a gas barrier layer, but is not preferred in the present invention because EVOH is sensitive to moisture and loses its gas barrier properties when exposed to humidity over a long period of time.

[0022] Thus, preferred materials to be used for the gas barrier layer are those resistant to moisture degradation. Resistant to moisture degradation means that the gas barrier properties are not substantially reduced by exposure to moisture. Examples of moisture resistant gas barrier layers include, but are not limited to Liquid Crystal Polymers (LCPs) and polyvinylidene chloride. More preferably, the gas barrier layer is made of a LCP and even more preferably a wholly aromatic LCP.

[0023] Liquid crystalline polymers (LCPs) are characterized as having a liquid crystalline phase above the temperature at which the polymers become molten. They have good gas barrier properties and are able to withstand high humidity environments. The LCPs used in the liners described herein are generally polyesters or poly(ester-amides), and generally comprise monomer units that include within their structures, exclusive of functional groups, one or more of the following aromatic nuclei: 1,4-phenylene, 1,3-phenylene, 4,4'-biphenylene, and 2,6- and/or 2,7-naphthylene. Some LCPs also contain monomer units that are derived from ethylene glycol. LCPs that may be used in this invention include the polymers that are available from Ticona and sold under the VECTRA trademark, LCPs available from BP-Amoco Chemicals and sold under the XYDAR trademark, and LCPs available from DuPont and sold under the ZENITE trademark.

**[0024]** Generally, the LCP's comprising wholly aromatic monomer units can be derived from one or more of the following monomers and generally at least two of the following monomers: terephthalic acid, isophthalic acid, 1,4-hydroquinone, resorcinol, 4-aminobenzoic acid, 3-aminobenzoic acid, 4-hydroxybenzoic acid, 3-hydroxybenzoic acid, 4-aminophenol, 3-aminophenol, 1,4-phenylenediamine, 4,4'-biphenol, 4,4'-biphenyldicarboxylic acid, 6-hydroxy-2-naphthoic acid, 2,6-naphthalenedicarboxylic acid, and 2,6-dihydroxynaphthalene.

**[0025]** Additional examples of gas barrier layer materials that may be used in this invention are blends of LCP with thermoplastics, preferably polyolefins or other gas barrier layer materials. Examples of polyolefins that may be blended with LCP include, but are not limited to polyethylene, polypropylene, ethylene-propylene copolymers, ethylene vinyl acetate (EVA), ethylene methyl acrylate, styrene-ethylene copolymers, EVOH, and the like. Preferred polyolefins that may be blended with LCP are polyethylene, polypropylene, polyvinylidene chloride, EVA, EVOH and mixtures thereof. Gas barrier layer materials that may be blended with LCP are polyvinylidene chloride, EVOH, polyethylene terephthalate, polyethylene naphthalate, cyclic olefin copolymers, polyamides such as MXD6 (a copolyamide of meta-xylylene-diamine and adipic acid produced by Mitsubishi Gas Chemical), polyacrylonitrile and mixtures thereof. The amount of LCP in the LCP blend may range from about 0.1 to about 99 wt.% based on the total weight of the blend.

**[0026]** It is preferred that a compatibilizer be used in the LCP blends. The task of a compatibilizer is to better achieve a more uniform dispersed blend such as by diminishing the surface tension and/or improving adhesion between the components. Any suitable compatibilizer may be used to achieve a uniform dispersed blend such as those described in WO 96/00752 and WO 93/24574, herein incorporated by reference. A preferred compatibilizer for use in the LCP blends is a functionalized polyolefin, where the functional groups included, but are not limited to a carboxyl group and its esters, a carboxylic anhydride group, a glycidyl group, an alkoxy silane group and combinations thereof. The amount of the compatibilizer may range from about 0.1 to about 30 wt.% based on the total weight of the LCP and the thermoplastic.

**[0027]** First outside layer **210** and second outside layer **212** can be made from the same or different materials such as thermoplastic elastomers, polyolefins and combinations thereof. A thermoplastic elastomer is a polymer having the processability of a thermoplastic material and the functional performance and properties of a thermoset rubber. Examples of thermoplastic elastomers include, but are not limited to, styrene block copolymers, elastomeric alloys, thermoplastic polyurethane, thermoplastic polyesters and thermoplastic polyamides. Polyolefins may also be considered thermoplastic elastomers. Thermoplastic elastomers are described starting on page 93 in Modern Plastics Handbook, published by McGraw-Hill, 1988.

**[0028]** The polyolefins used in the present invention for the first or second outer layer can be homopolymers, or copolymers comprising more than one monomer repeating unit. Examples of polyolefins that may be used include, but are not limited to, polyethylene, polypropylene, ethylene-propylene copolymers, ethylene vinyl acetate, ethylene methyl acrylate, styrene-ethylene copolymers and the like. Preferred polyolefins are polyethylene, polypropylene, and ethylene vinyl acetate.

**[0029]** Fig. 3 is another liner embodiment of the present invention providing an adhesive layer between the first or second outer layer, and inner gas barrier layer. Liner **202** in Fig. 3 comprises first outside layer **210**, second outside layer **212**, gas barrier layer **214** and at least one adhesive layers **216** and/or **218** positioned between outside layers **210** and/or **212** and gas barrier layer **214**. Again second outside layer **212** is the layer closest to the container and is thinner than first barrier layer **210**. The same materials described above may be used for outside layers **210** and **212**, and gas barrier layer **214**.

**[0030]** An adhesive is any substance that is capable of binding other substances together by surface attachment such as by a reactive bond (covalent or dipole-dipole) or a non-reactive means (chain entanglement with polymers). Any suitable adhesive may be used to bind outer layer **210** and **212** with gas barrier layer **214**. In the case when the gas barrier layer is a LCP, it is preferred that the adhesive layer is a functionalized polyolefin. Examples of suitable functional groups for the functionalized polyolefins include, but are not limited to, a carboxyl group and its esters, a carboxylic anhydride group, a glycidyl group, an alkoxy silane group and combinations thereof. A preferred adhesive layer is a terpolymer of ethylene, methyl acrylate and glycidyl methacrylate. Such adhesives for LCPs are disclosed in U.S. Patent Nos. 6,015,524 and 6,013,373, herein incorporated by reference.

**[0031]** The liner of the present invention may be made by any suitable method such as co-extrusion of the layers or forming films of the different layers separately and laminating them together. The multilayer film can then be "punched out" forming the liner. In a preferred method, the gas barrier layer is made up of a wholly aromatic LCP and is co-extruded with polyolefin outside layers.

**[0032]** Referring to Fig. 4, another embodiment of the present invention is closure **201** comprising base wall **207** attached to peripheral skirt **208**. Peripheral skirt **208** is adapted to attach to container **205**. Positioned inside the interior of closure **201** is liner **202**. Liner **202** may be positioned in the closure by any suitable method such as friction fit or gluing. When liner **202** is glued, first outer layer **210** is typically in direct contact with base wall **207**. Liner **202** may be any of the liners discussed herein such as those liners and liner materials described in Fig. 2 and Fig. 3. Liner **202** comprises first outside layer **210**, second outside layer **212** and gas barrier layer **214** positioned between first outside

layer **210** and second outside layer **212**. Liner **202** in Fig. 4 may be symmetrical or the second outside layer **212** may be thinner or thicker than first outside layer **210** as long as the gas barrier layer is a LCP, and preferably a wholly aromatic LCP. It is preferred that the LCP gas barrier layer be positioned in the closure such that it is less than about 150  $\mu\text{m}$ , more preferably less than about 75  $\mu\text{m}$  from the container to minimize the gas transmission rate. It should also be appreciated that multiple gas barrier layers and multiple outside layers may be used in this invention.

**[0033]** Base wall **207** and peripheral skirt **208** can be any material typically used in the closure art such as metals, e.g. aluminum, or plastic resins. The preferred plastic resins are moldable thermoplastic polymers such as polyethylene, polypropylene, ethylene vinyl acetate, polyethylene terephthalate, polyvinyl chloride and the like.

**[0034]** In addition, adhesive layers may be positioned between the gas barrier layer **214** and outside layers **210** and **212** as described in Fig. 3.

**[0035]** It should be appreciated that all Figures in this application may not be drawn to scale and thicknesses may be exaggerated for illustration purposes. It should also be appreciated that although Fig. 4 illustrates a screw type cap, any type of closure is contemplated under this application such as twist-off, pilfer proof, crown, lug, tear off, and ring pull.

**[0036]** Although not wishing to be bound by any theory, it is believed that the closure of the present invention using the asymmetric liner reduces gas transmission by reducing the vent area. The vent area is the thickness of the second outer layer **212** multiplied by the circumference of the liner. Since the vent area is the permeable area of the closure, any reduction in the vent area reduces the gas transmission rate. A gas barrier layer resistant to moisture degradation, (e.g., LCP) is preferred in the present invention because the gas barrier layer must be positioned closer to the contents of the container to reduce the vent area. Although moisture sensitive gas barrier layers such as EVOH can be used in the present invention, they are not preferred since their gas barrier properties are reduced under prolong contact with moisture.

**[0037]** Many features of the present invention will become apparent in the course of the following description of the exemplary embodiments, which are given for illustration of the invention and are not intended to be limiting thereof.

## EXAMPLES 1 TO 3

### Preparation of Liners in Examples 1-3

**[0038]** The liners of examples 1 to 3 below were prepared from multilayer plastic sheets produced by conventional sheet co-extrusion technology. Polymers used in the liners were fed to 3 extruders equipped with a multilayer feedblock and single manifold die. The feedbox was used to split and/or direct the different polymers to arrange the flows to form multiple layers. The polymer layers from the feedblock were then directed to an extrusion slot die to spread the layers both parallel and transverse to the flow direction of the polymers to form films. A 3 roll vertical stack was aligned linearly with the extrusion die slot to quench the molten polymer as it was cast. The 760 $\mu\text{m}$  sheet was then wound in rolls and subsequently die cut to form 38 mm round disks to be used as liners.

**[0039]** The EVA material used in the liners was an extrusion grade EVA containing about 9% vinyl acetate. The barrier layer was either ethylene vinyl alcohol (EVOH) or a wholly aromatic liquid crystal polymer (LCP) containing monomers derived from hydroxybenzoic acid, hydroxynaphthoic acid, terephthalic acid, aminophenol and biphenol. The adhesive layer was a terpolymer of ethylene, methyl acrylate and glycidyl methacrylate (E-MA-GMA).

**[0040]** The approximate thickness of the layers in examples 1 to 3 are shown in Table 1 below and were estimated based on the volumetric flow through the extruder.

Table 1

| Example | TOP EVA Thickness ( $\mu\text{m}$ ) | Adhesive Thickness ( $\mu\text{m}$ ) | Barrier Layer Thickness ( $\mu\text{m}$ ) | Adhesive Thickness ( $\mu\text{m}$ ) | *Bottom EVA Thickness ( $\mu\text{m}$ ) |
|---------|-------------------------------------|--------------------------------------|-------------------------------------------|--------------------------------------|-----------------------------------------|
| C-1 **  | 380                                 | 0                                    | 0                                         | 0                                    | 380                                     |
| C-2     | 330                                 | 25                                   | 50 (EVOH)                                 | 25                                   | 330                                     |
| C-3     | 360                                 | 5-10                                 | 18-20 (LCP)                               | 5-10                                 | 360                                     |

\*Bottom EVA is layer closest to the container

\*\* Monolayer, total thickness = 760  $\mu\text{m}$

## EXAMPLES 4 TO 9

### Preparation of Liners in Examples 4 to 9

**[0041]** Liner Examples 4 to 9 were also prepared using a co-extrusion process similar to that described above, with

the exception that the liners were made in two steps. First a symmetric 5 layer, thin cast film was prepared, then extrusion laminated to a monolayer EVA sheet.

**[0042]** The film was made using conventional cast film technology where a melt curtain extruded from a flat, vertically aligned die is drawn onto a single, rotating chrome polished casting roll. A draw down ratio (die gap / final sheet thickness) of approximately 4X was used for examples 4 to 7, while a draw down ratio of approximately 10X was used for examples 8 and 9.

**[0043]** These films were then extrusion laminated to an EVA sheet to form approximately 760  $\mu\text{m}$  thick liners. This was accomplished by mounting rolls of the films to a tension controlled "unwind" station, and feeding the film between the first and second rolls of a 3 roll stack used in conventional sheet extrusion technology. A molten sheet of EVA film was also fed between the second and third roll and adhesion of the film to the single layer EVA sheet was accomplished by "melting" the film to the molten EVA polymer where they meet between the rolls. The final sheet was cooled on the roll stack, then taken up on a winder for subsequent use. As with examples 1 to 3 described above, the laminated sheet was then die cut into 38-mm disks for use as liners.

**[0044]** The approximate thickness of the thin film layers (i.e., barrier layer, adhesive layers and thin EVA layer) used in preparing the liners in examples 4 to 9 are shown below in Table 2 and are estimated based on the draw down ratio and the volumetric flow through the film casting extruder. The thickness of the thicker EVA layer is the difference between the total 760  $\mu\text{m}$  liner thickness and the estimated thin film layers thickness.

Table 2

| Example | TOP EVA Thickness ( $\mu\text{m}$ ) | Adhesive Thickness ( $\mu\text{m}$ )** | Barrier Layer Thickness ( $\mu\text{m}$ )** | Adhesive Thickness ( $\mu\text{m}$ )** | *Bottom EVA Thickness ( $\mu\text{m}$ ) |
|---------|-------------------------------------|----------------------------------------|---------------------------------------------|----------------------------------------|-----------------------------------------|
| 4       | 700                                 | 5                                      | 5-10 (LCP)                                  | 5                                      | 50**                                    |
| 5       | 50**                                | 5                                      | 5-10 (LCP)                                  | 5                                      | 700                                     |
| 6       | 700                                 | 5                                      | 5-10 (LCP)                                  | 5                                      | 50**                                    |
| 7       | 50**                                | 5                                      | 5-10 (LCP)                                  | 5                                      | 700                                     |
| 8       | 725                                 | 5                                      | 5-10 (LCP)                                  | 5                                      | 25**                                    |
| 9       | 25**                                | 5                                      | 5-10 (LCP)                                  | 5                                      | 725                                     |

\*Bottom EVA is layer closest to the container

\*\* thin film layer thickness estimated by draw down ratio and volumetric flow

## EXAMPLES 10 TO 16

### Gas Transmission Rate Tests

**[0045]** Gas transmission rate measurements were conducted on the disk liners in examples 1 to 9 by the following procedure: (1) preparing the closures, (2) conditioning the closures for 1 week at 100% humidity and room temperature, and (3) testing the closures for gas transmission rates. Closures were prepared by inserting 760  $\mu\text{m}$  plastic liners of examples 1 to 9 into approximately 38 mm plastic polypropylene caps. The liners were held in place by a ridge or lip within the cap. The closures were applied to "barrier" PET bottles molded for use with a screw-on cap (torque spec: 24 in-lb.). The bottles were then cut off at 3 mm below the bottle "handling or transfer ring", which is located at approximately 25 mm from the top of the PET bottle.

**[0046]** The closures were conditioned by introducing small amounts of carbonated water to approximately 28 mm, cylindrical "manifolds", which were used as "special fixtures" for the test. The water was required to provide a 100% relative humidity (RH) environment to the inside of the closures. The manifolds were essentially small aluminum tubes, closed on one end, positioned vertically and fitted with vacuum grease O-rings to allow for "sealing" to the inside of cut-off PET bottle necks. The cut-off top of the bottles with closures attached were then clamped to the manifolds at transfer rings. Clamping directly on the thick, transfer rings was performed to provide a robust clamping area to allow for pressurization and to minimize  $\text{CO}_2$  permeability losses through the PET bottles. Pressurization to the inside of the closures was then accomplished by introducing pure, dry  $\text{CO}_2$  at 3.0 atmospheres through one of two side ports to the cylindrical manifold. These ports were located below the O-ring.

**[0047]** The outside atmosphere was maintained at 29°C and 75% RH by placing the manifold in an environmental chamber. The closures were then conditioned in this configuration for a minimum of seven (7) days prior to gas transmission rate testing.

**[0048]** The conditioned closures/bottles on manifolds were then tested for gas transmission rate using a MoCon C-IV

carbon dioxide test apparatus. The apparatus is a standard CO<sub>2</sub> detection device using infra-red (IR) technology. The conditioned closures/bottles on manifolds were first placed under aluminum capture volume containers. The aluminum capture volume containers are essentially inverted aluminum cups with two gas flow ports similar to those used for the cylindrical manifolds. These "capture containers" were then sealed to a "base" via vacuum grease and O-rings. A nitrogen carrier gas was then introduced into the capture containers, through one of the two ports, at a flow rate of approximately 50-75 cc/min via a mass flow meter. The gas flowed around the closure/bottle manifolds and exited from the other port to the IR detector. The gas flowed through the capture containers until a chart recorder tracing indicated a steady baseline ("zero"). During that purge time, the effluent gas stream contained a small, steady stream of nitrogen, as well as some CO<sub>2</sub> permeating from the pressurized closure/bottle at a rate to be determined.

**[0049]** The test instrument was then switched from the purge mode to the accumulation mode. The total test time for the accumulation mode was approximately sixty 60 minutes. The accumulation mode involved first measuring the IR response to the effluent gas as described above for thirty five minutes, then injecting a standard volumes of CO<sub>2</sub> (0.022 cc at standard pressure and temperature) into the capture container and detector loop. The detector response was determined as a difference between the IR detection slopes of the initial gas stream and the gas stream after introduction of the known quantity of CO<sub>2</sub> into the stream. The data were then reduced to a transmission rate.

**[0050]** The gas transmission rates for the liners in examples 1 to 9 are shown in Table 3 below.

Table 3

| Example | Liner Example No.      | Bottom Layer Thickness (μm) | CO <sub>2</sub> loss (cc/day-atm) |
|---------|------------------------|-----------------------------|-----------------------------------|
| C-10    | C-1 (No Barrier Layer) | N/A                         | 1.39                              |
| C-11    | C-2 (EVOH)             | 330                         | 0.32                              |
| 12      | 3 (LCP)                | 350                         | 0.09                              |
| 13      | 4 (LCP)                | 700                         | 0.17                              |
| 14      | 5 (LCP)                | 50                          | 0.12                              |
| 15      | 6 (LCP)                | 700                         | 0.54                              |
| 16      | 7 (LCP)                | 50                          | 0.09                              |
| 17      | 8 (LCP)                | 725                         | 0.21                              |
| 18      | 9 (LCP)                | 25                          | 0.11                              |

**[0051]** A comparison of example 12 with comparative example C-11 shows that a symmetric liner with a thin LCP (18-20 μm) as the gas barrier layer has a much lower gas transmission rate than a much thicker (50 μm) EVOH layer. These examples demonstrate the superior gas transmission properties of the LCP even at a much thinner thickness than the EVOH.

**[0052]** A comparison of asymmetrical liner examples 13 to 18 with a LCP thickness of 5-10 μm demonstrates that the gas transmission rate is reduced when the LCP is positioned closer to the container (i.e., thinner bottom EVA layer).

**[0053]** The foregoing is illustrative of the present invention and is not construed as limiting thereof. The invention is defined by the following claims with equivalents of the claims to be included therein.

## Claims

1. An asymmetric liner suitable for use in a container closure comprising:

a first layer;

a second layer wherein said second layer is positioned closer to a container than said first layer; and

a gas barrier layer between said first layer and said second layer;

wherein the thickness of said second layer is less than the thickness of said first layer.

2. The liner of claim 1 wherein said gas barrier layer is resistant to moisture degradation.

3. The liner of claim 2 wherein said gas barrier layer is selected from the group consisting of: liquid crystal polymer (LCP) and polyvinylidene chloride.

4. The liner of claim 2 wherein said gas barrier layer is a LCP.
5. The liner of claim 4 wherein said LCP is a wholly aromatic LCP.
- 5 6. The liner of claim 5 wherein said LCP is derived from at least one monomer selected from the group consisting of: terephthalic acid, isophthalic acid, 1,4-hydroquinone, resorcinol, 4-aminobenzoic acid, 3-aminobenzoic acid, 4-hydroxybenzoic acid, 3-hydroxybenzoic acid, 4-aminophenol, 3-aminophenol, 1,4-phenylenediamine, 4,4'-biphenol, 4,4'-biphenyldicarboxylic acid, 6-hydroxy-2-naphthoic acid, 2,6-naphthalenedicarboxylic acid, and 2,6-dihydroxynaphthalene.
- 10 7. The liner of claim 4 wherein said first layer and said second layer can be the same or different and selected from the group consisting of: thermoplastic elastomer, polyolefin and combinations thereof.
- 15 8. The liner of claim 7 wherein said first or second layer is a polyolefin.
9. The liner of claim 8 wherein said polyolefin is selected from the group consisting of: polyethylene, polypropylene, and ethylene vinyl acetate.
- 20 10. The liner of claim 4 further comprising an adhesive layer between said gas barrier layer and said first or second layer.
11. The liner of claim 10 wherein said adhesive layer is comprised of a functionalized polyolefin material.
- 25 12. The liner of claim 11 wherein said functionalized polyolefin material comprises at least one functional group selected from the group consisting of: a carboxyl group or its esters, a carboxylic anhydride group, a glycidyl group and an alkoxysilane group.
- 30 13. The liner of claim 11 wherein said functionalized polyolefin material is a terpolymer of ethylene, methyl acrylate and glycidyl methacrylate.
14. The liner of claim 4 wherein the thickness of said first layer is about 375  $\mu\text{m}$  to about 1250  $\mu\text{m}$  and the thickness of said second layer is less than about 150  $\mu\text{m}$ .
- 35 15. The liner of claim 4 wherein the thickness of said first layer is about 625  $\mu\text{m}$  to about 875  $\mu\text{m}$  and the thickness of said second layer is less than about 75  $\mu\text{m}$ .
16. The liner of claim 15 wherein the thickness of said barrier layer is between about 2 to about 15  $\mu\text{m}$ .
- 40 17. The liner of claim 16 wherein said first and said second layer is ethylene vinyl acetate.
18. A closure for a container comprising:
  - a base wall;
  - a peripheral skirt affixed to said base wall defining a closure interior, wherein said skirt is adapted to attach to said container; and
  - 45 a liner positioned inside said closure interior, said liner comprising:
    - a first layer;
    - a second layer; and
    - 50 a gas barrier layer between said first layer and said second layer;
    - wherein said gas barrier layer is a liquid crystal polymer (LCP).
19. The closure of claim 18 wherein said liner is asymmetric and wherein said LCP is a wholly aromatic LCP.
- 55 20. The closure of claim 18 wherein said gas barrier layer is a blend of a LCP with a thermoplastic.
21. The closure of claim 20 wherein said thermoplastic is a polyolefin selected from the group consisting of: polyethylene, polypropylene, polyvinylidene chloride, EVA, and mixtures thereof.



22. The closure of claim 20 wherein said thermoplastic is a gas barrier layer selected from the group consisting of: polyvinylidene chloride, EVOH, polyethylene terephthalate, polyethylene naphthalate, cyclic olefin copolymers, polyamides, polyacrylonitrile and mixtures thereof.
- 5 23. The closure of claim 20 wherein said blend further comprises a compatibilizer.
24. The closure of claim 19 wherein said second layer is the layer closest to said container and wherein the thickness of said second layer is less than the thickness of said first layer.
- 10 25. The closure of claim 18 wherein said second layer is positioned to contact said container.
26. The closure of claim 24 wherein said first layer is attached to said base wall.
- 15 27. The closure of claim 24 wherein said LCP is derived from at least one monomer selected from the group consisting of: terephthalic acid, isophthalic acid, 1,4-hydroquinone, resorcinol, 4-aminobenzoic acid, 3-aminobenzoic acid, 4-hydroxybenzoic acid, 3-hydroxybenzoic acid, 4-aminophenol, 3-aminophenol, 1,4-phenylenediamine, 4,4'-biphenol, 4,4'-biphenyldicarboxylic acid, 6-hydroxy-2-naphthoic acid, 2,6-naphthalenedicarboxylic acid, and 2,6-dihydroxynaphthalene.
- 20 28. The closure of claim 27 wherein said first or second layer is a polyolefin.
29. The closure of claim 28 wherein said polyolefin is selected from the group consisting of: polyethylene, polypropylene, and ethylene vinyl acetate.
- 25 30. The closure of claim 18 further comprising an adhesive layer between said gas barrier layer and said first or second layer.
31. The closure of claim 30 wherein said adhesive layer is comprised of a functionalized polyolefin material.
- 30 32. The closure of claim 31 wherein said functionalized polyolefin material comprises at least one functional group selected from the group consisting of a carboxyl group or its esters, a carboxylic anhydride group, a glycidyl group and an alkoxysilane group.
- 35 33. The closure of claim 28 wherein said functionalized polyolefin material is a terpolymer of ethylene, methyl acrylate and glycidyl methacrylate.
34. The closure of claim 24 wherein the thickness of said first layer is about 375  $\mu\text{m}$  to about 1250  $\mu\text{m}$  and the thickness of said second layer is less than about 150  $\mu\text{m}$ .
- 40 35. The closure of claim 24 wherein the thickness of said first layer is about 625  $\mu\text{m}$  to about 875  $\mu\text{m}$  and the thickness of said second layer is less than about 75  $\mu\text{m}$ .
36. The closure of claim 35 wherein the thickness of said barrier layer is between about 2 to about 15  $\mu\text{m}$ .
- 45 37. The closure of claim 36 wherein said first and said second layer is ethylene vinyl acetate.
38. The closure of claim 18 wherein said gas barrier layer is less than about 150  $\mu\text{m}$  from said container.
39. The closure of claim 18 wherein said gas barrier layer is less than about 75  $\mu\text{m}$  from said container.
- 50 40. The closure of claim 18 wherein said closure is selected from the group consisting of: screw, twist-off, pilfer proof, crown, lug, tear off, and ring pull.

FIG. 1

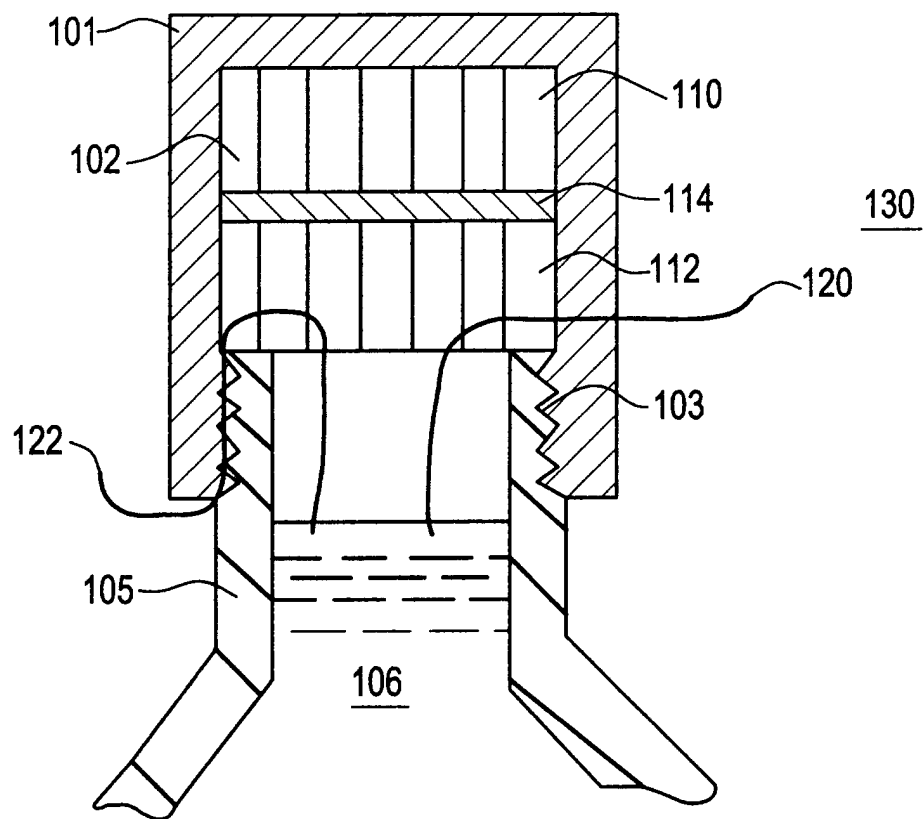


FIG. 2

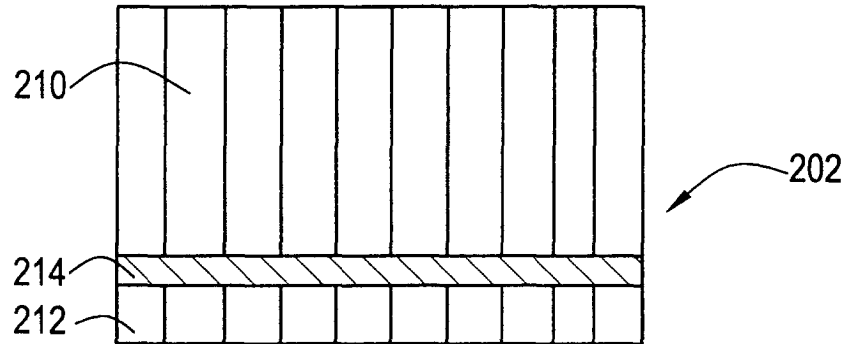


FIG. 3

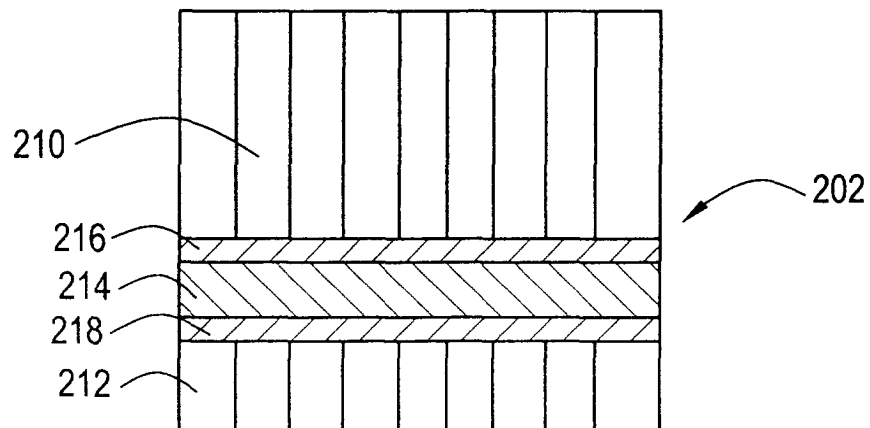


FIG. 4

