

by cutting an end seal, and the blotters removed. The blotterless pouches are rinsed with distilled water to remove any liquid nicotine that might be present on the surface of the sealant and excess water is removed from the pouches by shaking. Next, 5 ml of isopropanol spiked with an internal standard (propylene glycol n-propyl ether) is placed in each pouch which is then resealed with heat seals. The resealed pouches are placed on a shaker table for 90 minutes to facilitate nicotine extraction from the sealant. Finally, the pouch extracts are analyzed by gas chromatography and the amount of eluted nicotine is calculated for each pouch.

[00142] Nicotine Vapor Test

[00143] Ten pouches are made with each test film by heat sealing together two pieces of the sample film each measuring 3 x 3.5 inches on three sides with the same article contact surface facing each other. Next, 50 µl of pure nicotine is placed on a 1 x 1.25 inch piece of blotter paper. The blotter paper is then wrapped in perforated foil having approximately 20 needle perforations per side. The foil wrapped blotter paper is placed inside the pouch which is then hermetically sealed. The perforated foil wrapper prevents direct contact of the blotter absorbed nicotine with the sealant layer of the film.

[00144] The blotter containing pouches are stored at 100°F and 20% Relative Humidity (RH). Two pouches of each film structure are tested at recorded intervals e.g. days 1, 2, 8, 15 and 31 as follows. After the allotted time, two pouches are opened by cutting an end seal, and the foil covered blotters are removed. Next, 5 ml of isopropanol, spiked with an internal standard (propylene glycol n-propyl ether), is placed in each pouch and each blotterless pouch is resealed with heat seals. The resealed pouches are then placed on a shaker table for 90 minutes to facilitate nicotine extraction from the sealant. Finally, the pouch extracts are analyzed by gas chromatography and the amount of eluted nicotine is calculated for each pouch.

[00145] Eluted nicotine values are measured by the methods described above or tests similar thereto, unless otherwise specified.

[00146] Drug uptake test

[00147] Ten pouches are made with each test film by heat sealing together two pieces of the sample film each measuring 3 x 3.5 inches on three sides with the same article contact surface facing each

other. Next, a standard amount of the drug being tested is placed on a 1 x 1.25 inch piece of blotter paper and the blotter paper is placed inside the pouch which is then heat sealed.

[00148] The pouches are stored at 100° F and 20% RH and three pouches of each film structure are tested at reported intervals e.g. days 1, 7, 15 and 31. After the allotted time, three pouches are opened by cutting an end seal, and the blotters removed. The blotterless pouches are rinsed with distilled water to remove any drug residue that might be present on the surface of the sealant and excess water is removed from the pouches by shaking. Next, 5 ml of isopropanol spiked with an internal standard (propylene glycol n-propyl ether) is placed in each pouch which is then resealed with heat seals. The resealed pouches are placed on a shaker table for 90 minutes to facilitate drug extraction from the sealant. Finally, the pouch extracts are analyzed by gas chromatography and the amount of eluted drug is calculated for each pouch.

[00149] Drug Vapor Test

[00150] Ten pouches are made with each test film by heat sealing together two pieces of the sample film each measuring 3 x 3.5 inches on three sides with the same article contact surface facing each other. Next, a standard amount of the drug being tested is placed on a 1 x 1.25 inch piece of blotter paper. The blotter paper is then wrapped in perforated foil having approximately 20 needle perforations per side. The foil wrapped blotter paper is placed inside the pouch which is then hermetically sealed. The perforated foil wrapper prevents direct contact of the blotter absorbed drug with the sealant layer of the film.

[00151] The blotter containing pouches are stored at 100°F and 20% Relative Humidity (RH). Three pouches of each film structure are tested at recorded intervals e.g. days 1, 7, 15 and 31 as follows. After the allotted time, three pouches are opened by cutting an end seal, and the foil covered blotters are removed. Next, 5 ml of isopropanol, spiked with an internal standard (propylene glycol n-propyl ether), is placed in each pouch and each blotterless pouch is resealed with heat seals. The resealed pouches are then placed on a shaker table for 90 minutes to facilitate drug extraction from the sealant. Finally, the pouch extracts are analyzed by gas chromatography and the amount of eluted drug is calculated for each pouch.

- [00152] Eluted drug values are measured by the methods described above or tests similar thereto, unless otherwise specified.
- [00153] Raman Spectroscopy
- [00154] For purposes of illustration, a Raman Spectroscopy method for samples in direct contact with a nicotine composition is now described. One will understand that the method can be readily modified for use with indirect drug contact or for use with other drugs.
- [00155] Film Samples in direct contact with nicotine for a specified time were analyzed using a Confocal Raman microscope (Thermo Fisher DXRxi) using a 100x (numerical aperture: 0.90) objective, a laser wavelength of 532 nm (10 mW of power at sampling point) and an exposure time of 0.04 seconds per spectrum. The estimated spot size on the sample was 0.2 μm and the confocal aperture used was 25 μm . Spectra between wavenumbers 500-3500 cm^{-1} were collected. Spectra were collected in the form of a depth profile from a section of the film (100x100 μm) with a Raman image pixel size specified as 2 μm and the total number of scans was 10. As a result, each Raman image is a composite of results from 25,000 spectra. The Raman image was generated using proprietary software (Thermo Fisher Scientific) included with the Raman microscope used. Area under the peaks (wavenumber range: 1004-1064 cm^{-1}) was used to indicate relative nicotine concentration at each point on the generated Raman image on a rainbow scale (low: blue, high: red). Pure nicotine liquid has peaks at 1026 cm^{-1} and 1042 cm^{-1} .
- [00156] Following are examples given to illustrate the invention, but these examples should not be taken as limiting the scope. All percentages are by weight unless indicated otherwise.
- [00157] Films of 6, 7, 8, 9 or more layers are contemplated. The inventive multilayer films may include additional layers or polymers to add or modify various properties of the desired film such as heat sealability, interlayer adhesion, wrinkle resistance, puncture resistance, printability, toughness, gas and/or water barrier properties, abrasion resistance, printability, and optical properties such as gloss, haze, freedom from lines, streaks or gels. These layers may be formed by any suitable method including coextrusion, extrusion coating and lamination.
- [00158] Unless otherwise noted, the thermoplastic resins utilized in the present invention are generally commercially available in pellet form and, as generally recognized in the art, may be melt

blended or mechanically mixed by well-known methods using commercially available equipment including tumblers, mixers or blenders. Also, if desired, well known additives such as processing aids, slip agents, anti-blocking agents and pigments, and mixtures thereof may be incorporated into the film or applied to one or more surfaces thereof, e.g. by blending prior to extrusion, powdering, spraying, contact roller application, etc. Typically the resins and any desired additives are mixed and introduced to an extruder where the resins are melt plastified by heating and then transferred to an extrusion (or coextrusion) die. Extruder and die temperatures will generally depend upon the particular resin or resin containing mixtures being processed and suitable temperature ranges for commercially available resins are generally known in the art, or are provided in technical bulletins made available by resin manufacturers. Processing temperatures may vary depending upon other processing parameters chosen.

[00159] EXAMPLES 1-5

[00160] Examples 1-4 are comparative examples (not of the invention). Example 5 is an example according to the present invention. In all of the examples, a multilayer film is provided having a base film and connected sealant film. The sealant film has a surface layer which is designed to contact the article to be packaged e.g. a transdermal patch article, and to permit heat sealing of the multilayer film to form a container such as a pouch. The EAILDPE/COC sealant layer of the invention and the comparative sealant layers were either extrusion coated or adhesively laminated. In all of the examples 1-5, a multilayer base film having the following structure: OPET / Primer / PE / EAA / Foil was made and only the connected sealant film was varied.

[00161] Base film

[00162] The base film was comprised of five layers having an ordered structure of:

/Layer 1 / Layer 2 / Layer 3 / Layer 4 / Layer 5 / corresponding to:

/exterior layer 1 / primer layer 2 / bulk layer 3 / adhesive layer 4 / 0.2 layer 5 /; or more particularly,

/OPET/PEI/LDPE/EVA/Al Foil/.

- [00163] Layer 1 was a commercially available 0.92 mil, biaxially oriented polyethylene terephthalate (OPET) film corona treated on one side. The treated OPET film received a second corona treatment on the previously treated side prior to receiving an anchor coating of a water-based polyethyleneimine (PEI) primer (Layer 2) that was contact coated onto the corona treated side of the OPET film and dried just prior to lamination of the OPET film to 0.35 mil aluminum foil (Layer 5) using a coextrusion of LDPE (Layer 3) and EAA (Layer 4). Layers 3 and 4 were produced by the two-layer coextrusion of LDPE and EAA. The anchor coated side of the OPET film was laminated to 0.35 mil aluminum foil with a coextrusion of LDPE and EAA. The LDPE was a blend of 87.5 wt.% LDPE laminate resin and 12.5 wt.% of a white colorant in a carrier resin. The oxygen and moisture barrier was provided by a commercially available aluminum foil.
- [00164] Comparative Example 1
- [00165] In example 1, a sealant film of ionomer was extrusion coated onto a five layer base film made as described above. The aluminum foil surface of the multilayer base film having the structure OPET/primer/LDPE/EAA/foil was corona treated and then extrusion coated with ionomer. The ionomer used was a zinc salt of ethylene-methacrylate acid copolymer commercially available under the trademark Surlyn® 1652-1 and having a reported density of 0.940 g/cm³ and meh index of 4.5 g/10 min.
- [00166] The resultant six layer, multilayer film had the following structure: 0.92 mil OPET / primer / coex (0.42 mil LDPE / 0.1 mil EAA) / 0.35 mil foil 1.0 mil ionomer, and had a total nominal thickness of 2.8 mils (71 microns).
- [00167] Comparative Example 2
- [00168] The base film for example 2 was produced in the same manner as for example 1 except that the aluminum foil was not corona treated prior to the addition of the sealant film. In comparative example 2, a three-layer coextrusion of: EAA; LDPE; and an 80:20 wt% blend of LDPE:mLLDPE was extrusion coated onto the aluminum foil surface of the multilayer base film with the EAA layer adhered to and in direct contact with the aluminum foil. The resultant multilayer film had the following structure 0.92 mil OPET / primer / (0.42 mil LDPE / 0.1 mil

EAA) / 0.35 mil foil / 0.17 mil EAA / 0.65 mil LDPEI 0.43 mil LDPE:mLLDPE and a total thickness of 3.04 mils (77.2 microns).

[00169] Comparative Example 3

[00170] The base film for example 3 was produced in the same manner as for example 2. In comparative example 3, the sealant film was a commercially available, corona treated, cast APET film. The APET film received an additional corona treatment prior to adhesive lamination. The base and sealant films were laminated by coating the aluminum foil surface of the multilayer base film having the structure OPET/primer/LDPE/EAA/foil with a 2-part urethane adhesive using an analox roller followed by laminating contact to a corona retreated cast APET film . The resultant 7 layer film had the following structure: 0.92 mil OPET / primer / 0.42 mil LDPE / 0.1 mil EAA) / 0.35 mil foil/ 0.08 mil adhesive / 2 mil APET (inside) and a total thickness of 3.9 mils (99 microns).

[00171] Comparative Example 4

[00172] The base film for example 4 was produced in the same manner as for example 2 except that the LDPE/EAA coextrusion was applied slightly thicker. In comparative example 4, the sealant film was a corona treated polyacrylonitrile film. The polyacrylonitrile film received an additional corona treatment just prior to lamination. The aluminum foil surface of the multilayer base film having the structure OPET/primer/LDPE/EAA/foil was then coated with a 2-part urethane adhesive using an analox roller and the structure was adhesively laminated to the corona retreated polyacrylonitrile film. The resultant multilayer film had the following structure (outside) 0.92 mil OPET / primer / 0.56 mil LDPE / 0.1 mil EAA) / 0.35 mil foil / 0.07 mil Adhesive / 1.5 mil Barex (inside) and a total thickness of 3.5 mil.

[00173] Example 5 (Of the Invention)

[00174] The film structure in Example 5 is exemplary of a film according to the present invention. The base film for example 5 was produced in the same manner as for comparative example 2. In this example, the sealant film was a three-layer coextrusion of EAA, LDPE and Ethylene-norbornene copolymer (COC) which was extrusion coated onto the aluminum foil surface of the multilayer base film to produce an eight layer film having the structure: 0.92 mil OPET/primer/0.42 mil

LDPE 10.1 mil EAA 0.35 mil foil 0.17 mil EAA/0.65 mil LD/PE/0.43 mil COC and a total thickness of 3.0 mils (76 microns). The inventive film is well suited to package articles for collecting or administering a physiologically active substance such as transdermal drug delivery patches, or oral dissolvable thin strips and has advantageous moisture barrier, oxygen barrier, and low scalping properties as discussed below. The resultant multilayer film was tested for various properties which are reported below.

[00175] Scalping Tests for Examples 1-5

[00176] Each of the films made in Examples 1-5 were tested for nicotine scalping by a "Nicotine Direct Contact Test" and a "Nicotine Vapor Test". Properties are reported in **Table 2** below.

Table 2

Ex. No.	Sealant Layer	Ave. Sealant Thickness (mil)	Nicotine Direct Contact Test					Nicotine Vapor Test				
			Amount of Eluted Nicotine (mg)					Amount of Eluted Nicotine (mg)				
			Day 1	Day 2	Day 8	Day 15	Day 31	Day 1	Day 2	Day 8	Day 15	Day 31
1	Ionomer	1.0	17.1	15.3	16.7	24.0	22.0	8.5	11.9	15.8	25.2	23.7
2	LDPE:mLLDPE 80:20 wt.% blend	0.43	10.5	10.8	13.3	17.0	15.8	5.76	7.85	11.5	17.2	16.2
3	APET	2	12.6	10.5	12.0	13.1	11.2	1.73	2.47	Leak in Pouch	Leak in Pouch	2.3
4	polyacrylonitrile	1.5	0.05	0.00	0.00	0.03	0.03	0.21	0.36	0.49	0.70	1.08

5	COC	0.43	2.08	3.47	1.42	3.12	2.03	0.94	1.26	1.95	2.42	1.26
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[00177] Example 6 – Testing of additional agents

[00178] Tested Structures:

APET: 92ga OPET / 7.5# White PE Coex / 35ga Foil / 1.7# Adh. / 2mil APET
(35680-G)

CXB™: 92ga OPET / 9.6# White PE Coex / 35ga Foil / 1.7# Adh. / 2mil CXB
(LLDPE-COC) (35694-G)

Barex®: 92ga OPET / 9.6# White PE Coex / 35ga Foil / 1.7# Adh. / 2mil Barex®
(35434-G)

PE: 48ga OPET / 9.6# White PE Coex / 35ga Foil / 1.7# Adh. / 2mil EVA
(5% VA) (35775-G)

92ga OPET / 7.5# White PE Coex / 35ga Foil / 18# EAA/LDPE (35417)

Ionomer: 48ga OPET / 9.3# White PE Coex / 28.5ga Foil / 15# Ionomer (35698)

[00179] When choosing testing materials, PE based sealants were chosen as a negative control and Barex® was chosen as a positive control. The goal of an anti-scalping sealant is to perform better than PE and show close (if not matched) performance to Barex®

[00180] With Barex® being the gold standard for uptake, a goal of at least 85% of Barex® performance was set. Though each application will differ in barrier requirements, those that do require minimal uptake and are currently are in Barex® will require performance close to that of Barex® to minimize packaging risk.

[00181] In the case of Nicotine uptake testing, CXB™ performed at 95.2% Barex® performance with direct contact and 98% Barex® performance with indirect contact. In subsequent nicotine uptake studies, CXB™ had greater than 98% of Barex® performance

[00182] Estradiol Uptake, and HSP

[00183] Direct Contact

day	Ionomer	Barex	APET	35775- PE	CXB
1	0.0000	0.0000	0.0000	0.0000	0.0000
7	0.0000	0.0000	0.0000	0.0000	0.0000
18	0.0073	0.0000	0.0000	0.0048	0.0055
30	0.0051	0.0000	0.0137	0.0000	0.0088
60	0.0029	0.0000	0.0161	0.0058	0.0132

[00184] Very small amounts of estradiol can be detected in several of the samples. It is unclear at this point if the values are indicative of an accurate trend of uptake.

[00185] Indirect Contact (vapor contact)

day	Ionomer	Barex	APET	35775- PE	CXB
1	0.00000	0.00000	0.00000	0.00000	0.00000
7	0.00000	0.00000	0.00000	0.00000	0.00000
18	0.00065	0.00000	0.00000	0.00000	0.00000
30	0.00000	0.00000	0.00000	0.00000	0.00000
60	0.00000	0.00000	0.00296	0.01614	0.00000

[00186] In the indirect uptake test, PE and APET show detectable amounts of Estradiol while the other materials show no uptake. The estradiol values in this case remain very low.

[00187] HSP: (no RED value for Ionomer)

RED Values	CXB	Barex	PE (low Tg)	PET
Estradiol	1.62	0.97	3.12	0.46

[00188] **Raman:** No penetration of Estradiol could be detected with Raman Spectroscopy in the uptake samples.

[00189] Lidocaine Uptake, HSP, and Raman

[00190] Direct Contact

Direct Contact (avg mg of Lidocaine)					
day	Ionomer	Barex	APET	35775-PE	CXB
0	0.0000	0.0000	0.0000	0.0000	0.0000
1	0.3283	0.0467	0.0693	0.1559	0.0124
7	1.8896	0.1055	0.2392	0.5739	0.0214
18	1.9872	0.5642	0.3339	0.6513	0.0473
30	2.7984	0.1328	0.6924	0.8306	0.1347
60	2.85	0.43	1.19	0.72	0.25

[00191] Direct contact shows CXB as the best performance, even exceeding the performance of Barex®.

[00192] Indirect Contact (Vapor Contact)

Vapor Contact (avg mg of Lidocaine)					
day	Ionomer	Barex	APET	35775-PE	CXB
0	0.0000	0.0000	0.0000	0.0000	0.0000
1	0.0125	0.0090	0.0083	0.0137	0.0055
7	0.0400	0.0199	0.0194	0.0276	0.0075
14	0.0492	0.0352	0.0272	0.0536	0.0107
30	0.0664	0.0719	0.0506	0.0809	0.0209
60	0.3570	0.2999	0.1717	0.2452	0.1389

[00193] Again with vapor contact, CXB™ is the best performer.

[00194] HSP:

RED Values	CXB	Barex	PE (low Tg)	PET
Lidocaine	1.32	0.9	2.85	0.23

[00195] **Raman:** Permeation of Lidocaine could only be seen in Ionomer and PE after 28days of direct contact. PE permeation resulted in the Lidocaine diffusing all the way through the sealant layer and settling at the sealant/foil interface.

- [00196] Based on the results of the above examples, the inventors now believe that two factors play a role in permeation characteristics; namely, thermodynamic and kinetic interactions. Again, based on the results presented herein, the inventors believe that both of these interactions will, together, provide a more full understanding of the permeation properties of a sealant film relative to either factor in isolation. Thermodynamic interactions can be predicted through solubility modeling. Kinetic interactions are based on the structure of the polymer and the molecular weight of the active agent in the product. Assuming all transdermal drugs are low molecular weight, the polymer characteristics can be used to predict the kinetic interaction. In this case, T_g can be used as a factor for determining the rate at which a drug will diffuse through a polymer, with a higher T_g resulting in a lower diffusion rate. However, the T_g should be low enough to allow the polymer to be heat sealable. Thus the HSP RED value can be factored in, with higher RED values indicating lower solubilities (thermodynamic factor). The more soluble the drug is in the sealant, the more permeation will occur. Low permeation anti-scalping heat sealable films or layers can be obtained by balancing RED (thermodynamic) and T_g (kinetic factors).
- [00197] Based on the results presented herein, the inventors believe that films or layers comprising 90% or more of an ethylene norbornene copolymer and having a glass transition temperature of 50-138°C, an ethylene-norbornene comonomer content of 20-40 mole% ethylene and 30-60 mole% norbornene, or a glass transition temperature of 50-138°C and an ethylene-norbornene comonomer content of 20-40 mole% ethylene and 30-60 mole% norbornene can provide a heat-sealable film or layer that is anti-scalping with respect to a number of active pharmaceutical agents, particularly those having HPS RED values of 0.5 or greater, such as 0.6 or greater, 0.7 or greater, 0.8 or greater, 0.9 or greater, or 1 or greater.
- [00198] Various embodiments have been described above. Although the invention has been described with reference to these specific embodiments, the descriptions are intended to be illustrative and are not intended to be limiting. Various modifications and applications may occur to those skilled in the art without departing from the true spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. A film for packaging a product comprising a pharmaceutical active agent, the film comprising:

a product-contacting sealing layer comprising at least 90 wt. % of an ethylene norbornene copolymer or having a glass transition temperature in a range from 50°C to 110°C;

wherein the pharmaceutical active agent comprises a Hansen Solubility Parameter for the product-contacting sealing layer of 0.5 or greater.
2. A film according to claim 1, wherein the product-contacting sealing layer comprises at least 90 wt. % of an ethylene norbornene copolymer having a glass transition temperature in a range from 65°C to 110°C.
3. A film according to claim 1, wherein the pharmaceutical active agent comprises a Hansen Solubility Parameter for the polymeric sealing layer of 0.7 or greater.
3. A film according to claim 1, wherein the pharmaceutical active agent comprises a Hansen Solubility Parameter for the polymeric sealing layer of 1 or greater.
4. A film according to claim 1, wherein the pharmaceutical active agent is selected from the group consisting of fentanyl, nicotine, lidocaine, estradiol, clonidine, ethinyl estradiol, oxybutynin, buprenorphine, granisetron, methylphenidate, and scopolamine.

5. A film according to claim 1, wherein the pharmaceutical active agent is selected from the group consisting of nicotine, lidocaine, estradiol, clonidine, ethinyl estradiol, buprenorphine, granisetron, and scopolamine.
6. A film according to any one of claims 1-5, wherein the sealing layer comprises at least 95 wt. % ethylene norbornene copolymer.
7. A film according to any one of claims 1-5, wherein the sealing layer consists essentially of ethylene norbornene copolymer.
8. A film according to any one of the preceding claims, wherein the product comprising the pharmaceutical active agent comprises a transdermal patch comprising the pharmaceutical active agent.
9. A packaged pharmaceutical product, comprising:
a film according to any one of claims 1-8, wherein the a product-contacting sealing layer defines a sealed interior volume; and
the product comprising a pharmaceutical active agent disposed in the interior volume of the sealed package, wherein the pharmaceutical agent is in contact with the sealing layer.
10. A method for packaging a pharmaceutical product comprising a pharmaceutical active agent, the method comprising:
sealing the pharmaceutical product in an interior of a packaging film, wherein the film comprises a sealing layer comprising at least 90 wt. % of an ethylene norbornene copolymer having a glass transition temperature in a range from 65°C to 110°C,

wherein sealing the pharmaceutical product in the interior of the packaging film comprises placing the pharmaceutical agent in contact with the sealing layer, and

wherein the pharmaceutical active agent comprises a Hansen Solubility Parameter for the polymeric sealing layer of 0.5 or greater.

11. A method according to claim 10, wherein the pharmaceutical active agent comprises a Hansen Solubility Parameter for the polymeric sealing layer of 0.7 or greater.
12. A method according to claim 10, wherein the pharmaceutical active agent comprises a Hansen Solubility Parameter for the polymeric sealing layer of 1 or greater.
13. A method according to claim 10, wherein the pharmaceutical active agent is selected from the group consisting of fentanyl, nicotine, lidocaine, estradiol, clonidine, ethinyl estradiol, oxybutynin, buprenorphine, granisetron, methylphenidate, and scopolamine.
14. A method according to claim 10, wherein the pharmaceutical active agent is selected from the group consisting of nicotine, lidocaine, estradiol, clonidine, ethinyl estradiol, buprenorphine, granisetron, and scopolamine.
15. A method according to any one of claims 10-14, wherein the sealing layer comprises at least 95 wt. % ethylene norbornene copolymer.
16. A method according to any one of claims 10-15, wherein the sealing layer consists essentially of ethylene norbornene copolymer.

17. A method according to any one of claims 10-16, wherein the product comprising the pharmaceutical active agent comprises a transdermal patch comprising the pharmaceutical active agent.
18. A drug resistant, flexible, multilayer packaging film comprising:
- (a) a drug contact layer having at least 90 wt. % of an ethylene norbornene copolymer having a glass transition temperature of from 65°C to 110°C;
 - (b) a polyolefin bulk layer;
 - (c) a first intermediate adhesive layer;
 - (d) an oxygen barrier layer having an oxygen transmission rate of less than 0.01 cm³/100 inches²/24 hours at 1 atmosphere and 23°C;
 - (e) a second intermediate adhesive layer; and
 - (f) an exterior protective layer comprising a polymer selected from the group consisting of paper, oriented polyester, amorphous polyester, polyamide, polyolefin, nylon, polypropylene, or copolymers, or blends thereof,
- wherein said multilayer film has the following properties:
- a water vapor transmission rate (WTVR) of less than 0.01 g/ 100 square inches per 24 hours at 23°C and 1 atmosphere.
19. A multilayer film as defined in claim 18, wherein said contact layer comprises at least 95 wt. % ethylene norbornene copolymer,
20. A multilayer film as defined in claim 18, wherein said contact layer consists essentially of ethylene norbornene copolymer.

21. A packaged pharmaceutical product comprising:
a multilayer film as defined in claim 18, wherein said film is formed into a flexible container; and
a transdermal patch sealed within the container.
22. A packaged pharmaceutical product as defined in claim 21, wherein said patch is a nicotine or fentanyl drug delivery patch.
23. A drug resistant, flexible, multilayer packaging film comprising a drug contact layer having at least 90 wt. % of an ethylene norbornene copolymer having a glass transition temperature of from 55°C to 110°C.
24. A film according to claim 23, wherein the film has a water vapor transmission rate (WTVR) of less than 0.1 g/ 100 square inches per 24 hours at 23°C and 1 atmosphere.
25. A film according to claim 23 or claim 24, wherein the film has an oxygen transmission rate of less than 0.01 cm³/100 inches²/24 hours at 1 atmosphere and 23°C.
26. A film according to any one of claims 23-25, further comprising an exterior protective layer comprising a polymer selected from the group consisting of paper, oriented polyester, amorphous polyester, polyamide, polyolefin, nylon, polypropylene, or copolymers, or blends thereof.
27. A film according to any one of claims 23-26, wherein the film further comprises a polyolefin bulk layer between the drug contact layer and the exterior protective layer.

28. A film according to any one of claims 23-27, wherein the contact layer comprises at least 95 wt. % ethylene norbornene copolymer.
29. A film according to any one of claims 23-27, wherein the contact layer consists essentially of ethylene norbornene copolymer.
30. A packaged pharmaceutical product comprising:
a film according to any one or claims 23-29, wherein the film is formed into a flexible container; and
a product comprising a pharmaceutical active agent, wherein the pharmaceutical active agent is in contact with the drug contact layer of the film.
31. A packaged pharmaceutical product according to claim 30, wherein the pharmaceutical active agent comprises a Hansen Solubility Parameter for the drug contacting layer of 0.5 or greater.
32. A packaged pharmaceutical product according to claim 30, wherein the pharmaceutical active agent comprises a Hansen Solubility Parameter for the drug contacting layer of 0.7 or greater.
33. A packaged pharmaceutical product according to claim 30, wherein the pharmaceutical active agent comprises a Hansen Solubility Parameter for the drug contacting layer of 1 or greater.
34. A packaged pharmaceutical product according to any one of claims 30-33, wherein the pharmaceutical active agent is selected from the group consisting

of fentanyl, nicotine, lidocaine, estradiol, clonidine, ethinyl estradiol, oxybutynin, buprenorphine, granisetron, methylphenidate, and scopolamine.

35. A packaged pharmaceutical product according to any one of claims 30-33, wherein the pharmaceutical active agent is selected from the group consisting of nicotine, lidocaine, estradiol, clonidine, ethinyl estradiol, buprenorphine, granisetron, and scopolamine.
36. A packaged pharmaceutical product according to any one of claims 30-35, wherein the product comprising the pharmaceutical active agent comprises a transdermal patch comprising the pharmaceutical active agent.
37. A packaged pharmaceutical product according to claim 36, wherein the patch is a nicotine or fentanyl drug delivery patch.

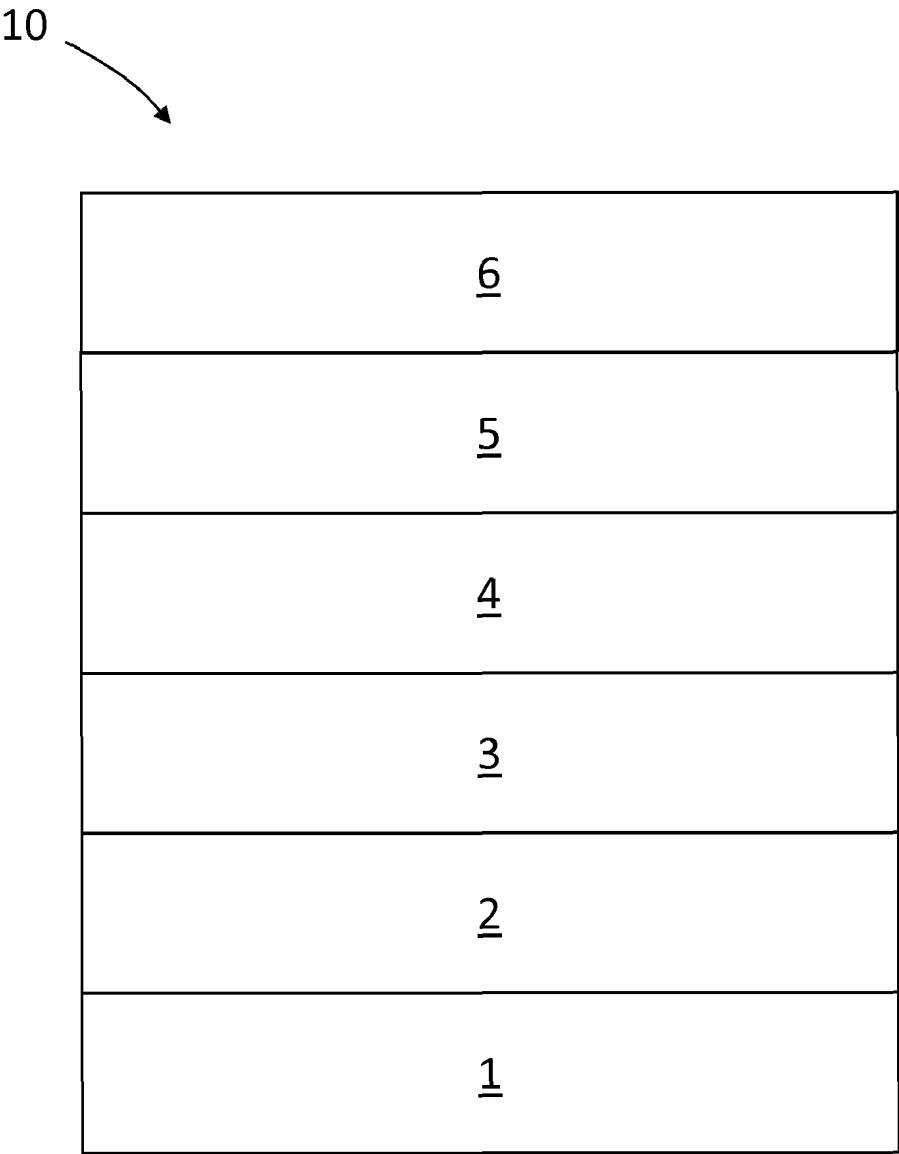


FIG. 1

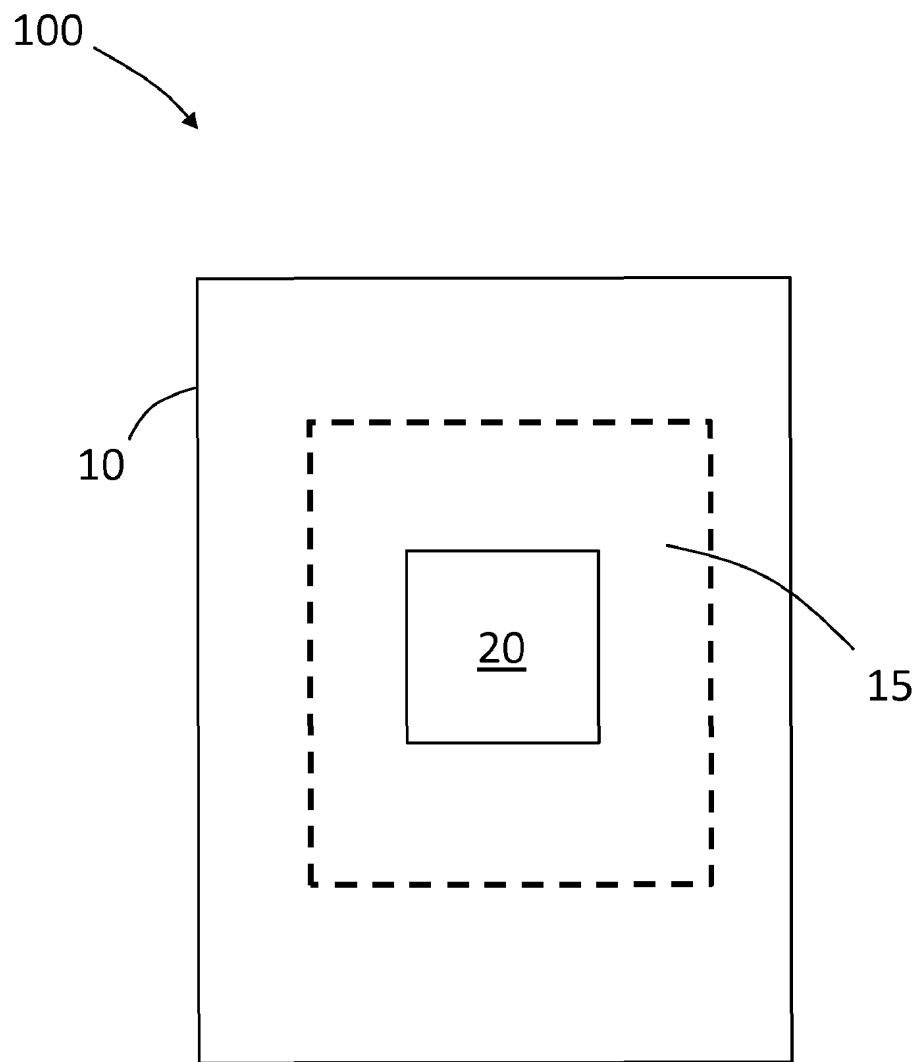


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/015246

A. CLASSIFICATION OF SUBJECT MATTER

INV. B32B7/12 B32B27/08 B32B27/10 B32B27/32 B32B27/34
B32B27/36 A61J1/10

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B32B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/208685 A1 (RIVERS BRIAN PATRICK [US] ET AL) 20 August 2009 (2009-08-20) paragraphs [0006], [0007], [0064] - [0075], [0105] - [0108], [0114] - [0116], [0133], [0140] -----	1-12, 15-20, 23-25, 30-33
X	US 2006/198973 A1 (JESTER RANDY D [US]) 7 September 2006 (2006-09-07) paragraphs [0001], [0007] - [0009], [0042], [0047], [0050], [0062]; claims 1,2,6,22; figures 1,1a -----	1-8, 23-29
A	US 2006/046006 A1 (BASTION BRADLEY J [US] ET AL) 2 March 2006 (2006-03-02) the whole document ----- -/-	1-37



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

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"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

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Date of the actual completion of the international search

28 April 2015

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European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Ibarrola Torres, O

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/015246

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/101946 A2 (CARTOTECNICA VENETA SPA [IT]; PARISI SALVATORE [IT]; MENEGHETTI GIOVAN) 28 August 2008 (2008-08-28) page 1 page 18, last line - page 19, line 21; claims 1,5, 6, 10, 12, 14, 15; figure 1 -----	1-37

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/015246

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009208685 A1	20-08-2009	US 2009208685 A1	20-08-2009
		WO 2009105205 A1	27-08-2009

US 2006198973 A1	07-09-2006	NONE	

US 2006046006 A1	02-03-2006	NONE	

WO 2008101946 A2	28-08-2008	EP 2117838 A2	18-11-2009
		WO 2008101946 A2	28-08-2008



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- (71) **Applicant:** PERFECSEAL, INC. [US/US]; 3500 North Main Street, Oshkosh, WI 54901 (US).
- (72) **Inventors:** PRISCAL, Michael, D.; 3485 Dekalb Lane, Neenah, WI 54956 (US). PUGUH, Arthya; 1700 Dublin Trail Apt. #122, Neenah, WI 54956 (US).
- (74) **Agent:** HALL, Tom, J.; Bemis Company, Inc., Office Of Intellectual Property Counsel, P.O. Box 669, Neenah, WI 54957 (US).
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BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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(54) **Title:** BLISTER PACKAGING COMPONENTS

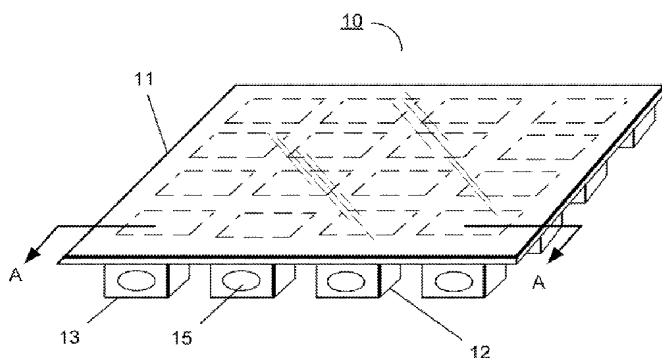


FIG. 1

(57) **Abstract:** The present invention relates to blister components for blister packages formed from multilayer thermoplastic films. In one preferred embodiment of the present invention, the blister component has a layer sequence configuration of A/B/C/B/A. Preferably, layer A is a first exterior layer comprising cyclic olefin copolymer (COC), layer B is an interior layer comprising a high density polyethylene (HDPE), a blend of high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), or a bimodal high density polyethylene having a distribution of a low molecular weight region and a high molecular weight region (HDPE-Bimodal), or a high density polyethylene having a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil), layer C is a central core layer. Alternatively, the blister component has a layer sequence configuration of A/B/C/B/D, where layer D is a second exterior layer.



BLISTER PACKAGING COMPONENTS

BACKGROUND OF THE INVENTION

- [01]** The present invention relates generally to blister packaging and more particularly, to blister components for blister packaging formed from multilayer thermoplastic films where a low moisture vapor transmission rate is desired.
- [02]** Blister packaging is employed widely for commercial packaging of food products, personal care products, and human health products such as pharmaceuticals, and medical devices or precision instruments. The use of this type of packaging has become widespread mainly due to the ability in incorporate suitable moisture, dust, UV and/or gas barriers into the packages when such properties are desired for maintaining the product contained therein. For example, blister packaging is extensively used in the pharmaceutical industry for packaging of medicaments or the like in capsule, lozenge, or pill form because the integrity of the medicament can be maintained through the proper selection of materials used to form the packages.
- [03]** For preparing blister packages or so-called push through packages, generally a thermoplastic film is first processed by vacuum forming or pneumatic forming so as to form blisters or cavities thereon, namely portions having a predetermined contour corresponding to each specific article to be received therein. After the so-blistered film has been solidified, each blister is charged with each piece of the article to be packaged and a second or lidding film is then covered over each blister and sealed to the first film. The second lidding film is often a laminate material which can be ruptured by a simple finger-rupture or peeled off from the first film to allow access to a packaged item. Conventional materials used for forming the blistered film have included transparent plastics such as polyvinylchloride (PVC), polyvinylidene chloride (PVdC) and polychlorotrifluoroethylene (PCTFE), commonly referred to as ACLAR®

(Honeywell/Allied Signal). Packaging for pharmaceuticals or other moisture-sensitive articles require not only low moisture permeability but also other properties such as chemical inertness, clarity, rigidity, or uniform thickness. The use of polyvinylchloride (PVC) and polyvinylidene chloride (PVdC) have been shown to have poor and/or insufficient moisture-proofing properties required by the pharmaceutical industry. While ACLAR® exhibits relatively low moisture vapor transmission, its use in blister packaging is inherently costly.

- [04] There is therefore a need in the art for improved blister packaging materials which provides sufficient moisture vapor barrier and chemical inertness properties and is aesthetically pleasing enough to present the products contained therein while being cost effective to be manufactured.

SUMMARY OF THE INVENTION

- [05] The present invention is directed to blister components for blister packages formed from a multilayer thermoplastic film. As used throughout this disclosure, the term "blister component" refers to multilayer thermoplastic film or a roll of multilayer thermoplastic film both of which may be thermoformed, partially thermoformed or not thermoformed at all. In one embodiment of the present invention, the sequence of layers in the multilayer thermoplastic film of the blister component is palindromic. As used throughout this application, the term "palindromic" refers to a multilayer film, the layers of which are substantially symmetrical. Non-limiting examples of palindromic films are film or sheet having the layer sequence of configurations: A/B/A or A/B/B/A or A/B/C/B/A or A/B/C/D/C/B/A or A/B/C/B/D/B/C/B/A or A/B/E/D/E/B/C/B/E/D/E/B/A, etc. An example of a layer sequence configuration of a non-palindromic film would be A/B/C or A/B/C/A. A palindromic thermoplastic film may be coextruded as a symmetrical cast or blown film using coextrusion methods generally well known in the art. An alternative method of producing palindromic films is by the use of

blown coextrusion of non-symmetrical film or sheet structures followed by collapsing the blown bubble around a central core layer.

- [06]** In another embodiment of the present invention, the sequence of layers in the multilayer thermoplastic film of the blister component is non-palindromic.
- [07]** In one generic embodiment, the thermoformed blister component of the present invention may be characterized as a palindromic film formed from a non-symmetrical film having a generic layer sequence configuration of A/B/C which is coextruded by blown film coextrusion techniques and collapsed upon itself to produce a layer sequence configuration of A/B/C/B/A. In this embodiment, the thermoformed blister component includes a film where layer A is an exterior layer comprising a cyclic olefin copolymer (COC), layer B is an interior layer comprising a high density polyethylene (HDPE), a blend of high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin, a bimodal high density polyethylene having a distribution of a low molecular weight region and a high molecular weight region, or a high density polyethylene (HDPE) and has a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil), and layer C is a central core layer. The central core layer C may be any suitable polymeric material which can be blown coextruded and collapsed upon itself. One non-limiting example of such materials is ethylene vinyl acetate copolymer (EVA).
- [08]** In another generic embodiment, the thermoformed blister component of the present invention may be characterized as a non-palindromic film having a layer sequence configuration of A/B/C/B/D which is coextruded by blown film coextrusion techniques and is not collapsed upon itself. In this embodiment, the thermoformed blister component includes a film where layer A is an exterior layer comprising a material selected from the group consisting of cyclic olefin copolymer (COC), layer B is an interior layer comprising a high density polyethylene (HDPE), a blend of high density polyethylene, high density

polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), a bimodal high density polyethylene having a distribution of a low molecular weight region and a high molecular weight region (HDPE-Bimodal), or a high density polyethylene and has a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil), layer C is a central core layer, and D is an exterior layer comprising a different material than layer A and is selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA). Core layer C may be any thermoplastic material. In one preferred embodiment, core layer C comprises ethylene vinyl acetate copolymer (EVA).

- [09] It should be understood that in the above-described generic embodiments, the thermoformed blister component may include additional film layers.
- [10] The blister packages of the present invention may also include a lidding component which is heat-sealable to the exterior layer A of the blister component. In one embodiment, the lidding component comprises a thermoplastic resin heat-sealable to cyclic olefin copolymer.

BRIEF DESCRIPTION OF THE DRAWINGS

- [11] Further features and advantages of the present invention will become apparent from the following detailed description, taken in combination with the appended drawings, in which:
- [12] FIG. 1 illustrates a schematic view of one embodiment of a blister package according to the present invention.

- [13]** FIG. 2 illustrates an exploded view taken along line A-A of FIG. 1 depicting the blister and lidding components of the present invention.
- [14]** FIG. 3 illustrates a cross-sectional view of one embodiment of a blister component according to the present invention.
- [15]** FIG. 4 illustrates a cross-sectional view of another embodiment of a blister component according to the present invention.
- [16]** FIG. 5 illustrates a cross-sectional view of one embodiment of a lidding component according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

- [17]** In accordance with the practice of the present invention, a representative blister package **10** as described herein is shown in FIGS. 1 and 2. Package **10** of the present invention comprises a thermoformed blister component **11** and a lidding component **12**, the former provided with one or more thermoformed pockets **13** surrounded by sealed flange regions **14**. Pocket **13** defines an individual compartment for receiving a product **15**, such as a tablet.
- [18]** In accordance with an important aspect of the present invention, the thermoformed blister component **11** comprises a multilayer thermoplastic film. It will be appreciated that the multilayer thermoplastic film of the thermoformed blister component **11** may include any number of film layers and film layer compositions depending upon both functional and aesthetic requirements of the blister component. It is desirable that multilayer thermoplastic film includes one or more film layers which are barrier materials and substantially chemically inert when in contact with a product. The term "barrier" refers to a material that controls permeability of one or more elements through a film structure including moisture, chemicals, heat, odor and oxygen or other gases. As it relates to the present invention, a barrier material can be provided by a single film layer or

multiple film layers acting individually or in concert with each other, respectively. The phrase “substantially chemically inert” refers to materials that generally are not reactive with the product with which it comes into contact with and does not leech chemical ingredients into the product with which it comes into contact. Preferably, thermoformed blister component **11** comprises a multilayer thermoplastic film which provides an average water vapor transmission rate of less than 0.500 g/m²/day or less than 0.250 g/m²/day or less than 150 g/m²/day or about 0.131 or about 0.110 g/m²/day at 100° F (37.8° C) and 90% relative humidity having a thickness of about 10 mil (254 micron) before being thermoformed. The aforementioned features of the present invention may be achieved by a multilayer thermoplastic film comprising at least 3 or 4 or 5 or 6 or 7 or 8 or 9 or 10 or 11 or 12 or 13 or more layers.

- [19] In one embodiment as depicted in FIG. 3, thermoformed blister component **11** comprises a multilayer thermoplastic film **100** comprising a five-layer structure of a first exterior layer **101**, a first interior layer **102**, a central core layer **103**, a second interior layer **104**, and a second exterior layer **105**. In one embodiment, first and second exterior layers **101** and **105** comprise the same materials. In another embodiment, first and second exterior layers **101** and **105** comprise different materials.
- [20] For example, in one preferred embodiment, first and second exterior layers **101** and **105** each comprise the same material of cyclic olefin copolymer (COC), a first and second interior layers **102** and **104** each comprise high density polyethylene (HDPE), a blend of a high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), a high density polyethylene (HDPE) and has a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil), or a bimodal high density polyethylene having a distribution of a low molecular weight region and a high molecular weight region (HDPE-Bimodal), and a core layer **103** comprising ethylene vinyl

acetate copolymer (EVA). Alternatively, the first exterior layer **101** comprises cyclic olefin copolymer (COC) and the second exterior layer **105** comprises a different material than first exterior layer **101** which is selected from the group consisting of polypropylene (PP), aromatic polyesters such as, but not limited to, polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG), aliphatic polyesters such as, but not limited to, polylactic acid (PLA); polyhydroxyalkonates including but not limited to polyhydroxypropionate, poly(3-hydroxybutyrate) (PH3B), poly(3-hydroxyvalerate) (PH3V), poly(4-hydroxybutyrate) (PH4B), poly(4-hydroxyvalerate) (PH4V), poly(5-hydroxyvalerate) (PH5V), poly(6-hydroxydodecanoate) (PH6D); or polystyrenes such as, but not limited to, high impact polystyrene (HIPS), general purpose polystyrene (GPPS), and styrene block copolymer (SBC).

- [21]** As used herein, the phrase “cyclic olefin copolymer” refers to copolymers having at least one norbornene structural moiety within the repeating backbone of the polymer. Suitable COCs for use in the present invention may have a heat deflection temperature under load (0.45 MPa) of about 75° C or 130° C or 150° C, or 170° C. Exemplary of commercially available cyclic olefin copolymers include, but are not limited to, the TOPAS® family of resins which is supplied by Celanese Corporation (Irving, TX, USA).
- [22]** As used throughout this application, the term “polypropylene” refers to a homopolymer or copolymer having a propyl or C-3 linkage between monomer units. A non-limiting example of a suitable propylene copolymer is Propylene 4170 available from Total Petrochemicals USA, Inc. (Houston, Tex.). Other non-limiting examples of polypropylenes include Polypropylene 3287WZ, which is available from Total Petrochemicals USA, Inc. (Houston, Tex.); and H02C-00 Polypropylene Homopolymer, which is available from Ineos Olefins & Polymers USA (League City, Tex.).

[23] As used throughout this application, the term "polyester" refers to a homopolymer or copolymer having an ester linkage between monomer units which may be formed, for example, by condensation polymerization reactions between a dicarboxylic acid and a diol. The ester linkage can be represented by the general formula: $[O-R-OC(O)-R'-C(O)]_n$ where R and R' are the same or different alkyl (or aryl) group and may be generally formed from the polymerization of dicarboxylic acid and diol monomers containing both carboxylic acid and hydroxyl moieties. The dicarboxylic acid (including the carboxylic acid moieties) may be linear or aliphatic (e.g., lactic acid, oxalic acid, maleic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, and the like) or may be aromatic or alkyl substituted aromatic (e.g., various isomers of phthalic acid, such as paraphthalic acid (or terephthalic acid), isophthalic acid and naphthalic acid). Specific examples of a useful diol include but are not limited to ethylene glycol, propylene glycol, trimethylene glycol, 1,4-butane diol, neopentyl glycol, cyclohexane diol and the like. Polyesters may include a homopolymer or copolymer of alkyl-aromatic esters including but not limited to polyethylene terephthalate (PET), amorphous polyethylene terephthalate (APET), crystalline polyethylene terephthalate (CPET), glycol-modified polyethylene terephthalate (PETG) and polybutylene terephthalate; a copolymer of terephthalate and isophthalate including but not limited to polyethylene terephthalate/isophthalate copolymer. Aliphatic esters include but not limited to polylactic acid (PLA); polyhydroxyalkonates including but not limited to polyhydroxypropionate, poly(3-hydroxybutyrate) (PH3B), poly(3-hydroxyvalerate) (PH3V), poly(4-hydroxybutyrate) (PH4B), poly(4-hydroxyvalerate) (PH4V), poly(5-hydroxyvalerate) (PH5V), poly(6-hydroxydodecanoate) (PH6D); and blends of any of these materials. A non-limiting example of PETG is Eastar™ Copolyester 6763, which is also available from Eastman Chemical Company (Kingsport, Tenn.).

- [24] As used herein, the term "polylactic acid" is used synonymously throughout this disclosure to describe homopolymers or copolymers having an ester linkage between monomer units and can be represented by the general formula: $[\text{---OCH(R)C(O)}]_n$ where $R=\text{CH}_3$. Polylactic acid may be fabricated by polymerizing lactic acid, which is mostly produced from by carbohydrate fermentation of corn. Polylactic acid may be also produced by polymerization of lactide which obtained by condensation of two lactic acid molecules. Polylactic acid has a glass transition temperature of ranges from 50-80° C. while the melting temperature ranges from 130-180° C. Polylactic acid is known by those skilled in the art and fully disclosed in U.S. Pat. Nos. 5,698,322; 5,142,023; 5,760,144; 5,593,778; 5,807,973; and 5,010,145, the entire disclosure of each of which is hereby incorporated by reference. Examples of commercially available polylactic acid are sold under the trademark NatureWorks™ PLA Polymer in grades 4031-D, 4032-D, and 4041-D from Cargill Dow LLC, Minneapolis, Minn., U.S.A.
- [25] As used throughout this application, the term "polystyrene" or "PS" refers to a homopolymer or copolymer having at least one styrene repeating linkage (such as benzene (i.e., C_6H_5) having an ethylene substituent) within the repeating backbone of the polymer. The styrene linkage can be represented by the general formula: $[\text{CH}_2\text{---CH}_2(\text{C}_6\text{H}_5)]_n$. Polystyrene may be formed by any method known to those skilled in the art. Examples of styrenic polymers include but are not limited to high impact polystyrene (HIPS), general purpose polystyrene (GPPS) and styrene block copolymer (SBC). HIPS is sometimes called rubber-modified polystyrene and is normally produced by copolymerization of styrene and a synthetic rubber. (See Wagner, et al., "Polystyrene," The Wiley Encyclopedia of Packaging Technology, Second Edition, 1997, pp. 768-771 (John Wiley & Sons, Inc., New York, New York), which is incorporated in its entirety in this application by this reference.) Examples of HIPS include but are not limited to Impact Polystyrene 825E and Impact Polystyrene 945E, both of which are available from Total Petrochemicals USA, Inc; EB6025 Rubber Modified High Impact

Polystyrene, which is available from Chevron Phillips Company (The Woodlands, Texas); and 6210 High Impact Polystyrene, which is available from Ineos Nova LLC (Channahon, Illinois). GPPS is often called crystal polystyrene, as a reference to the clarity of the resin. Examples of GPPS include but are not limited to Crystal Polystyrene 524B and Crystal Polystyrene 525B, both of which are available from Total Petrochemicals USA, Inc. Styrene block copolymers (SBC) include styrene butadiene copolymers (SB). The styrene-butadiene copolymers that are suitable for packaging applications are those resinous block copolymers that typically contain a greater proportion of styrene than butadiene and that are predominantly polymodal with respect to molecular weight distribution. (See Hartsock, "Styrene-Butadiene Copolymers," The Wiley Encyclopedia of Packaging Technology, Second Edition, 1997, pp. 863-864 (John Wiley & Sons, Inc., New York, New York), which is incorporated in its entirety in this application by this reference.) A non-limiting example of SB is DK13 K-Resin[®] Styrene-Butadiene Copolymer, which is available from Chevron Phillips Chemical Company (The Woodlands, Texas).

- [26] In one preferred embodiment, first and second exterior layers **101** and **105** each comprise at least 50% or at least 60% or at least 70% or at least 80% or at least 90% or at least 95% cyclic olefin copolymer (COC) relative to the total weight of the layer, and first and second interior layers **102** and **104** each comprise high density polyethylene (HDPE).
- [27] As used herein, the phrase "high density polyethylene" or "HDPE" refers to homopolymers of ethylene that have densities of about 0.960 g/cm³ to about 0.970 g/cm³ as well as copolymers of ethylene and an alpha-olefin (such as 1-butene or 1-hexene) that have densities of about 0.940 g/cm³ to about 0.958 g/cm³. In contrast, a low density polyethylene (LDPE) generally has a density of about 0.915 g/cm³ to about 0.930 g/cm³. HDPE is inclusive of polymers made with Ziegler or Phillips type catalysts and polymers made with single-site

metallocene catalysts. A non-limiting example of high density polyethylene includes Alathon® M6020 from Equistar Chemicals LP (Houston, Tex.). Other specific non-limiting examples of HDPE include Alathon® M6020 available from Equistar Chemicals LP (Houston, Tex.); Alathon® L5885 available from Equistar Chemicals LP (Houston, Tex.); ExxonMobil™ HDPE HD 7925.30 available from ExxonMobil Chemical Company (Houston, Tex.); and ExxonMobil™ HDPE HD 7845.30 available from ExxonMobil Chemical Company (Houston, Tex.).

[28] In another preferred embodiment, first exterior layer **101** comprises at least 50%, 60%, 70%, 80%, 90%, 95% relative to the total weight of the layer of cyclic olefin copolymer (COC), second exterior layer **105** comprises at least 50%, 60%, 70%, 80%, 90%, 95% of relative to the total weight of the layer of a different material selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate PETG) or polylactic acid (PLA), and first and second interior layers **102** and **104** each comprise high density polyethylene (HDPE) and has a thickness of at least 20% or at least 25% or at least 30% or at least 35% of the total thickness of the multilayer thermoplastic film **100**.

[29] In still another preferred embodiment, first exterior layer **101** comprises at least 50%, 60%, 70%, 80%, 90%, 95% relative to the total weight of the layer of cyclic olefin copolymer (COC), second exterior layer **105** comprises at least 50%, 60%, 70%, 80%, 90%, 95% of relative to the total weight of the layer of a different material selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate PETG) and polylactic acid (PLA), and first

and second interior layers **102** and **104** each comprise high density polyethylene (HDPE) and has a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil).

[30] In another preferred embodiment, first and second interior layers **102** and **104** each comprise a blend of a high density polyethylene and a high density polyethylene nucleation additive (HDPE-Blend). As used herein, the phrase "nucleation additive" means a material that increases high density polyethylene crystallinity as a result of its incorporation into HDPE. Such nucleation additives typically provide better control over crystallization rates. Examples of nucleation additives include minerals such as chalk, talc, clay, kaolin, silicates and the like, and organic agents such as salts of aliphatic or aromatic carboxylic acids, aromatic salts, metallic salts of aromatic phosphorous compounds, quinaridones, and aromatic amides. Further examples include zinc glycerolate, calcium glycerolate, calcium hexahydrophthalate, zinc hexahydrophthalate, salts and the like, and mixtures thereof. In one embodiment, the nucleation additive comprises calcium hexahydrophthalate. In one embodiment, the nucleation additive is present in each interior layer of HDPE from about 0.2% to about 3.5% by weight of the layer.

[31] In still another preferred embodiment, first exterior layer **101** comprises at least 50%, 60%, 70%, 80%, 90%, 95% relative to the total weight of the layer of cyclic olefin copolymer (COC), second exterior layer **105** comprises at least 50%, 60%, 70%, 80%, 90%, 95% of relative to the total weight of the layer of a different material selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) or polylactic acid (PLA). In this embodiment, first and second interior layers **102** and **104** each comprise a blend of a high density polyethylene, a high density polyethylene nucleation additive

and/or a hydrocarbon resin (HDPE-Blend). The hydrocarbon resin may be present in first and second interior layers **102** and **104** from about 3% to about 16% by weight of the layer. As used herein, the phrase "hydrocarbon resin" refers to a product produced by polymerization from coal tar, petroleum, and turpentine feed stocks, as defined by ISO Standard 472, "Plastics – Vocabulary" incorporated by reference herein to the extent that it teaches hydrocarbon resins. A hydrocarbon resin may comprise any of those hydrocarbon resins disclosed in U.S. Pat. No. 6,432,496, issued Aug. 13, 2002, or in U.S. Patent Application 2008/0286547, published Nov. 20, 2008, both of which are incorporated in their entireties in this application by this reference. More specifically, as a non-limiting example, the hydrocarbon resin may include petroleum resins, terpene resins, styrene resins, cyclopentadiene resins, saturated alicyclic resins or mixtures of such resins. Additionally, as a non-limiting example, the hydrocarbon resin may comprise hydrocarbon resin derived from the polymerization of olefin feeds rich in dicyclopentadiene (DCPD), from the polymerization of olefin feeds produced in the petroleum cracking process (such as crude C₉ feed streams), from the polymerization of pure monomers (such as styrene, α -methylstyrene, 4-methylstyrene, vinyltoluene or any combination of these or similar pure monomer feedstocks), from the polymerization of terpene olefins (such as α -pinene, β -pinene or d-limonene) or from a combination of such. The hydrocarbon resin may be fully or partially hydrogenated. Specific examples of hydrocarbon resins include but are not limited to Plastolyn[®] R1140 Hydrocarbon Resin available from Eastman Chemical Company (Kingsport, Tenn.), Regalite[®] T1140 available from Eastman Chemical Company (Kingsport, Tenn.), Arkon[®] P-140 available from Arakawa Chemical Industries, Limited (Osaka, Japan) and Piccolyte[®] S135 Polyterpene Resins available from Hercules Incorporated (Wilmington, Del.).

- [32] In yet another preferred embodiment, first exterior layer **101** comprises at least 50%, 60%, 70%, 80%, 90%, 95% relative to the total weight of the layer of cyclic olefin copolymer (COC), second exterior layer **105** comprises at least 50%, 60%,

70%, 80%, 90%, 95% of relative to the total weight of the layer of a different material selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA), and first and second interior layers **102** and **104** each comprise high density polyethylene having a bi-modal molecular weight having a distribution of a low molecular weight region and a high molecular weight region (HDPE-Bimodal).

- [33]** In one preferred embodiment, the central core layer **103** comprises an ethylene vinyl acetate copolymer (EVA) and more preferably, an ethylene vinyl acetate copolymer (EVA) having a 12% by weight vinyl acetate content. Non-limiting examples of EVA include Escorene™ Ultra LD 705.MJ available from ExxonMobil Chemical Company (Houston, Tex.), Escorene™ Ultra LD 768.MJ available from ExxonMobil Chemical Company (Houston, Tex.) and Ateva® 2861AU available from Celanese Corporation (Edmonton, Alberta, Canada).
- [34]** These five-layer embodiments described above may include, but are not limited to the following layer sequences and general layer compositions: COC / HDPE / EVA / HDPE / COC; COC / HDPE-Blend / EVA / HDPE-Blend / COC; COC / HDPE-Bimodal / EVA / HDPE-Bimodal / COC; COC / HDPE / EVA / HDPE / PP; COC / HDPE-Blend / EVA / HDPE-Blend / PP; COC / HDPE-Bimodal / EVA / HDPE-Bimodal / PP; COC / HDPE / EVA / HDPE / PETG; COC / HDPE-Blend / EVA / HDPE-Blend / PETG; COC / HDPE-Bimodal / EVA / HDPE-Bimodal / PETG; COC / HDPE / EVA / HDPE / APET; COC / HDPE-Blend / EVA / HDPE-Blend / APET; COC / HDPE-Bimodal / EVA / HDPE-Bimodal / APET; COC / HDPE / EVA / HDPE / PET; COC / HDPE-Blend / EVA / HDPE-Blend / PET; COC / HDPE-Bimodal / EVA / HDPE-Bimodal / PET; COC / HDPE / EVA / HDPE / OPET; COC / HDPE-Blend / EVA / HDPE-Blend / OPET; COC / HDPE-Bimodal

/ EVA / HDPE-Bimodal / OPET; COC / HDPE / EVA / HDPE / PLA; COC / HDPE-Blend / EVA / HDPE-Blend / PLA; COC / HDPE-Bimodal / EVA / HDPE-Bimodal / PLA; COC / HDPE / EVA / HDPE / HIPS; COC / HDPE-Blend / EVA / HDPE-Blend / HIPS; COC / HDPE-Bimodal / EVA / HDPE-Bimodal / HIPS; COC / HDPE / EVA / HDPE / GPPS; COC / HDPE-Blend / EVA / HDPE-Blend / GPPS; COC / HDPE-Bimodal / EVA / HDPE-Bimodal / GPPS; COC / HDPE / EVA / HDPE / SBC; COC / HDPE-Blend / EVA / HDPE-Blend / SBC; and COC / HDPE-Bimodal / EVA / HDPE-Bimodal / SBC.

- [35] It should be understood that the above examples may further include a tie layer comprising a tie layer material between a high density polyethylene layer and the second exterior layer comprising polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) or polylactic acid (PLA). The phrase "tie layer material" may include, but not limited to, unmodified polyolefins such as polyethylenes and ethylene vinyl acetate copolymers, unmodified ester copolymers such as ethylene acrylate copolymers and ethylene methacrylate copolymers and unmodified ethylene acid copolymers such as ethylene acrylic acid copolymers and blends thereof. Tie layer materials may also include modified polyolefins including, but not limited to anhydride modified polyethylenes, anhydride modified ethylene vinyl acetate copolymers, modified ester copolymers such as anhydride modified ethylene acrylate copolymers, modified ethylene acid copolymers such as anhydride modified ethylene acrylic acid copolymers and blends thereof. Tie layer materials may further include a blend of an unmodified polyolefin or unmodified ester copolymer or unmodified ethylene acid copolymer and a modified polyolefin or modified ester copolymer or modified ethylene acid copolymer. In a preferred embodiment, a tie layer may be present between a layer comprising high density polyethylene and the second exterior layer

comprising polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) or polylactic acid (PLA).

- [36]** In another preferred embodiment as depicted in FIG. 4, thermoformed blister component **11** comprises a multilayer palindromic thermoplastic film **200** which comprises a thirteen-layer symmetrical structure of a first exterior layer **201**, a first interior layer **202**, a second interior layer **203**, a third interior layer **204**, a fourth interior layer **205**, a fifth interior layer **206**, a sixth interior layer **207**, a central core layer **208**, a seventh interior layer **209**, an eighth interior layer **210**, a ninth interior layer **211**, a tenth interior layer **212**, an eleventh interior layer **213**, and a second exterior layer **214**. In this embodiment, film **200** comprises two exterior layers each comprising cyclic olefin copolymer (COC), two discrete interior layers each comprising ethylene vinyl alcohol copolymer (EVOH), and four discrete interior layers each comprising high density polyethylene (HDPE). This thirteen-layer embodiment has the following layer sequence and general layer composition: COC / HDPE / tie / EVOH / tie / HDPE / EVA / HDPE / tie / EVOH / tie / HDPE / COC.
- [37]** The total thickness of multilayer thermoplastic films of the thermoformed blister component **11** of the present invention is generally from about 12.7 μm (0.5 mil) to about 508 μm (20 mil), typically from about 50.8 μm (2 mil) to about 254 μm (10 mil), most typically from about 76.2 μm (3 mil) to about 203.2 μm (8 mil).
- [38]** In accordance with the practice of the present invention, one embodiment of a lidding component **12** of the present invention is depicted in FIG. 5. In this embodiment, lidding component **12** comprises a laminate **300** having a first exterior layer **301**, an interior layer **302** and a second exterior layer **303**. Preferably, second exterior layer **303** comprises a thermoplastic resin heat-

sealable to cyclic olefin copolymer, first exterior layer **301** comprises a metal foil such as aluminum, and interior layer **302** comprises a tie or adhesive material bonding exterior layers **301** and **303** together.

- [39]** The above description and the following examples illustrate certain embodiments of the present invention and are not to be interpreted as limiting. Selection of particular embodiments, combinations thereof, modifications, and adaptations of the various embodiments, conditions and parameters normally encountered in the art will be apparent to those skilled in the art and are deemed to be within the spirit and scope of the present invention.

WORKING EXAMPLES

THERMOFORMED BLISTER COMPONENT-PALINDROMIC FILM EXAMPLES

- [40]** The following example illustrates a certain particular embodiment of palindromic multilayer thermoplastic film structure suitable for use in the present invention and is not to be interpreted as limiting. In the following example, polymeric resin composition percentages are based on the total weight of each film layer. In the following example, the film structure was produced using a single-bubble coextrusion apparatus and method which are well known to those skilled in the art. The single-bubble blown coextrusion film apparatus included a multi-manifold circular die head for bubble blown film through which a non-palindromic film composition was forced through and formed into a cylindrical bubble. The film bubble was immediately quenched e.g., via cooled water bath, solid surface and/or air, and then ultimately collapsed onto itself and formed into a palindromic film.

Example 1-1

- [41] Example 1-1 is one embodiment of a palindromic thermoplastic film **100** as illustrated in FIG. 3 having a structure and layer compositions as described below:
- [42] Layer **101** was 100% by weight of a cyclic olefin copolymer (COC) having density of 1010 kg/m³, a heat deflection temperature under load (0.45 MPa) of about 75° C and a glass transition temperature of 78° C. Exemplary of such a commercially available COC is TOPAS® 8007S-04 supplied by Celanese Corporation (Irving, TX, USA). This layer had a thickness of approximately 15.24 µm (0.60 mil).
- [43] Layer **102** was a blend of 99% by weight of a high density polyethylene (HDPE) having density of 0.966 g/cm³ and 1% by weight of a high density polyethylene masterbatch comprising 4% by weight of a high density polyethylene nucleation additive. Exemplary of a commercially available HDPE is SURPASS® HP167-AB supplied by Nova Chemical Company (Joffre, Alberta, Canada). SURPASS® HP167-AB is believed to be an example of a bimodal high density polyethylene having a distribution of a low molecular weight region and a high molecular weight region. Exemplary of a commercially available high density polyethylene masterbatch having a 4% high density polyethylene nucleation additive is POLYBATCH® CLR 124 supplied by A. Schulman (Fairlawn, OH, USA). This layer had a thickness of approximately 50.8 µm (2 mil).
- [44] Layer **103** was a blend of 50% by weight of an ethylene vinyl acetate copolymer (EVA) having a 12% by weight vinyl acetate comonomer content, a density of 0.93 g/cm³ and a melt flow rate (190° C/2.16 kg) of 0.35 g/10 min, and 50% by weight of an ethylene vinyl acetate copolymer (EVA) having a 26.2% by weight vinyl acetate comonomer content, a density of 0.951 g/cm³ and a melt flow rate (190° C/2.16 kg) of 2.3 g/10 min. Exemplary of such EVAs is ELVAX® 3135x supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA) and ESCORENE™ Ultra LD 768.MJ supplied by Exxon Mobil Chemical Company

(Baytown, TX, USA), respectively. This layer had a thickness of approximately 8.13 μm (0.32 mil).

- [45] Layer **104** was a blend of 99% by weight of a high density polyethylene (HDPE) having density of 0.966 g/cm^3 and 1% by weight of a high density polyethylene masterbatch comprising 4% by weight of a high density polyethylene nucleation additive. Exemplary of a commercially available HDPE is SURPASS® HP167-AB supplied by Nova Chemical Company (Joffre, Alberta, Canada). Exemplary of a commercially available high density polyethylene masterbatch having a 4% high density polyethylene nucleation additive is POLYBATCH® CLR 124 supplied by A. Schulman (Fairlawn, OH, USA). This layer had a thickness of approximately 50.8 μm (2 mil).
- [46] Layer **105** was 100% by weight of a cyclic olefin copolymer (COC) having density of 1010 kg/m^3 , a heat deflection temperature under load (0.45 MPa) of about 75° C and a glass transition temperature of 78° C. Exemplary of such a commercially available COC is TOPAS® 8007S-04 supplied by Celanese Corporation (Irving, TX, USA). This layer had a thickness of approximately 15.24 μm (0.60 mil).
- [47] The film as described above had a total thickness of approximately 152.4 μm (6 mil) and an average water vapor transmission rate of 0.131 $\text{g}/\text{m}^2/\text{day}$ at 100° F (37.8° C) and 90% relative humidity having a thickness of about 10 mil (254 micron) before being thermoformed.

LIDDING COMPONENT

- [48] The following examples illustrate certain particular embodiments of a film for use as a lidding component structure suitable and are not to be interpreted as limiting. In the following examples, polymeric resin composition percentages are based on the total weight of each film layer. In the following examples, the film structures were produced using an extrusion coating apparatus and methods

which are well known to those skilled in the art. The extrusion coating apparatus includes a multi-manifold flat die head through which a two-layer film composition was forced and extrusion coated onto the shiny surface of a metallic foil. The metallic foil was pre-treated prior to extrusion coating by printing a primer coat onto the matte surface of the foil.

Example 2-1

- [49] Example 2-1 is one embodiment of a laminate **300** of a lidding component film **12** as illustrated in FIG. 5 having a structure and layer compositions as described below:
- [50] Layer **301** was an aluminum foil. This layer had a thickness of approximately 25.4 μm (1 mil).
- [51] Layer **302** was 100% by weight of an ethylene acrylic acid copolymer (EAA) having a density of 0.94 g/cm³, a melting point of 78° C, and a melt flow rate (190° C/2.16 kg) of 10 g/10 min. Exemplary of such a commercially available EAA is NUCREL[®] 3990 supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA).
- [52] Layer **303** (heat-seal layer) was a blend of 96% by weight of a modified ethylene acrylic acid copolymer (mod-EAA) having a density of 1.02 g/cm³, a melting point of 97° C, and a melt flow rate (190° C/2.16 kg) of 13 g/10 min, and 4% by weight of a masterbatch comprising an ethylene methacrylate copolymer (mod-EMA) having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of between 3 and 8 g/10 min, and a 1% by weight of a chill roll release additive. Exemplary of such a commercially available mod-EAA having a density of 1.02 g/cm³, a melting point of 97° C, and a melt flow rate (190° C/2.16 kg) of 13 g/10 min is APPEEL[®] 20D828 supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA). Exemplary of such a commercially available mod-EMA

is Ampacet 100578 Chill Roll Cop MB supplied by Ampacet Corporation, Inc. (Tarrytown, NY, USA).

Example 2-2

- [53] Example 2-2 is another embodiment of a laminate **300** of a lidding component film **12** as illustrated in FIG. 5 having a structure and layer compositions as described below:
- [54] Layer **301** and **302** were equivalent to those described above in Example 2-1.
- [55] Layer **303** (heat-seal layer) was a blend of 86% by weight of a modified ethylene acrylic acid copolymer (mod-EAA) having a density of 1.02 g/cm³, a melting point of 97° C, and a melt flow rate (190° C/2.16 kg) of 13 g/10 min; 10% by weight of a modified ethylene acrylate copolymer (mod-EMA) having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of 2.0 g/10 min, and a melting point of 91° C; and 4% by weight of a masterbatch comprising an ethylene methacrylate copolymer (mod-EMA) having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of between 3 and 8 g/10 min, and a 1% by weight of a chill roll release additive. Exemplary of such a commercially available mod-EAA having a density of 1.02 g/cm³, a melting point of 97° C, and a melt flow rate (190° C/2.16 kg) of 13 g/10 min is APPEEL[®] 20D828 supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA). Exemplary of such a commercially available mod-EMA having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of 2.0 g/10 min, and a melting point of 91° C is BYNEL[®] 22E780 supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA). Exemplary of such a commercially available masterbatch mod-EMA having a chill roll release additive is Ampacet 100578 Chill Roll Cop MB supplied by Ampacet Corporation, Inc. (Tarrytown, NY, USA).

Example 2-3

- [56] Example 2-3 is another embodiment of a laminate **300** of a lidding component film **12** as illustrated in FIG. 5 having a structure and layer compositions as described below:
- [57] Layer **301** and **302** were equivalent to those described above in Example 2-1.
- [58] Layer **303** (heat-seal layer) was a blend of 85% by weight of a modified ethylene acrylic acid copolymer (mod-EAA) having a density of 1.02 g/cm³, a melting point of 97° C, and a melt flow rate (190° C/2.16 kg) of 13 g/10 min; 10% by weight of a modified ethylene acrylate copolymer (mod-EMA) having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of 2.0 g/10 min, and a melting point of 91° C; 4% of a masterbatch comprising an ethylene methacrylate copolymer (mod-EMA) having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of between 3 and 8 g/10 min, and a 1% by weight of a chill roll release additive; and 1% by weight of a high density polyethylene masterbatch comprising 1% by weight of a high density polyethylene nucleation additive. Exemplary of such a commercially available mod-EAA having a density of 1.02 g/cm³, a melting point of 97° C, and a melt flow rate (190° C/2.16 kg) of 13 g/10 min is APPEEL[®] 20D828 supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA). Exemplary of such a commercially available mod-EMA having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of 2.0 g/10 min, and a melting point of 91° C is BYNEL[®] 22E780 supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA). Exemplary of such a commercially available masterbatch mod-EMA having a chill roll release additive is Ampacet 100578 Chill Roll Cop MB supplied by Ampacet Corporation, Inc. (Tarrytown, NY, USA). Exemplary of such a commercially available masterbatch of a high density polyethylene masterbatch comprising 1% by weight of a high density polyethylene nucleation additive is POLYBATCH[®] CLR 122 supplied by A. Schulman (Fairlawn, OH, USA).

[59] The blister packages of the present invention can be manufactured using methods known in the art. Generally, the blister cavities are thermoformed from the blister components of the present invention in-line just prior to filling the cavities with a product to be packaged. The lidding component is then unwound from a roll and brought into contact with the formed and filled blister component such that the heat-seal layer of the lidding component contacts the blister component. The lidding and blister components are heat sealed, typically using a heated platen. Some areas of the package may not be sealed to provide a starting point for peeling off the lidding component prior to removing the product. If the lidding component is not pre-printed, printing is generally done just before heat sealing. After heat-sealing, the individual blisters may be perforated using methods known in the art so that they can be removed at point of use.

What is claimed:

1. A blister component for a blister package, comprising:

a multilayer thermoplastic film comprising:
 - i. a first exterior layer comprising cyclic olefin copolymer (COC);
 - ii. two interiors layers each comprising a high density polyethylene (HDPE);
 - iii. a central core layer; and
 - iv. a second exterior layer comprising a material selected from the group consisting of cyclic olefin copolymer (COC), polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA).
2. A component according to claim 1, wherein the multilayer thermoplastic film is palindromic.
3. A component according to claim 1, wherein the two interiors layers each further comprise a high density polyethylene nucleation additive.
4. A component according to claim 3, wherein the two interiors layers each further comprise a hydrocarbon resin.

5. A component according to claim 1, wherein the two interiors layers each have a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil).
6. A component according to claim 1, wherein the two interiors layers each comprise a bimodal high density polyethylene having a distribution of a low molecular weight region and a high molecular weight region.
7. A component according to claim 1, wherein the central core layer comprises an ethylene vinyl acetate copolymer.
8. A component according to claim 1, wherein the central core layer comprises an ethylene vinyl acetate copolymer having a 12% by weight vinyl acetate content.
9. A blister component for a blister package, comprising:
a multilayer thermoplastic film comprising:
 - i. a first exterior layer comprising cyclic olefin copolymer (COC);
 - ii. two interiors layers each comprising a high density polyethylene;
 - iii. a central core layer; and
 - iv. a second exterior layer comprising a material selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene

terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA).

10. A component according to claim 9, wherein the two interiors layers each further comprise a high density polyethylene nucleation additive.
11. A component according to claim 10, wherein the two interiors layers each further comprise a hydrocarbon resin.
12. A component according to claim 9, wherein the central core layer comprises an ethylene vinyl acetate copolymer.
13. A component according to claim 11, wherein the central core layer comprises an ethylene vinyl acetate copolymer having a 12% by weight vinyl acetate content.
14. A blister component for a blister package, comprising:
a multilayer thermoplastic film comprising:
 - i. a first exterior layer comprising cyclic olefin copolymer (COC);
 - ii. two interiors layers each comprising a high density polyethylene and has a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil);
 - iii. a central core layer;

- iv. a second exterior layer comprising a material selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA).
- 15. A component according to claim 13, wherein each of the two interiors layers has a thickness of at least 20% of the total thickness of the multilayer thermoplastic film.
 - 16. A component according to claim 13, wherein each of the two interiors layers has a thickness of at least 25% of the total thickness of the multilayer thermoplastic film.
 - 17. A component according to claim 13, wherein each of the two interiors layers has a thickness of at least 30% of the total thickness of the multilayer thermoplastic film.
 - 18. A component according to claim 13, wherein each of the two interiors layers has a thickness of at least 35% of the total thickness of the multilayer thermoplastic film.

19. A component according to claim 13, wherein the central core layer comprises an ethylene vinyl acetate copolymer.
20. A component according to claim 18, wherein the central core layer comprises an ethylene vinyl acetate copolymer having a 12% by weight vinyl acetate content.
21. A blister component for a blister package, comprising:
a multilayer thermoplastic film comprising:
 - i. a first exterior layer comprising cyclic olefin copolymer (COC);
 - ii. two interiors layers each comprising a bimodal high density polyethylene having a distribution of a low molecular weight region and a high molecular weight region;
 - iii. a central core layer; and
 - iv. a second exterior layer comprising a material selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA).
22. A component according to claims 1 to 21, wherein each of the two interiors layers comprises a high density polyethylene having a density of at least about 0.96 g/cm³.

23. A component according to claims 1 to 21, wherein the cyclic olefin copolymer is formed from norbornene and ethylene monomers.
24. A component according to claims 1 to 21, wherein the cyclic olefin copolymer has a heat deflection temperature under load (0.45 MPa) of about 75° C.
25. A component according to claims 1 to 21, wherein the central core layer is in direct contact with the two interiors layers.
26. A component according to claims 1 to 21, wherein each of the two interiors layers is in direct contact with an exterior layer.
27. A component according to claims 1 to 21, wherein the multilayer thermoplastic film has an average water vapor transmission rate of 0.131 g/m²/day at 100° F (37.8° C) and 90% relative humidity having a thickness of about 10 mil (254 micron) before being thermoformed.
28. A component according to claims 1 to 21, wherein the multilayer thermoplastic film has an average water vapor transmission rate of 0.110 g/m²/day at 100° F (37.8° C) and 90% relative humidity having a thickness of about 10 mil (254 micron) before being thermoformed.

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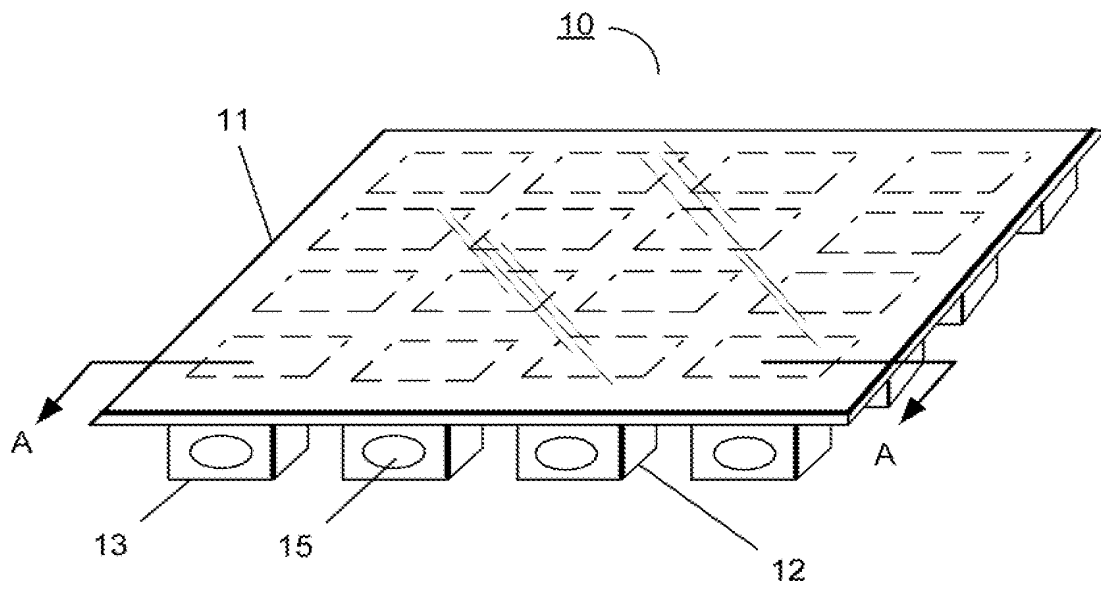
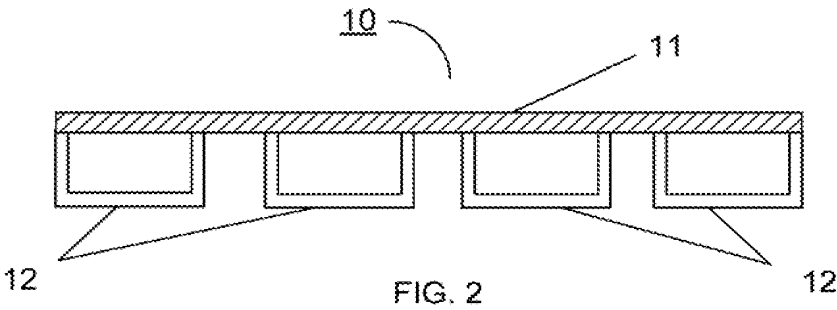


FIG. 1



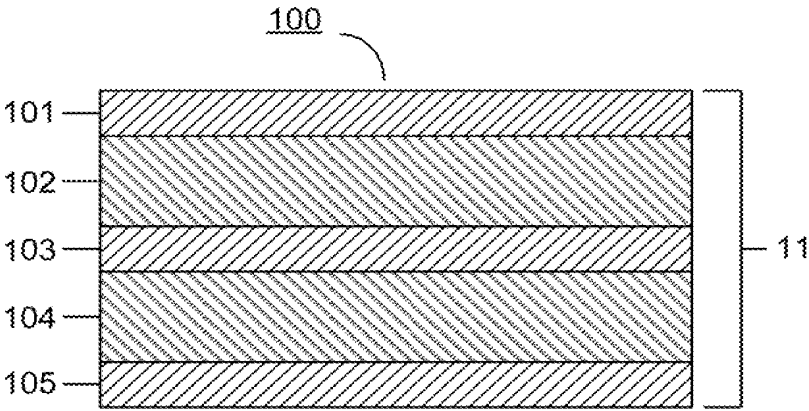


FIG. 3

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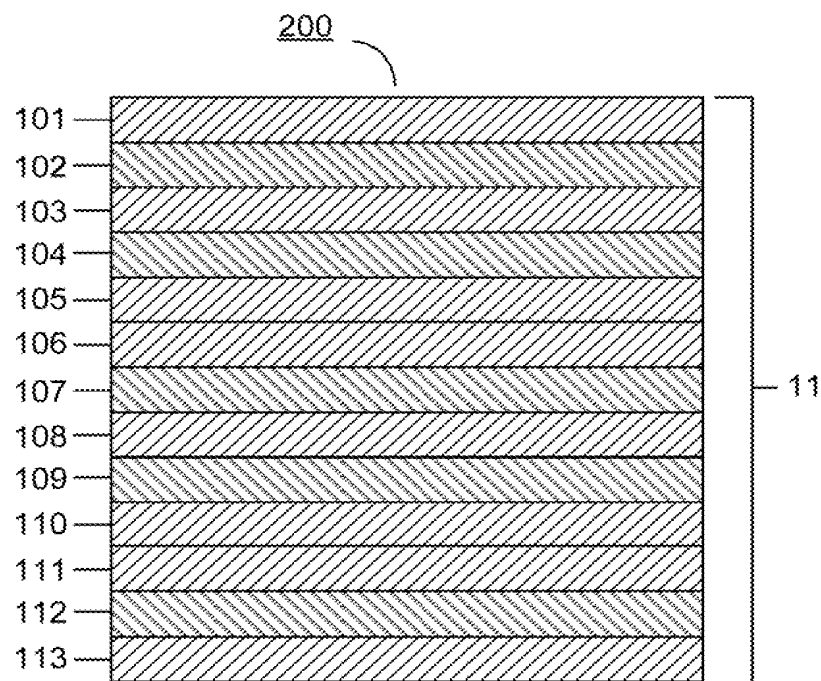


FIG. 4

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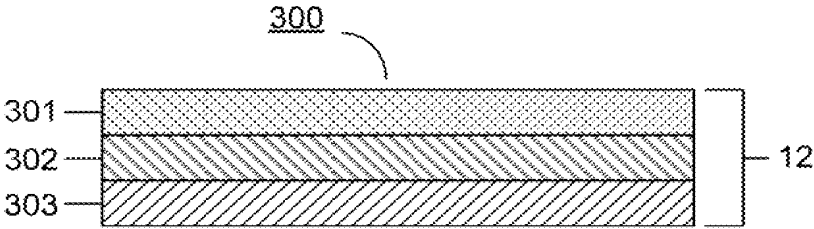


FIG. 5

INTERNATIONAL SEARCH REPORT

014/041212 03.11.2014

International application No.

PCT/US2014/041212

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B65D 75/36 (2014.01)

CPC - B65D 75/36 (2014.09)

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)

IPC(8) - B32B 27/32; B65D 75/327, 75/36 (2014.01)

CPC - B32B 27/32; B65D 75/327, 75/36 (2014.09)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 428/35.7, 35.8, 35.9, 461, 500, 515, 516, 523

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Orbit, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,783,273 A (YAMAMOTO et al) 21 July 1998 (21.07.1998) entire document	1-20
Y	US 2007/0212539 A1 (YAMADA et al) 13 September 2007 (13.09.2007) entire document	1-8, 11
Y	WO 2007/104513 A1 (NILSEN et al) 20 September 2007 (20.09.2007) entire document	6, 21
Y	US 2005/0186373 A1 (RHEE et al) 25 August 2005 (25.08.2005) entire document	7, 8, 12, 13, 19, 20
Y	WO 2013/116445 A1 (HAUSMANN et al) 08 August 2013 (08.08.2013) entire document	9-21

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

* 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

15 September 2014

Date of mailing of the international search report

03 NOV 2014

Name and mailing address of the ISA/US

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Authorized officer:

Blaine R. Copenheaver

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Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 22-28
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.



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- (71) **Applicant:** PERFECSEAL, INC. [US/US]; 3500 North Main Street, Oshkosh, WI 54901 (US).
- (72) **Inventors:** PUGUH, Arthya; 1700 Dublin Trail Apt. #122, Neenah, WI 54956 (US). OSBORN, Christopher L.; W168 N10345 Wildrose Lane, Germantown, WI 53022 (US).
- (74) **Agent:** HALL, Tom J.; Bemis Company, Inc., Office of Intellectual Property Counsel, P.O. Box 669, Neenah, WI 54957 (US).

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- (84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

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(54) **Title:** BLISTER PACKAGING COMPONENTS

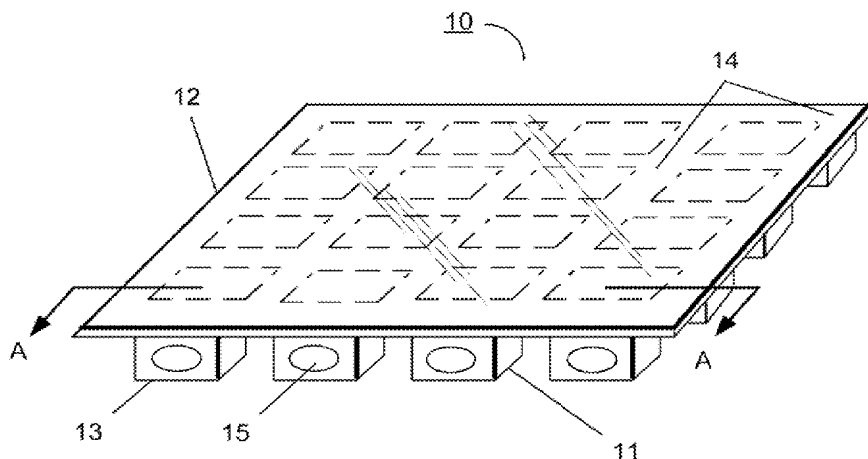


FIG. 1

(57) **Abstract:** The present invention relates to blister components for blister packages formed from multilayer thermoplastic films. In one embodiment of the present invention, the blister component includes layer sequence of A/B/A where layer A is an exterior layer comprising a cyclic olefin copolymer (COC), and layer B is an interior layer comprising a high density polyethylene (HDPE), or a blend of a high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HD-PE-Blend).

BLISTER PACKAGING COMPONENTS

BACKGROUND OF THE INVENTION

- [01] The present invention relates generally to blister packaging and more particularly, to blister components for packaging packages formed from multilayer thermoplastic films where a low moisture vapor transmission rate is desired.
- [02] Blister packaging is employed widely for commercial packaging of food products, personal care products, and human health products such as pharmaceuticals, and medical devices or precision instruments. The use of this type of packaging has become widespread mainly due to the ability in incorporate suitable moisture, dust, UV and/or gas barriers into the packages when such properties are desired for maintaining the product contained therein. For example, blister packaging is extensively used in the pharmaceutical industry for packaging of medicaments or the like in capsule, lozenge, or pill form because the integrity of the medicament can be maintained through the proper selection of materials used to form the packages.
- [03] For preparing blister packages or so-called push through packages, generally a thermoplastic film is first processed by vacuum forming or pneumatic forming so as to form blisters or cavities thereon, namely portions having a predetermined contour corresponding to each specific article to be received therein. After the so-blistered film has been solidified, each blister is charged with each piece of the article to be packaged and a second or lidding film is then covered over each blister and sealed to the first film. The second lidding film is often a laminate material which can be ruptured by a simple finger-rupture or peeled off from the first film to allow access to a packaged item. Conventional materials used for forming the blistered film have included transparent plastics such as polyvinylchloride (PVC), polyvinylidene chloride (PVdC) and polychlorotrifluoroethylene (PCTFE), commonly referred to as ACLAR®

(Honeywell/Allied Signal). Packaging for pharmaceuticals or other moisture-sensitive article requires not only low moisture permeability but also other properties such as chemical inertness, clarity, rigidity, or uniform thickness. The use of polyvinylchloride (PVC) and polyvinylidene chloride (PVdC) have been shown to have poor and/or insufficient moisture-proofing properties required by the pharmaceutical industry. While ACLAR® exhibits relatively low moisture vapor transmission, its use in blister packaging is inherently costly.

- [04] There is therefore a need in the art for improved blister packaging materials which provides sufficient moisture vapor barrier and chemical inertness properties and is aesthetically pleasing enough to present the products contained therein while being cost effective to be manufactured.

SUMMARY OF THE INVENTION

- [05] The present invention is directed to blister components for blister packages formed from a multilayer film. As used throughout this disclosure, the term "blister component" refers to multilayer thermoplastic film or a roll of multilayer thermoplastic film both of which may be thermoformed, partially thermoformed or not thermoformed at all. In one embodiment of the present invention, the sequence of layers in the multilayer thermoplastic film of the blister component is palindromic. As used throughout this application, the term "palindromic" refers to a multilayer film, the layers of which are substantially symmetrical. Non-limiting examples of palindromic films are film or sheet having the layer sequence of configurations: A/B/A or A/B/B/A or A/C/B/C/A or A/C/D/B/D/C/A or A/D/C/D/B/D/C/D/A, etc. An example of a layer sequence configuration of a non-palindromic film would be A/B/C or A/C/B/A. A palindromic thermoplastic film may be coextruded as a symmetrical cast or blown film using coextrusion methods generally well known in the art. An alternative method of producing palindromic films is by the use of blown coextrusion of non-symmetrical film or sheet structures followed by collapsing the blown bubble around a central core

layer. In one embodiment of the present invention, a non-symmetrical film having a layer sequence configuration of A/B is coextruded by blown film coextrusion techniques and collapsed upon itself.

- [06] In another embodiment of the present invention, the sequence of layers in the multilayer thermoplastic film of the blister component is non-palindromic.
- [07] In one generic embodiment, the thermoformed blister component of the present invention may be characterized as a palindromic film formed from a non-symmetrical film having a layer sequence configuration of A/B which is coextruded by blown film coextrusion techniques and collapsed upon itself to produce a layer sequence configuration of A/B/A. In this embodiment, the thermoformed blister component includes a film where layer A is an exterior layer comprising a cyclic olefin copolymer (COC) and layer B is a central core layer comprising high density polyethylene (HDPE), or a blend of a high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), a bimodal high density polyethylene having a molecular weight distribution of a low molecular weight region and a high molecular weight region (HDPE-Bimodal), or a high density polyethylene (HDPE) and has a thickness of between 50 μm to 254 μm (2 mil to 10 mil).
- [08] In an alternative generic embodiment of the present invention, the thermoformed blister component a palindromic film formed from a non-symmetrical film having a layer sequence configuration of A/C/B which is coextruded by blown film coextrusion techniques and collapsed upon itself to produce a layer sequence configuration of A/C/B/C/A. In this embodiment, layer A is an exterior layer comprising a cyclic olefin copolymer (COC), layer B is a central core layer comprising high density polyethylene (HDPE) or a blend of a high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), a bimodal high density polyethylene having a molecular weight distribution of a low molecular weight region and a high

molecular weight region (HDPE-Bimodal), or a high density polyethylene (HDPE) and has a thickness of between 50 μm to 254 μm (2 mil to 10 mil), and C is an interior layer comprising a tie or adhesive material bonding layers A and B together.

- [09]** In still another generic embodiment, the thermoformed blister component of the present invention may be characterized as a non-palindromic film having a layer sequence configuration of A/B/D which is coextruded by blown film coextrusion techniques and is not collapsed upon itself. In this embodiment, the thermoformed blister component includes a film where layer A is a first exterior layer comprising cyclic olefin copolymer (COC), layer B is a central core layer comprising a blend of a high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), a bimodal high density polyethylene having a molecular weight distribution of a low molecular weight region and a high molecular weight region (HDPE-Bimodal), or a high density polyethylene (HDPE) and has a thickness of between 50 μm to 254 μm (2 mil to 10 mil), and D is a second exterior layer comprising a different material than A and is selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA).
- [10]** It should be understood that in the above-described generic embodiments, the thermoformed blister component may include additional film layers.
- [11]** The blister packages of the present invention may also include a lidding component which is heat-sealable to the exterior layer A of the blister component. In one embodiment, the lidding component comprises a thermoplastic resin heat-sealable to cyclic olefin copolymer.

BRIEF DESCRIPTION OF THE DRAWINGS

- [12] Further features and advantages of the present invention will become apparent from the following detailed description, taken in combination with the appended drawings, in which:
- [13] FIG. 1 illustrates a schematic view of one embodiment of a blister package according to the present invention.
- [14] FIG. 2 illustrates an exploded view taken along line A-A of FIG. 1 depicting the blister and lidding components of the present invention.
- [15] FIG. 3 illustrates a cross-sectional view of one embodiment of a blister component according to the present invention.
- [16] FIG. 4 illustrates a cross-sectional view of another embodiment of a blister component according to the present invention.
- [17] FIG. 5 illustrates a cross-sectional view of one embodiment of a lidding component according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

- [18] In accordance with the practice of the present invention, a representative blister package **10** as described herein is shown in FIGS. 1 and 2. Package **10** of the present invention comprises a thermoformed blister component **11** and a lidding component **12**, the former provided with one or more thermoformed pockets **13** surrounded by sealed flange regions **14**. Pocket **13** defines an individual compartment for receiving a product **15**, such as a tablet.
- [19] In accordance with an important aspect of the present invention, the thermoformed blister component **11** comprises a multilayer film. It will be appreciated that film of thermoformed blister component **11** may include any

number of film layers and film layer compositions depending upon both functional and aesthetic requirements of the blister component. It is desirable that the multilayer thermoplastic film include one or more film layers which are barrier materials and substantially chemically inert when in contact with a product. The term "barrier" refers to a material that controls permeability of one or more elements through a film structure including moisture, chemicals, heat, odor and oxygen or other gases. As it relates to the present invention, a barrier material can be provided by a single film layer or multiple film layers acting individually or in concert with each other, respectively. The phrase "substantially chemically inert" refers to materials that generally are not reactive with the product with which it comes into contact with and does not leech chemical ingredients into the product with which it comes into contact. Preferably, thermoformed blister component **11** comprises a multilayer film which provides an average water vapor transmission rate of less than 0.500 g/m²/day or less than 0.250 g/m²/day or less than 150 g/m²/day or about 0.131 g/m²/day at 100° F (37.8° C) and 90% relative humidity having a thickness of about 10 mil (254 micron) before being thermoformed. The aforementioned features of the present invention may be achieved by a multilayer film **100** comprising at least 3 or 4 or 5 or 6 or 7 or 8 or 9 or 10 or 11 or 12 or 13 or more layers.

- [20] In one embodiment as depicted in FIG. 3, thermoformed blister component **11** comprises a multilayer palindromic film **100** comprising at least a three-layer structure of a first exterior layer **101**, a central core layer **102**, and a second exterior layer **103**. In one embodiment, first and second exterior layers **101** and **103** comprise the same materials. In another embodiment, first and second exterior layers **101** and **103** comprise different materials. In every embodiment, the central core layer **102** comprises high density polyethylene.
- [21] For example, in a preferred embodiment, thermoformed blister component **11** comprises a multilayer palindromic film **100** having a first and second exterior

layers **101** and **103** each comprising cyclic olefin copolymer (COC). As used herein, the phrase "cyclic olefin copolymer" refers to copolymers having at least one norbornene structural moiety within the repeating backbone of the polymer. Exemplary of commercially available cyclic olefin copolymers include, but are not limited to, the TOPAS[®] family of resins which is supplied by Celanese Corporation (Irving, TX, USA). Suitable COCs for use in the present invention may have a heat deflection temperature under load (0.45 MPa) of about 75° C or 130° C or 150° C, or 170° C. First and second exterior layers **101** and **103** may each comprises at least 50% or at least 60% or at least 70% or at least 80% or at least 90% or at least 95% cyclic olefin copolymer (COC) relative to the total weight of the layer. In this embodiment, the central core layer **102** comprises a high density polyethylene (HDPE).

[22] As used herein, the phrase "high density polyethylene" or "HDPE" refers to homopolymers of ethylene that have densities of about 0.960 g/cm³ to about 0.970 g/cm³ as well as copolymers of ethylene and an alpha-olefin (such as 1-butene or 1-hexene) that have densities of about 0.940 g/cm³ to about 0.958 g/cm³. In contrast, a low density polyethylene (LDPE) generally has a density of about 0.915 g/cm³ to about 0.930 g/cm³. HDPE is inclusive of polymers made with Ziegler or Phillips type catalysts and polymers made with single-site metallocene catalysts. A non-limiting example of high density polyethylene includes Alathon[®] M6020 from Equistar Chemicals LP (Houston, Tex.). Other specific non-limiting examples of HDPE include Alathon[®] M6020 available from Equistar Chemicals LP (Houston, Tex.); Alathon[®] L5885 available from Equistar Chemicals LP (Houston, Tex.); ExxonMobil[™] HDPE HD 7925.30 available from ExxonMobil Chemical Company (Houston, Tex.); and ExxonMobil[™] HDPE HD 7845.30 available from ExxonMobil Chemical Company (Houston, Tex.).

[23] In another preferred embodiment, thermoformed blister component **11** comprises a multilayer palindromic film **100** having first and second exterior layers **101** and

103 each comprising cyclic olefin copolymer (COC), and a central core layer **102** comprising a high density polyethylene and a high density polyethylene nucleation additive. As used herein, the phrase "nucleation additive" means a material that increases high density polyethylene crystallinity as a result of its incorporation into HDPE. Such nucleation additives typically provide better control over crystallization rates. Examples of nucleation additives include minerals such as chalk, talc, clay, kaolin, silicates and the like, and organic agents such as salts of aliphatic or aromatic carboxylic acids, aromatic salts, metallic salts of aromatic phosphorous compounds, quinaridones, and aromatic amides. Further examples include zinc glycerolate, calcium glycerolate, calcium hexahydrophthalate, zinc hexahydrophthalate, salts and the like, and mixtures thereof. In one embodiment, the nucleation additive comprises calcium hexahydrophthalate. In one embodiment, the nucleation additive is present in each interior layer of HDPE from about 0.2% to about 3.5% by weight of the layer.

- [24] In another preferred embodiment, thermoformed blister component **11** comprises a multilayer palindromic film **100** having first and second exterior layers **101** and **103** each comprising cyclic olefin copolymer (COC), and a central core layer **102** comprising a high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin.
- [25] As used herein, the phrase "hydrocarbon resin" refers to a product produced by polymerization from coal tar, petroleum, and turpentine feed stocks, as defined by ISO Standard 472, "Plastics – Vocabulary" incorporated by reference herein to the extent that it teaches hydrocarbon resins. The hydrocarbon resin may be present in central core layer **102** from about 3% to about 16% by weight of the layer. A hydrocarbon resin may comprise any of those hydrocarbon resins disclosed in U.S. Pat. No. 6,432,496, issued Aug. 13, 2002, or in US Patent Application 2008/0286547, published Nov. 20, 2008, both of which are

incorporated in their entireties in this application by this reference. More specifically, as a non-limiting example, the hydrocarbon resin may include petroleum resins, terpene resins, styrene resins, cyclopentadiene resins, saturated alicyclic resins or mixtures of such resins. Additionally, as a non-limiting example, the hydrocarbon resin may comprise hydrocarbon resin derived from the polymerization of olefin feeds rich in dicyclopentadiene (DCPD), from the polymerization of olefin feeds produced in the petroleum cracking process (such as crude C₉ feed streams), from the polymerization of pure monomers (such as styrene, α -methylstyrene, 4-methylstyrene, vinyltoluene or any combination of these or similar pure monomer feedstocks), from the polymerization of terpene olefins (such as α -pinene, β -pinene or d-limonene) or from a combination of such. The hydrocarbon resin may be fully or partially hydrogenated. Specific examples of hydrocarbon resins include but are not limited to Plastolyn[®] R1140 Hydrocarbon Resin available from Eastman Chemical Company (Kingsport, Tenn.), Regalite[®] T1140 available from Eastman Chemical Company (Kingsport, Tenn.), Arkon[®] P-140 available from Arakawa Chemical Industries, Limited (Osaka, Japan) and Piccolyte[®] S135 Polyterpene Resins available from Hercules Incorporated (Wilmington, Del.). It should be understood that the central core layer of high density polyethylene may include a blend of high density polyethylene and a hydrocarbon resin with no high density polyethylene nucleation additive present.

- [26] In another preferred embodiment, thermoformed blister component **11** comprises a multilayer non-palindromic film **100** having a first exterior layer **101** comprising cyclic olefin copolymer (COC), a second exterior layer **103** comprising a material which is different than first exterior layer **101** and is a material selected from the group consisting of polypropylene (PP), polystyrenes such as, but not limited to, high impact polystyrene (HIPS), general purpose polystyrene (GPPS), and styrene block copolymer (SBC), aromatic polyesters such as, but not limited to, polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET),

amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and aliphatic polyesters such as, but not limited to, polylactic acid (PLA); polyhydroxyalkonates including but not limited to polyhydroxypropionate, poly(3-hydroxybutyrate) (PH3B), poly(3-hydroxyvalerate) (PH3V), poly(4-hydroxybutyrate) (PH4B), poly(4-hydroxyvalerate) (PH4V), poly(5-hydroxyvalerate) (PH5V), poly(6-hydroxydodecanoate) (PH6D); and a central core layer **102** comprising a blend of high density polyethylene, a high density polyethylene nucleation additive, and optionally, a hydrocarbon resin (HDPE-Blend).

- [27] In another preferred embodiment, thermoformed blister component **11** comprises a multilayer non-palindromic film **100** having a first exterior layer **101** comprising cyclic olefin copolymer (COC), a second exterior layer **103** comprising a material which is different than first exterior layer **101** and is a material selected from the group consisting of polypropylene (PP), polystyrenes such as, but not limited to, high impact polystyrene (HIPS), general purpose polystyrene (GPPS), and styrene block copolymer (SBC), aromatic polyesters such as, but not limited to, polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and aliphatic polyesters such as, but not limited to, polylactic acid (PLA); polyhydroxyalkonates including but not limited to polyhydroxypropionate, poly(3-hydroxybutyrate) (PH3B), poly(3-hydroxyvalerate) (PH3V), poly(4-hydroxybutyrate) (PH4B), poly(4-hydroxyvalerate) (PH4V), poly(5-hydroxyvalerate) (PH5V), poly(6-hydroxydodecanoate) (PH6D); and a central core layer **102** comprising a high density polyethylene having a bi-modal molecular weight distribution of a low molecular weight region and a high molecular weight region (HDPE-Bimodal).
- [28] As used throughout this application, the term "polypropylene" refers to a homopolymer or copolymer having a propyl or C-3 linkage between monomer

units. A non-limiting example of a suitable propylene copolymer is Propylene 4170 available from Total Petrochemicals USA, Inc. (Houston, Tex.). Other non-limiting examples of polypropylenes include Polypropylene 3287WZ, which is available from Total Petrochemicals USA, Inc. (Houston, Tex.); and H02C-00 Polypropylene Homopolymer, which is available from Ineos Olefins & Polymers USA (League City, Tex.).

- [29]** As used throughout this application, the term "polyester" refers to a homopolymer or copolymer having an ester linkage between monomer units which may be formed, for example, by condensation polymerization reactions between a dicarboxylic acid and a diol. The ester linkage can be represented by the general formula: $[O-R-OC(O)-R'-C(O)]_n$ where R and R' are the same or different alkyl (or aryl) group and may be generally formed from the polymerization of dicarboxylic acid and diol monomers containing both carboxylic acid and hydroxyl moieties. The dicarboxylic acid (including the carboxylic acid moieties) may be linear or aliphatic (e.g., lactic acid, oxalic acid, maleic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, and the like) or may be aromatic or alkyl substituted aromatic (e.g., various isomers of phthalic acid, such as paraphthalic acid (or terephthalic acid), isophthalic acid and naphthalic acid). Specific examples of a useful diol include but are not limited to ethylene glycol, propylene glycol, trimethylene glycol, 1,4-butane diol, neopentyl glycol, cyclohexane diol and the like. Polyesters may include a homopolymer or copolymer of alkyl-aromatic esters including but not limited to polyethylene terephthalate (PET), amorphous polyethylene terephthalate (APET), crystalline polyethylene terephthalate (CPET), glycol-modified polyethylene terephthalate (PETG) and polybutylene terephthalate; a copolymer of terephthalate and isophthalate including but not limited to polyethylene terephthalate/isophthalate copolymer. Aliphatic polyesters include but not limited to polylactic acid (PLA); polyhydroxyalkonates including but not limited to polyhydroxypropionate, poly(3-hydroxybutyrate) (PH3B), poly(3-hydroxyvalerate) (PH3V), poly(4-

hydroxybutyrate) (PH4B), poly(4-hydroxyvalerate) (PH4V), poly(5-hydroxyvalerate) (PH5V), poly(6-hydroxydodecanoate) (PH6D); and blends of any of these materials. A non-limiting example of PETG is Eastar™ Copolyester 6763, which is also available from Eastman Chemical Company (Kingsport, Tenn.).

[30] As used herein, the term "polylactic acid" is used synonymously throughout this disclosure to describe homopolymers or copolymers having an ester linkage between monomer units and can be represented by the general formula: $[-OCH(R)C(O)-]_n$ where $R=CH_3$. Polylactic acid may be fabricated by polymerizing lactic acid, which is mostly produced from by carbohydrate fermentation of corn. Polylactic acid may be also produced by polymerization of lactide which obtained by condensation of two lactic acid molecules. Polylactic acid has a glass transition temperature of ranges from 50-80° C. while the melting temperature ranges from 130-180° C. Polylactic acid is known by those skilled in the art and fully disclosed in U.S. Pat. Nos. 5,698,322; 5,142,023; 5,760,144; 5,593,778; 5,807,973; and 5,010,145, the entire disclosure of each of which is hereby incorporated by reference. Examples of commercially available polylactic acid are sold under the trademark NatureWorks™ PLA Polymer in grades 4031-D, 4032-D, and 4041-D from Cargill Dow LLC, Minneapolis, Minn., U.S.A.

[31] As used throughout this application, the term "polystyrene" or "PS" refers to a homopolymer or copolymer having at least one styrene repeating linkage (such as benzene (i.e., C_6H_5) having an ethylene substituent) within the repeating backbone of the polymer. The styrene linkage can be represented by the general formula: $[CH_2-CH_2(C_6H_5)]_n$. Polystyrene may be formed by any method known to those skilled in the art. Examples of styrenic polymers include but are not limited to high impact polystyrene (HIPS), general purpose polystyrene (GPPS) and styrene block copolymer (SBC). HIPS is sometimes called rubber-modified polystyrene and is normally produced by copolymerization of styrene and a

synthetic rubber. (See Wagner, et al., "Polystyrene," The Wiley Encyclopedia of Packaging Technology, Second Edition, 1997, pp. 768-771 (John Wiley & Sons, Inc., New York, New York), which is incorporated in its entirety in this application by this reference.) Examples of HIPS include but are not limited to Impact Polystyrene 825E and Impact Polystyrene 945E, both of which are available from Total Petrochemicals USA, Inc; EB6025 Rubber Modified High Impact Polystyrene, which is available from Chevron Phillips Company (The Woodlands, Texas); and 6210 High Impact Polystyrene, which is available from Ineos Nova LLC (Channahon, Illinois). GPPS is often called crystal polystyrene, as a reference to the clarity of the resin. Examples of GPPS include but are not limited to Crystal Polystyrene 524B and Crystal Polystyrene 525B, both of which are available from Total Petrochemicals USA, Inc. Styrene block copolymers (SBC) include styrene butadiene copolymers (SB). The styrene-butadiene copolymers that are suitable for packaging applications are those resinous block copolymers that typically contain a greater proportion of styrene than butadiene and that are predominantly polymodal with respect to molecular weight distribution. (See Hartsock, "Styrene-Butadiene Copolymers," The Wiley Encyclopedia of Packaging Technology, Second Edition, 1997, pp. 863-864 (John Wiley & Sons, Inc., New York, New York), which is incorporated in its entirety in this application by this reference.) A non-limiting example of SB is DK13 K-Resin® Styrene-Butadiene Copolymer, which is available from Chevron Phillips Chemical Company (The Woodlands, Texas).

- [32] In still another preferred embodiment, thermoformed blister component **11** comprises a multilayer non-palindromic film **100** having a first exterior layer **101** comprising cyclic olefin copolymer (COC), a second exterior layer **103** comprising a material which is different than first exterior layer **101** and is selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene

terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA), and a central core layer **102** comprising a high density polyethylene having a thickness of between 50 μm to 254 μm (2 mil to 10 mil).

[33] These three-layer embodiments described above may include, but are not limited to the following layer sequences and general layer compositions: COC / HDPE / COC; COC / HDPE-Blend / COC; COC / HDPE-Bimodal / COC; COC / HDPE / PP; COC / HDPE-Blend / PP; COC / HDPE-Bimodal / PP; COC / HDPE / PETG; COC / HDPE-Blend / PETG; COC / HDPE-Bimodal / PETG; COC / HDPE / APET; COC / HDPE-Blend / APET; COC / HDPE-Bimodal / APET; COC / HDPE / PET; COC / HDPE-Blend / PET; COC / HDPE-Bimodal / PET; COC / HDPE / OPET; COC / HDPE-Blend / OPET; COC / HDPE-Bimodal / OPET; COC / HDPE / PLA; COC / HDPE-Blend / PLA; COC / HDPE-Bimodal / PLA; COC / HDPE / HIPS; COC / HDPE-Blend / HIPS; COC / HDPE-Bimodal / HIPS; COC / HDPE / GPPS; COC / HDPE-Blend / GPPS; COC / HDPE-Bimodal / GPPS; COC / HDPE / SBC; COC / HDPE-Blend / SBC; and COC / HDPE-Bimodal / SBC.

[34] In another generic embodiment as depicted in FIG. 4, thermoformed blister component **11** comprises a multilayer film **200** comprises a five-layer symmetrical structure of a first exterior layer **201**, a central core layer **202**, a second exterior layer **203**, and two interior layers **204** and **205** each positioned between an exterior layer and the central core layer. In this embodiment, first and second exterior layers **201** and **203** each comprise a cyclic olefin copolymer (COC) as described above for layer **101** and **103** for film **100**. Central core layer **202** comprises a high density polyethylene (HDPE) or a blend of a high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), or a high density polyethylene where the core layer has a thickness of between 50 μm to 254 μm (2 mil to 10 mil), or a high density polyethylene having a bi-modal molecular weight distribution of a low

molecular weight region and a high molecular weight region as described above for central core layer **102** for film **100**. Interior layers **204** and **205** each comprise a tie layer material (tie) which bonds the exterior layers to the central core layer.

- [35] It should be understood that the phrase "tie layer material" may include, but not limited to, unmodified polyolefins such as polyethylenes and ethylene vinyl acetate copolymers, unmodified ester copolymers such as ethylene acrylate copolymers and ethylene methacrylate copolymers and unmodified ethylene acid copolymers such as ethylene acrylic acid copolymers and blends thereof. Tie layer materials may also include modified polyolefins including, but not limited to anhydride modified polyethylenes, anhydride modified ethylene vinyl acetate copolymers, modified ester copolymers such as anhydride modified ethylene acrylate copolymers, modified ethylene acid copolymers such as anhydride modified ethylene acrylic acid copolymers and blends thereof. Tie layer materials may further include a blend of an unmodified polyolefin or unmodified ester copolymer or unmodified ethylene acid copolymer and a modified polyolefin or modified ester copolymer or modified ethylene acid copolymer.
- [36] In another generic embodiment as depicted in FIG. 4, thermoformed blister component **11** comprises a multilayer film **200** comprises a five-layer non-symmetrical structure of a first exterior layer **201**, a central core layer **202**, a second exterior layer **203**, and two interior layers **204** and **205** each positioned between an exterior layer and the central core layer. In this embodiment, the first exterior layer **201** comprises a cyclic olefin copolymer (COC), the second exterior layer **203** comprising a different material than first exterior layer **201** which is selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA), central

core layer **202** comprises a blend of high density polyethylene, high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), and two interior layers **204** and **205** each comprising a tie layer material.

[37] In still another generic embodiment as depicted in FIG. 4, thermoformed blister component **11** comprises a multilayer film **200** comprises a five-layer non-symmetrical structure of a first exterior layer **201**, a central core layer **202**, a second exterior layer **203**, and two interior layers **204** and **205** each positioned between an exterior layer and the central core layer. In this embodiment, first exterior layer **201** comprises a cyclic olefin copolymer (COC), a second exterior layer **203** comprising a different material than first exterior layer **201** which is selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA), central core layer **202** comprises a high density polyethylene having a thickness of between 50 μm to 254 μm (2 mil to 10 mil), and two interior layers **204** and **205** each comprising a tie layer material.

[38] In still another generic embodiment as depicted in FIG. 4, thermoformed blister component **11** comprises a multilayer film **200** comprises a five-layer non-symmetrical structure of a first exterior layer **201**, a central core layer **202**, a second exterior layer **203**, and two interior layers **204** and **205** each positioned between an exterior layer and the central core layer. In this embodiment, first exterior layer **201** comprises a cyclic olefin copolymer (COC), a second exterior layer **203** comprising a different material than first exterior layer **201** which is selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene

terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA), central core layer **202** comprises a bi-modal high density polyethylene having a molecular weight distribution of a low molecular weight region and a high molecular weight region (HDPE-Bimodal), and two interior layers **204** and **205** each comprising a tie layer material.

[39] These five-layer embodiments described above may include, but are not limited to the following layer sequences and general layer compositions: COC / tie / HDPE / tie / COC; COC / tie / HDPE-Blend / tie / COC; COC / tie / HDPE-Bimodal / tie / COC; COC / tie / HDPE / tie / PP; COC / tie / HDPE-Blend / tie / PP; COC / tie / HDPE-Bimodal / tie / PP; COC / tie / HDPE / tie / PETG; COC / tie / HDPE-Blend / tie / PETG; COC / tie / HDPE-Bimodal / tie / PETG; COC / tie / HDPE / tie / APET; COC / tie / HDPE-Blend / tie / APET; COC / tie / HDPE-Bimodal / tie / APET; COC / tie / HDPE / tie / PET; COC / tie / HDPE-Blend / tie / PET; COC / tie / HDPE-Bimodal / tie / PET; COC / tie / HDPE / tie / OPET; COC / tie / HDPE-Blend / tie / OPET; COC / tie / HDPE-Bimodal / tie / OPET; COC / tie / HDPE / tie / PLA; COC / tie / HDPE-Blend / tie / PLA; COC / tie / HDPE-Bimodal / tie / PLA; COC / tie / HDPE / tie / HIPS; COC / tie / HDPE-Blend / tie / HIPS; COC / tie / HDPE-Bimodal / tie / HIPS; COC / tie / HDPE / tie / GPPS; COC / tie / HDPE-Blend / tie / GPPS; COC / tie / HDPE-Bimodal / tie / GPPS; COC / tie / HDPE / tie / SBC; COC / tie / HDPE-Blend / tie / SBC; and COC / tie / HDPE-Bimodal / tie / SBC.

[40] Those skilled in the art will recognize that a tie layer material may not be needed to bond a cyclic olefin copolymer (COC) to a high density polyethylene. Therefore, while the above examples illustrate symmetrical film structures having at least five layers, a tie layer between cyclic olefin copolymer (COC) and high density polyethylene may be omitted and thus, four-layer film structures can be formed as well.

- [41] It should be understood that in the above-described generic embodiments, the thermoformed blister component may include additional film layers.
- [42] While it should be understood that each film layer of films **100** and **200** may each have any thickness as desired, it is preferable that the thickness of each of the central core layer layers **102** and **202** is at least 40% or at least 45% or at least 50%, or at least 55%, or at least 60%, or at least 65% of the total thickness of the palindromic thermoplastic films **100** and **200**, respectively.
- [43] The total thickness of multilayer films of the thermoformed blister component **11** of the present invention is generally from about 12.7 μm (0.5 mil) to about 508 μm (20 mil), typically from about 50.8 μm (2 mil) to about 254 μm (10 mil), most typically from about 76.2 μm (3 mil) to about 203.2 μm (8 mil).
- [44] In accordance with the practice of the present invention, one embodiment of a lidding component **12** of the present invention is depicted in FIG. 5. In this embodiment, lidding component **12** comprises a laminate **300** having a first exterior layer **301**, an interior layer **302** and a second exterior layer **303**. Preferably, second exterior layer **303** comprises a thermoplastic resin heat-sealable to cyclic olefin copolymer, first exterior layer **301** comprises a metal foil such as aluminum, and interior layer **302** comprises a tie or adhesive material bonding exterior layers **301** and **303** together.
- [45] The above description and the following examples illustrate certain embodiments of the present invention and are not to be interpreted as limiting. Selection of particular embodiments, combinations thereof, modifications, and adaptations of the various embodiments, conditions and parameters normally encountered in the art will be apparent to those skilled in the art and are deemed to be within the spirit and scope of the present invention.

WORKING EXAMPLES

THERMOFORMED BLISTER COMPONENT-PALINDROMIC FILM EXAMPLES

- [46] The following example illustrates a certain particular embodiment of palindromic film structure suitable for use in the present invention and is not to be interpreted as limiting. In the following example, polymeric resin composition percentages are based on the total weight of each film layer. In the following example, the film structure was produced using a single-bubble coextrusion apparatus and method which are well known to those skilled in the art. The single-bubble blown coextrusion film apparatus included a multi-manifold circular die head for bubble blown film through which a non-palindromic film composition was forced through and formed into a cylindrical bubble. The film bubble was immediately quenched e.g., via cooled water bath, solid surface and/or air, and then ultimately collapsed onto itself and formed into a palindromic film.

Example 1-1

- [47] Example 1-1 is one embodiment of a palindromic thermoplastic film **200** as illustrated in FIG. 4 having a structure and layer compositions as described below:
- [48] Layer **201** was 100% by weight of a cyclic olefin copolymer (COC) having density of 1010 kg/m³, a heat deflection temperature under load (0.45 MPa) of about 75° C and a glass transition temperature of 130° C. Exemplary of such a commercially available COC is TOPAS® 6013F-04 supplied by Celanese Corporation (Irving, TX, USA). This layer had a thickness of approximately 36.2 µm (1.4 mil).
- [49] Layer **204** was a blend of 80% by weight of a maleic anhydride modified ethylene elastomer and 20% by weight of a high density polyethylene (HDPE). Exemplary of a commercially available maleic anhydride modified ethylene elastomer is ADMER® SE810 having a density of 0.89 g/cm³ and a melt flow index (190° C/2.16 kg) of 7.2 g/ 10 min supplied by Mitsui Chemicals America, Inc. (Rye

Brook, NY, USA). Exemplary of a commercially available HDPE is SURPASS[®] HP167-AB supplied by Nova Chemical Company (Joffre, Alberta, Canada). SURPASS[®] HP167-AB is believed to be an example of a bimodal high density polyethylene having a distribution of a low molecular weight region and a high molecular weight region. Exemplary of a commercially available high density polyethylene is POLYBATCH[®] CLR 124 supplied by A. Schulman (Fairlawn, OH, USA). This layer had a thickness of approximately 6.0 μm (0.24 mil).

- [50] Layer **202** was 100% by weight a high density polyethylene (HDPE). This layer had a thickness of approximately 156.8 μm (6.18 mil).
- [51] Layer **205** was a blend of 80% by weight of a maleic anhydride modified ethylene elastomer and 20% by weight of a high density polyethylene (HDPE). This layer had a thickness of approximately 6.0 μm (0.24 mil).
- [52] Layer **203** was 100% by weight of a cyclic olefin copolymer (COC) having density of 1010 kg/m³, a heat deflection temperature under load (0.45 MPa) of about 75° C and a glass transition temperature of 130° C. Exemplary of such a commercially available COC is TOPAS[®] 6013F-04 supplied by Celanese Corporation (Irving, TX, USA). This layer had a thickness of approximately 36.2 μm (1.4 mil).
- [53] The film as described above had a total thickness of approximately 241.3 μm (9.5 mil).

Example 1-2

- [54] Example 1-2 is another embodiment of a palindromic thermoplastic film **200** as illustrated in FIG. 4 having the same structure and same layer compositions as described above for Example 1-1, except for the following layer thickness:
- [55] Layer **201** had a thickness of 28.7 μm (1.13 mil).

- [56] Layer **204** had a thickness of 4.7 μm (0.19 mil).
- [57] Layer **202** had a thickness of 124 μm (4.88 mil).
- [58] Layer **205** had a thickness of 4.7 μm (0.19 mil).
- [59] Layer **203** had a thickness of 28.7 μm (1.13 mil).
- [60] The film as described above had a total thickness of approximately 190.5 μm (7.5 mil).

LIDDING COMPONENT

- [61] The following examples illustrate certain particular embodiments of a film for use as a lidding component structure suitable and are not to be interpreted as limiting. In the following examples, polymeric resin composition percentages are based on the total weight of each film layer. In the following examples, the film structures were produced using an extrusion coating apparatus and methods which are well known to those skilled in the art. The extrusion coating apparatus includes a multi-manifold flat die head through which a two-layer film composition was forced and extrusion coated onto the shiny surface of a metallic foil. The metallic foil was pre-treated prior to extrusion coating by printing a primer coat onto the matte surface of the foil.

Example 2-1

- [62] Example 2-1 is one embodiment of a laminate **300** of a lidding component film **12** as illustrated in FIG. 5 having a structure and layer compositions as described below:
- [63] Layer **301** was an aluminum foil. This layer had a thickness of approximately 25.4 μm (1 mil).

- [64] Layer **302** was 100% by weight of an ethylene acrylic acid copolymer (EAA) having a density of 0.94 g/cm³, a melting point of 78° C, and a melt flow rate (190° C/2.16 kg) of 10 g/10 min. Exemplary of such a commercially available EAA is NUCREL[®] 3990 supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA).
- [65] Layer **303** (heat-seal layer) was a blend of 86% by weight of a modified ethylene acrylic acid copolymer (mod-EAA) having a density of 1.02 g/cm³, a melting point of 97° C, and a melt flow rate (190° C/2.16 kg) of 13 g/10 min; 10% by weight of a modified ethylene acrylate copolymer (mod-EMA) having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of 2.0 g/10 min, and a melting point of 91° C; and 4% of a masterbatch comprising an ethylene methacrylate copolymer (mod-EMA) having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of between 3 and 8 g/10 min, and a 1% by weight of a chill roll release additive. Exemplary of such a commercially available mod-EAA having a density of 1.02 g/cm³, a melting point of 97° C, and a melt flow rate (190° C/2.16 kg) of 13 g/10 min is APPEEL[®] 20D828 supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA). Exemplary of such a commercially available mod-EMA having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of 2.0 g/10 min, and a melting point of 91° C is BYNEL[®] 22E780 supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA). Exemplary of such a commercially available masterbatch mod-EMA having a chill roll release additive is Ampacet 100578 Chill Roll Cop MB supplied by Ampacet Corporation, Inc. (Tarrytown, NY, USA).

Example 2-2

- [66] Example 2-2 is another embodiment of a laminate **300** of a lidding component film **12** as illustrated in FIG. 5 having a structure and layer compositions as described below:

- [67] Layer **301** and **302** were equivalent to those described above in Example 2-1.
- [68] Layer **303** (heat-seal layer) was a blend of 86% by weight of a modified ethylene acrylic acid copolymer (mod-EAA) having a density of 1.02 g/cm³, a melting point of 97° C, and a melt flow rate (190° C/2.16 kg) of 13 g/10 min; 10% by weight of a modified ethylene acrylate copolymer (mod-EMA) having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of 2.0 g/10 min, and a melting point of 91° C; and 4% by weight of a masterbatch comprising an ethylene methacrylate copolymer (mod-EMA) having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of between 3 and 8 g/10 min, and a 1% by weight of a chill roll release additive. Exemplary of such a commercially available mod-EAA having a density of 1.02 g/cm³, a melting point of 97° C, and a melt flow rate (190° C/2.16 kg) of 13 g/10 min is APPEEL[®] 20D828 supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA). Exemplary of such a commercially available mod-EMA having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of 2.0 g/10 min, and a melting point of 91° C is BYNEL[®] 22E780 supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA). Exemplary of such a commercially available masterbatch mod-EMA having a chill roll release additive is Ampacet 100578 Chill Roll Cop MB supplied by Ampacet Corporation, Inc. (Tarrytown, NY, USA).

Example 2-3

- [69] Example 2-3 is another embodiment of a laminate **300** of a lidding component film **12** as illustrated in FIG. 5 having a structure and layer compositions as described below:
- [70] Layer **301** and **302** were equivalent to those described above in Example 2-1.
- [71] Layer **303** (heat-seal layer) was a blend of 85% by weight of a modified ethylene acrylic acid copolymer (mod-EAA) having a density of 1.02 g/cm³, a melting point of 97° C, and a melt flow rate (190° C/2.16 kg) of 13 g/10 min; 10% by weight of

a modified ethylene acrylate copolymer (mod-EMA) having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of 2.0 g/10 min, and a melting point of 91° C; 4% of a masterbatch comprising an ethylene methacrylate copolymer (mod-EMA) having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of between 3 and 8 g/10 min, and a 1% by weight of a chill roll release additive; and 1% by weight of a high density polyethylene masterbatch comprising 1% by weight of a high density polyethylene nucleation additive. Exemplary of such a commercially available mod-EAA having a density of 1.02 g/cm³, a melting point of 97° C, and a melt flow rate (190° C/2.16 kg) of 13 g/10 min is APPEEL[®] 20D828 supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA). Exemplary of such a commercially available mod-EMA having a density of 0.94 g/cm³, a melt flow rate (190° C/2.16 kg) of 2.0 g/10 min, and a melting point of 91° C is BYNEL[®] 22E780 supplied by E.I. du Pont de Nemours and Company, Inc. (Wilmington, DE, USA). Exemplary of such a commercially available masterbatch mod-EMA having a chill roll release additive is Ampacet 100578 Chill Roll Cop MB supplied by Ampacet Corporation, Inc. (Tarrytown, NY, USA). Exemplary of such a commercially available masterbatch of a high density polyethylene masterbatch comprising 1% by weight of a high density polyethylene nucleation additive is POLYBATCH[®] CLR 122 supplied by A. Schulman (Fairlawn, OH, USA).

- [72] The blister packages of the present invention can be manufactured using methods known in the art. Generally, the blister cavities are thermoformed from the blister components of the present invention in-line just prior to filling the cavities with a product to be packaged. The lidding component is then unwound from a roll and brought into contact with the formed and filled blister component such that the heat-seal layer of the lidding component contacts the blister component. The lidding and blister components are heat sealed, typically using a heated platen. Some areas of the package may not be sealed to provide a starting point for peeling off the lidding component prior to removing the product.

If the lidding component is not pre-printed, printing is generally done just before heat sealing. After heat-sealing, the individual blisters may be perforated using methods known in the art so that they can be removed at point of use.

What is claimed:

1. A blister component for a blister package, comprising:

a multilayer thermoplastic film comprising:
 - i. two exterior layers comprising a cyclic olefin copolymer (COC); and
 - ii. a central core layer comprising a high density polyethylene (HDPE).
2. A component according to claim 1, wherein the multilayer thermoplastic film is palindromic.
3. A component according to claim 1, wherein the central core layer comprises a high density polyethylene nucleation additive.
4. A component according to claim 3, wherein the central core layer comprises a hydrocarbon resin.
5. A component according to claim 1, wherein the central core layer has a thickness of between 50 μm to 254 μm (2 mil to 10 mil).
6. A component according to claim 1, wherein the central core layer comprises a bimodal high density polyethylene having a molecular weight distribution of a low molecular weight region and a high molecular weight region.

7. A component according to claim 1, wherein the central core layer is in direct contact with both exterior layers.
8. A component according to claim 1, wherein the multilayer thermoplastic film comprises two interior layers each comprising a tie layer material.
9. A component according to claim 8, wherein each of the two interior layers are in direct contact an exterior layer.
10. A component according to claim 8, wherein each of the two interior layers are in direct contact the central core layer.
11. A component according to claim 8, wherein the two interior layers each comprise a blend of a maleic anhydride modified ethylene elastomer and high density polyethylene.
12. A component according to claim 1, wherein the central core layer has a thickness of at least 40% of the total thickness of the multilayer thermoplastic film
13. A component according to claim 1, wherein the central core layer has a thickness of at least 45% of the total thickness of the multilayer thermoplastic film.

14. A component according to claim 1, wherein the central core layer has a thickness of at least 50% of the total thickness of the multilayer thermoplastic film.
15. A component according to claim 1, wherein the central core layer has a thickness of at least 55% of the total thickness of the multilayer thermoplastic film.
16. A component according to claim 1, wherein the central core layer has a thickness of at least 60% of the total thickness of the multilayer thermoplastic film.
17. A component according to claim 1, wherein the central core layer has a thickness of at least 65% of the total thickness of the multilayer thermoplastic film.
18. A component according to claim 1, wherein the central core layer has a thickness of at least 75% of the total thickness of the multilayer thermoplastic film.
19. A blister component for a blister package, comprising:
a multilayer thermoplastic film comprising:
 - i. a first exterior layer comprising cyclic olefin copolymer (COC);
 - ii. a second exterior layer comprising a material selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene

- terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA); and
- iii. a central core layer comprising a blend of high density polyethylene and a high density polyethylene nucleation additive.
20. A component according to claim 19, wherein the central core layer comprises a hydrocarbon resin.
21. A blister component for a blister package, comprising:
- a multilayer thermoplastic film comprising:
- i. a first exterior layer comprising cyclic olefin copolymer (COC);
- ii. a second exterior layer comprising a material selected from the group consisting of polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA); and
- iii. a central core layer comprising high density polyethylene having a thickness of between 50 μm to 254 μm (2 mil to 10 mil).
22. A component according to claims 1 to 21, wherein the central core layer comprises a high density polyethylene having a density of at least about 0.96 g/cm^3 .

23. A component according to claims 1 to 21, wherein the cyclic olefin copolymer is formed from norbornene and ethylene monomers.
24. A component according to claims 1 to 21, wherein the cyclic olefin copolymer has a heat deflection temperature under load (0.45 MPa) of about 75° C.
25. A component according to claims 1 to 21, wherein the cyclic olefin copolymer has a heat deflection temperature under load (0.45 MPa) of about 130° C.
26. A component according to claims 1 to 21, wherein the cyclic olefin copolymer has a heat deflection temperature under load (0.45 MPa) of about 150° C.
27. A component according to claims 1 to 21, wherein the cyclic olefin copolymer has a heat deflection temperature under load (0.45 MPa) of about 170° C.
28. A component according to claims 1 to 21, wherein the thermoplastic resin of the lidding component comprises a blend of modified ethylene acrylate copolymer resins.
29. A component according to claims 1 to 21, wherein the multilayer thermoplastic film comprises at least 5 layers.

1/5

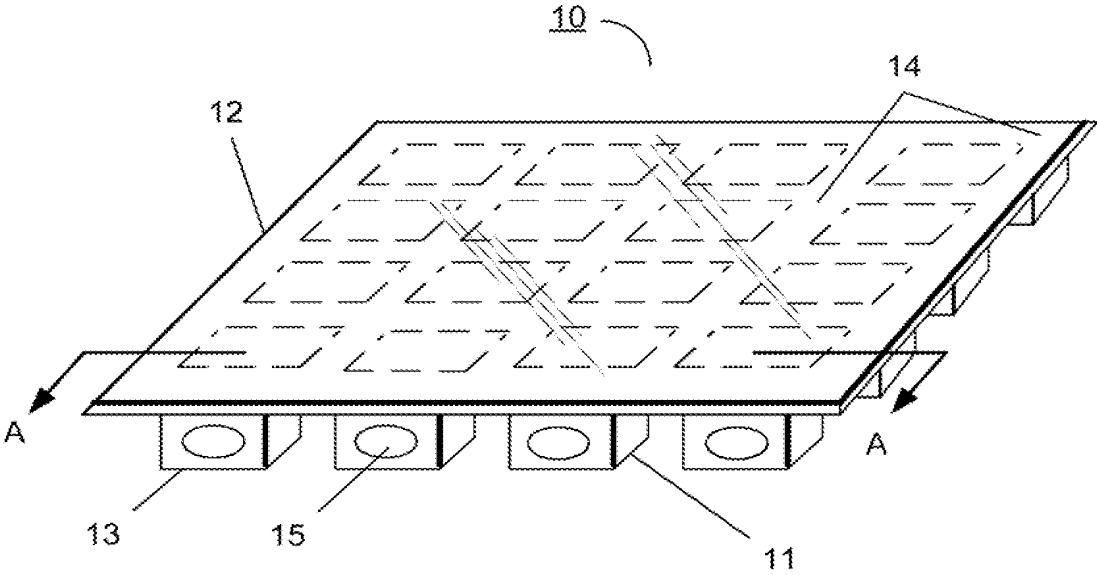
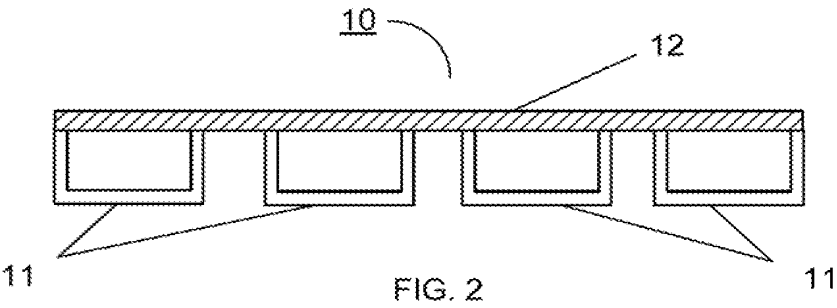


FIG. 1



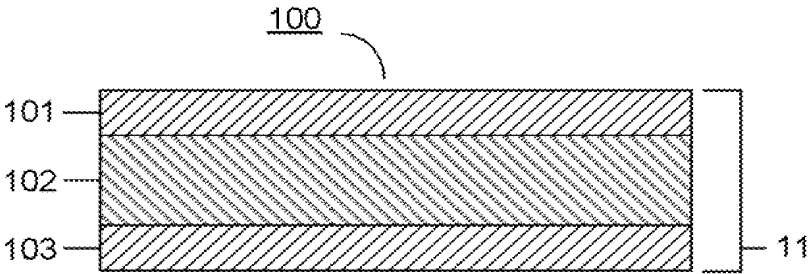


FIG. 3

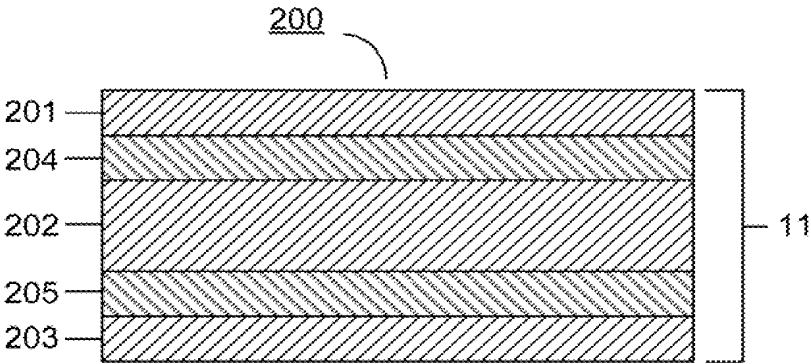


FIG. 4

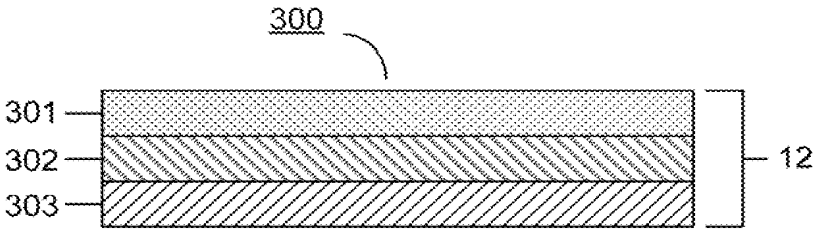


FIG. 5

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B65D 75/36 (2014.01)

CPC - B65D 75/36 (2014.09)

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)

IPC(8) - B32B 27/32; B65D 75/327, 75/36 (2014.01)

CPC - B32B 27/32; B65D 75/327, 75/36 (2014.09)

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

USPC - 428/35.7, 35.8, 35.9, 461, 500, 515, 516, 523

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Orbit, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---	US 5,783,273 A (YAMAMOTO et al) 21 July 1998 (21.07.1998) entire document	1-3, 5, 7, 12-18
Y		4, 6, 8-11, 19, 20
X ---	WO 2013/116445 A1 (HAUSMANN et al) 08 August 2013 (08.08.2013) entire document	21
Y		19, 20
Y	US 2007/0212539 A1 (YAMADA et al) 13 September 2007 (13.09.2007) entire document	4, 8-10, 20
Y	WO 2007/104513 A1 (NILSEN et al) 20 September 2007 (20.09.2007) entire document	6
Y	WO 2012/037180 A1 (BONEKAMP et al) 22 March 2012 (22.03.2012) entire document	11

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

* 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

15 September 2014

Date of mailing of the international search report

24 OCT 2014

Name and mailing address of the ISA/US

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P.O. Box 1450, Alexandria, Virginia 22313-1450

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Authorized officer:

Blaine R. Copenheaver

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 22-29
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.



- (51) **International Patent Classification:**
B32B 27/00 (2006.01) *B65D 83/04* (2006.01)
- (21) **International Application Number:**
PCT/US2014/041260
- (22) **International Filing Date:**
6 June 2014 (06.06.2014)
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- (71) **Applicant:** PERFECSEAL, INC. [US/US]; 3500 North Main Street, Oshkosh, WI 54901 (US).
- (72) **Inventors:** HAEDT, Ed, L.; 2162 Carlton Road, Oshkosh, WI 54904 (US). PRISCAL, Michael, D.; 3485 Dekalb Lane, Neenah, WI 54956 (US).
- (74) **Agent:** HALL, Tom, J.; Bemis Company, Inc., Office of Intellectual Property Counsel, P.O. Box 669, Neenah, WI 54957 (US).
- (81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) **Title:** BLISTER PACKAGING COMPONENTS

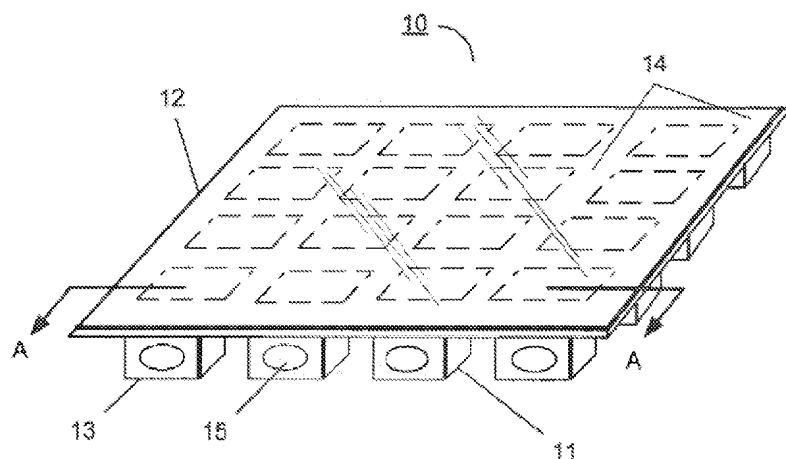


FIG. 1

(57) **Abstract:** The present invention relates to blister components for blister packages formed from multilayer thermoplastic films. In one embodiment of the present invention, the thermoformed blister component comprises a first exterior layer of polyvinylchloride (PVC) or polyvinylidene chloride; one interior layer comprising a blend of a high density polyethylene, high density polyethylene nucleation additive and optionally, a hydrocarbon resin, or a high density polyethylene and has a thickness of between 50 m to 254 m (2 mil to 10 mil); and a second exterior layer comprising a material selected from the group consisting of polyvinylchloride, polyvinylidene chloride, cyclic olefin copolymer, polypropylene, high impact polystyrene, general purpose polystyrene, styrene block copolymer, polyethylene terephthalate, oriented polyethylene terephthalate, amorphous polyethylene terephthalate, glycol-modified polyethylene terephthalate and polylactic acid.

BLISTER PACKAGING COMPONENTS

BACKGROUND OF THE INVENTION

- [01]** The present invention relates generally to blister packaging and more particularly, to blister components for blister packages formed from multilayer thermoplastic films where a low moisture vapor transmission rate is desired.
- [02]** Blister packaging is employed widely for commercial packaging of food products, personal care products, and human health products such as pharmaceuticals, and medical devices or precision instruments. The use of this type of packaging has become widespread mainly due to the ability to incorporate suitable moisture, dust, UV and/or gas barriers into the packages when such properties are desired for maintaining the product contained therein. For example, blister packaging is extensively used in the pharmaceutical industry for packaging of medicaments or the like in capsule, lozenge, or pill form because the integrity of the medicament can be maintained through the proper selection of materials used to form the packages.
- [03]** For preparing blister packages or so-called push through packages, generally a thermoplastic film is first processed by vacuum forming or pneumatic forming so as to form blisters or cavities thereon, namely portions having a predetermined contour corresponding to each specific article to be received therein. After the so-blistered film has been solidified, each blister is charged with each piece of the article to be packaged and a second or lidding film is then covered over each blister and sealed to the first film. The second lidding film is often a laminate material which can be ruptured by a simple finger-rupture or peeled off from the first film to allow access to a packaged item. Conventional materials used for forming the blistered film have included transparent plastics such as polyvinylchloride (PVC), polyvinylidene chloride (PVdC) and polychlorotrifluoroethylene (PCTFE), commonly referred to as ACLAR®

(Honeywell/Allied Signal). Packaging for pharmaceuticals or other moisture-sensitive articles require not only low moisture permeability but also other properties such as chemical inertness, clarity, rigidity, or uniform thickness. The use of polyvinylchloride (PVC) and polyvinylidene chloride (PVdC) have been shown to have poor and/or insufficient moisture-proofing properties required by the pharmaceutical industry. While ACLAR[®] exhibits relatively low moisture vapor transmission, its use in blister packaging is inherently costly.

- [04] There is therefore a need in the art for improved blister packaging materials which provides sufficient moisture vapor barrier and chemical inertness properties and is aesthetically pleasing enough to present the products contained therein while being cost effective to be manufactured.

SUMMARY OF THE INVENTION

- [05] The present invention is directed to blister components for blister packages formed from a multilayer film. As used throughout this disclosure, the term "blister component" refers to multilayer thermoplastic film or a roll of multilayer thermoplastic film both of which may be thermoformed, partially thermoformed or not thermoformed at all. In one embodiment of the present invention, the sequence of layers in the multilayer thermoplastic film of the blister component is palindromic. As used throughout this application, the term "palindromic" refers to a multilayer film, the layers of which are substantially symmetrical. Non-limiting examples of palindromic films are film or sheet having the layer sequence of configurations: A/B/A or A/B/B/A or A/C/B/C/A or A/C/D/B/D/C/A or A/D/C/D/B/D/C/D/A, etc. An example of a layer sequence configuration of a non-palindromic film would be A/B/C or A/C/B/A. A palindromic or non-palindromic thermoplastic film may be formed using extrusion lamination methods generally well known in the art.

- [06]** For example, in one generic embodiment, the thermoformed blister component of the present invention may be characterized as palindromic which is coextruded by extrusion lamination techniques to produce a layer sequence configuration of A/B/A. In this embodiment, the thermoformed blister component includes a film where layer A is an exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC), and a layer B which is a central core layer comprising a blend of high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), or a high density polyethylene (HDPE) and has a thickness of between 50 μm to 406 μm (2 mil to 16 mil). In one preferred embodiment, each exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC) has a thickness of less than 127 μm (5 mil), and more preferably, between 19 μm to 50 μm (0.75 mil to 4 mil).
- [07]** In an alternative generic embodiment of the present invention, the thermoformed blister component is a palindromic film which is formed by extrusion lamination and/or extrusion coating techniques to produce a layer sequence configuration of A/C/B/C/A. In this embodiment, layer A is an exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC), a layer B is a central core layer comprising a blend of high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), or a high density polyethylene (HDPE) and has a thickness of between 50 μm to 406 μm (2 mil to 16 mil), and C is a tie layer comprising a tie or an adhesive material bonding layers A and B together. In one preferred embodiment, each exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC) has a thickness of less than 127 μm (5 mil), and more preferably, between 19 μm to 50 μm (0.75 mil to 4 mil).
- [08]** In another generic embodiment, the thermoformed blister component of the present invention may be characterized as a palindromic film which is formed by

extrusion lamination and/or extrusion coating techniques to produce a layer sequence configuration of A/B/D/B/A. In this embodiment, the thermoformed blister component includes a film where layer A is an exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC), a layer B is an interior layer comprising a blend of a high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), or a high density polyethylene (HDPE) and has a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil), layer D is a central core layer. In one preferred embodiment, core layer D comprises ethylene vinyl acetate copolymer (EVA). In one preferred embodiment, each exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC) has a thickness of less than 127 μm (5 mil), and more preferably, between 19 μm to 50 μm (0.75 mil to 4 mil)..

- [09]** In another generic embodiment, the thermoformed blister component of the present invention may be characterized as a palindromic which is formed by extrusion lamination and/or extrusion coating techniques to produce a layer sequence configuration of A/C/B/D/B/C/A. In this embodiment, the thermoformed blister component includes a layer A which is an exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC), a layer B which is an interior layer comprising a blend of a high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), or a high density polyethylene (HDPE) and has a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil), a layer C which is a tie layer comprising a tie or an adhesive material bonding layers A and B together, and a layer D which is a central core layer. In one preferred embodiment, core layer D comprises an ethylene vinyl acetate copolymer (EVA). In one preferred embodiment, each exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC) has a thickness of less than 127 μm (5 mil), and more preferably, between 19 μm to 50 μm (0.75 mil to 4 mil).

- [10] In other embodiments of the present invention, the sequence of layers in the multilayer thermoplastic film of the blister component is non-palindromic.
- [11] For example, in one generic embodiment, the thermoformed blister component of the present invention may be characterized as a non-palindromic film which is formed by extrusion lamination and/or extrusion coating techniques to produce a layer sequence configuration of A/B/E. In this embodiment, the thermoformed blister component includes a layer A which is a first exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC), a layer B which is a central core layer comprising a blend of high density polyethylene, high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend) or a high density polyethylene (HDPE) and has a thickness of between 50 μm to 406 μm (2 mil to 16 mil), and a layer E which is a second exterior layer comprising a material selected from the group consisting of cyclic olefin copolymer (COC), polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA). In one preferred embodiment, the first exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC) has a thickness of less than 127 μm (5 mil), and more preferably, between 19 μm to 50 μm (0.75 mil to 4 mil).
- [12] In an alternative generic embodiment of the present invention, the thermoformed blister component is a non-palindromic film formed from extrusion lamination and/or extrusion coating methods to produce layer sequence having a layer configuration of A/C/B/C/E. In this embodiment, layer A is a first exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC), a layer B which is a central core layer comprising a blend of high density polyethylene, a high density polyethylene nucleation additive and/or a hydrocarbon resin (HDPE-

Blend), or a high density polyethylene (HDPE) and has a thickness of between 50 μm to 406 μm (2 mil to 16 mil), a layer C which is a tie layer comprising a tie or an adhesive material bonding layers A and B, and layers B and E together, and a layer E which is a second exterior layer comprising a material selected from the group consisting of cyclic olefin copolymer (COC), polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA). In one preferred embodiment, the first exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC) has a thickness of less than 127 μm (5 mil), and more preferably, between 19 μm to 50 μm (0.75 mil to 4 mil).

- [13]** In another alternative generic embodiment of the present invention, the thermoformed blister component a non-palindromic film formed by extrusion lamination and/or extrusion coating techniques to produce a non-symmetrical film having a layer sequence configuration of A/B/D/B/E. In this embodiment, layer A is a first exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC), a layer B is an interior layer comprising a blend of high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), or a high density polyethylene (HDPE) and has a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil), a layer D which is a core layer, and a layer E which is a second exterior layer comprising a material selected from the group consisting of cyclic olefin copolymer (COC), polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA). In one embodiment, core layer D comprises an ethylene acetate copolymer (EVA). In one preferred embodiment, the first exterior layer

comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC) has a thickness of less than 127 μm (5 mil), and more preferably, between 19 μm to 50 μm (0.75 mil to 4 mil).

- [14]** In still another alternative generic embodiment of the present invention, the thermoformed blister component a non-palindromic film formed by extrusion lamination and/or extrusion coating methods to produce a non-symmetrical film having a layer sequence configuration of A/C/B/D/B/C/E. In this embodiment, layer A is a first exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC), a layer B which is an interior layer comprising a blend of high density polyethylene, a high density polyethylene nucleation additive and optionally, a hydrocarbon resin (HDPE-Blend), or a high density polyethylene (HDPE) and has a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil, C is a tie layer comprising a tie or adhesive material bonding layers A and B, and layers B and E together, a layer D which is a core layer, and a layer E which is a second exterior layer comprising a material selected from the group consisting of cyclic olefin copolymer (COC), polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA). In one preferred embodiment, core layer D comprises an ethylene vinyl acetate copolymer (EVA). In one preferred embodiment, the first exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC) has a thickness of less than 127 μm (5 mil), and more preferably, between 19 μm to 50 μm (0.75 mil to 4 mil).
- [15]** It should be understood that in the above-described generic embodiments, the thermoformed blister component may include additional film layers.

- [16]** The blister packages of the present invention also include a lidding component which is heat-sealable to the first exterior layer A of the blister component. In one preferred embodiment, the lidding component comprises a thermoplastic resin heat-sealable to polyvinylchloride (PVC) or polyvinylidene chloride (PVdC).

BRIEF DESCRIPTION OF THE DRAWINGS

- [17]** Further features and advantages of the present invention will become apparent from the following detailed description, taken in combination with the appended drawings, in which:
- [18]** FIG. 1 illustrates a schematic view of one embodiment of a blister package according to the present invention.
- [19]** FIG. 2 illustrates an exploded view taken along line A-A of FIG. 1 depicting the blister and lidding components of the present invention.
- [20]** FIG. 3a illustrates a cross-sectional view of one embodiment of a three-layer blister component according to the present invention.
- [21]** FIG. 3b illustrates a cross-sectional view of an embodiment of another three-layer blister component according to the present invention.
- [22]** FIG. 4a illustrates a cross-sectional view of an embodiment of a five-layer blister component according to the present invention.
- [23]** FIG. 4b illustrates a cross-sectional view of an embodiment of another five-layer blister component according to the present invention.
- [24]** FIG. 4c illustrates a cross-sectional view of an embodiment of another five-layer blister component according to the present invention.
- [25]** FIG. 4d illustrates a cross-sectional view of an embodiment of another five-layer blister component according to the present invention.

- [26] FIG. 5a illustrates a cross-sectional view of an embodiment of a seven-layer blister component according to the present invention.
- [27] FIG. 5b illustrates a cross-sectional view of an embodiment of another seven-layer blister component according to the present invention.
- [28] FIG. 6 illustrates a cross-sectional view of one embodiment of a lidding component according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

- [29] In accordance with the practice of the present invention, a representative blister package **10** as described herein is shown in FIGS. 1 and 2. Package **10** of the present invention comprises a thermoformed blister component **11** and a lidding component **12**, the former provided with one or more thermoformed pockets **13** surrounded by sealed flange regions **14**. Pocket **13** defines an individual compartment for receiving a product **15**, such as a tablet.
- [30] In accordance with an important aspect of the present invention, the thermoformed blister component **11** comprises a multilayer film. It will be appreciated that film of thermoformed blister component **11** may include any number of film layers and film layer compositions depending upon both functional and aesthetic requirements of the blister component. It is desirable that the multilayer thermoplastic film include one or more film layers which are barrier materials and substantially chemically inert when in contact with a product. The term "barrier" refers to a material that controls permeability of one or more elements through a film structure including moisture, chemicals, heat, odor and oxygen or other gases. As it relates to the present invention, a barrier material can be provided by a single film layer or multiple film layers acting individually or in concert with each other, respectively. The phrase "substantially chemically inert" refers to materials that generally are not reactive with the product with which it comes into contact with and does not leech chemical ingredients into the

product with which it comes into contact. Preferably, thermoformed blister component **11** comprises a multilayer film which provides an average water vapor transmission rate of less than $0.500 \text{ g/m}^2/\text{day}$ or less than $0.250 \text{ g/m}^2/\text{day}$ or less than $150 \text{ g/m}^2/\text{day}$ or about $0.131 \text{ g/m}^2/\text{day}$ or about $0.110 \text{ g/m}^2/\text{day}$ at 100° F (37.8° C) and 90% relative humidity having a thickness of about 10 mil (254 micron) before being thermoformed. The aforementioned features of the present invention may be achieved by a multilayer film comprising at least 3 or 4 or 5 or 6 or 7 or 8 or 9 or 10 or 11 or 12 or 13 or more layers.

THERMOFORMED BLISTER COMPONENT

- [31]** As used herein, the phrase "high density polyethylene" or "HDPE" refers to homopolymers of ethylene that have densities of about 0.960 g/cm^3 to about 0.970 g/cm^3 as well as copolymers of ethylene and an alpha-olefin (such as 1-butene or 1-hexene) that have densities of about 0.940 g/cm^3 to about 0.958 g/cm^3 . In contrast, a low density polyethylene (LDPE) generally has a density of about 0.915 g/cm^3 to about 0.930 g/cm^3 . HDPE is inclusive of polymers made with Ziegler or Phillips type catalysts and polymers made with single-site metallocene catalysts. A non-limiting example of high density polyethylene includes Alathon[®] M6020 from Equistar Chemicals LP (Houston, Tex.). Other specific non-limiting examples of HDPE include Alathon[®] L5885 available from Equistar Chemicals LP (Houston, Tex.); ExxonMobil[™] HDPE HD 7925.30 available from ExxonMobil Chemical Company (Houston, Tex.); and ExxonMobil[™] HDPE HD 7845.30 available from ExxonMobil Chemical Company (Houston, Tex.).
- [32]** As used herein, the phrase "nucleation additive" means a material that increases high density polyethylene crystallinity as a result of its incorporation into HDPE. Such nucleation additives typically provide better control over crystallization rates. Examples of nucleation additives include minerals such as chalk, talc, clay, kaolin, silicates and the like, and organic agents such as salts of aliphatic or

aromatic carboxylic acids, aromatic salts, metallic salts of aromatic phosphorous compounds, quinaridones, and aromatic amides. Further examples include zinc glycerolate, calcium glycerolate, calcium hexahydrophthalate, zinc hexahydrophthalate, salts and the like, and mixtures thereof. In one embodiment, the nucleation additive comprises calcium hexahydrophthalate. In one embodiment, the nucleation additive is present in each interior layer of HDPE from about 0.2% to about 3.5% by weight of the layer.

- [33]** As used herein, the phrase "hydrocarbon resin" refers to a product produced by polymerization from coal tar, petroleum, and turpentine feed stocks, as defined by ISO Standard 472, "Plastics – Vocabulary" incorporated by reference herein to the extent that it teaches hydrocarbon resins. The hydrocarbon resin may be present in an interior or core layer of high density polyethylene from about 3% to about 16% by weight of the layer. A hydrocarbon resin may comprise any of those hydrocarbon resins disclosed in U.S. Pat. No. 6,432,496, issued Aug. 13, 2002, or in US Patent Application 2008/0286547, published Nov. 20, 2008, both of which are incorporated in their entireties in this application by this reference. More specifically, as a non-limiting example, the hydrocarbon resin may include petroleum resins, terpene resins, styrene resins, cyclopentadiene resins, saturated alicyclic resins or mixtures of such resins. Additionally, as a non-limiting example, the hydrocarbon resin may comprise hydrocarbon resin derived from the polymerization of olefin feeds rich in dicyclopentadiene (DCPD), from the polymerization of olefin feeds produced in the petroleum cracking process (such as crude C₉ feed streams), from the polymerization of pure monomers (such as styrene, α -methylstyrene, 4-methylstyrene, vinyltoluene or any combination of these or similar pure monomer feedstocks), from the polymerization of terpene olefins (such as α -pinene, β -pinene or d-limonene) or from a combination of such. The hydrocarbon resin may be fully or partially hydrogenated. Specific examples of hydrocarbon resins include but are not limited to Plastolyn[®] R1140 Hydrocarbon Resin available from Eastman

Chemical Company (Kingsport, Tenn.), Regalite[®] T1140 available from Eastman Chemical Company (Kingsport, Tenn.), Arkon[®] P-140 available from Arakawa Chemical Industries, Limited (Osaka, Japan) and Piccolyte[®] S135 Polyterpene Resins available from Hercules Incorporated (Wilmington, Del.)

- [34]** As used throughout this application, the term "polypropylene" refers to a homopolymer or copolymer having a propyl or C-3 linkage between repeating units. A non-limiting example of a suitable propylene copolymer is Propylene 4170 available from Total Petrochemicals USA, Inc. (Houston, Tex.). Other non-limiting examples of polypropylenes include Polypropylene 3287WZ, which is available from Total Petrochemicals USA, Inc. (Houston, Tex.); and H02C-00 Polypropylene Homopolymer, which is available from Ineos Olefins & Polymers USA (League City, Tex.).
- [35]** As used throughout this application, the term "polyester" refers to a homopolymer or copolymer having an ester linkage between repeating units which may be formed, for example, by condensation polymerization reactions between a dicarboxylic acid and a diol. The ester linkage can be represented by the general formula: $[O-R-OC(O)-R'-C(O)]_n$ where R and R' are the same or different alkyl (or aryl) group and may be generally formed from the polymerization of dicarboxylic acid and diol monomers containing both carboxylic acid and hydroxyl moieties. The dicarboxylic acid (including the carboxylic acid moieties) may be linear or aliphatic (e.g., lactic acid, oxalic acid, maleic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, and the like) or may be aromatic or alkyl substituted aromatic (e.g., various isomers of phthalic acid, such as paraphthalic acid (or terephthalic acid), isophthalic acid and naphthalic acid). Specific examples of a useful diol include but are not limited to ethylene glycol, propylene glycol, trimethylene glycol, 1,4-butane diol, neopentyl glycol, cyclohexane diol and the like. Polyesters may include a homopolymer or copolymer of alkyl-aromatic esters including but not limited to polyethylene

terephthalate (PET), amorphous polyethylene terephthalate (APET), crystalline polyethylene terephthalate (CPET), glycol-modified polyethylene terephthalate (PETG) and polybutylene terephthalate; a copolymer of terephthalate and isophthalate including but not limited to polyethylene terephthalate/isophthalate copolymer; a homopolymer or copolymer of aliphatic esters including but not limited to polylactic acid (PLA); polyhydroxyalkonates including but not limited to polyhydroxypropionate, poly(3-hydroxybutyrate) (PH3B), poly(3-hydroxyvalerate) (PH3V), poly(4-hydroxybutyrate) (PH4B), poly(4-hydroxyvalerate) (PH4V), poly(5-hydroxyvalerate) (PH5V), poly(6-hydroxydodecanoate) (PH6D); and blends of any of these materials. A non-limiting example of PETG is Eastar™ Copolyester 6763, which is also available from Eastman Chemical Company (Kingsport, Tenn.).

[36] As used herein, the term "polylactic acid" is used synonymously throughout this disclosure to describe homopolymers or copolymers having an ester linkage between monomer units and can be represented by the general formula: $[-OCH(R)C(O)-]_n$ where $R=CH_3$. Polylactic acid may be fabricated by polymerizing lactic acid, which is mostly produced from by carbohydrate fermentation of corn. Polylactic acid may be also produced by polymerization of lactide which obtained by condensation of two lactic acid molecules. Polylactic acid has a glass transition temperature of ranges from 50-80° C while the melting temperature ranges from 130-180° C. Polylactic acid is known by those skilled in the art and fully disclosed in U.S. Pat. Nos. 5,698,322; 5,142,023; 5,760,144; 5,593,778; 5,807,973; and 5,010,145, the entire disclosure of each of which is hereby incorporated by reference. Examples of commercially available polylactic acid are sold under the trademark NatureWorks™ PLA Polymer in grades 4031-D, 4032-D, and 4041-D from Cargill Dow LLC, Minneapolis, Minn., U.S.A.

[37] As used throughout this application, the term "polystyrene" or "PS" refers to a homopolymer or copolymer having at least one styrene repeating linkage (such

as benzene (i.e., C_6H_5) having an ethylene substituent) within the repeating backbone of the polymer. The styrene linkage can be represented by the general formula: $[CH_2-CH_2(C_6H_5)]_n$. Polystyrene may be formed by any method known to those skilled in the art. Examples of styrenic polymers include but are not limited to high impact polystyrene (HIPS), general purpose polystyrene (GPPS) and styrene block copolymer (SBC). HIPS is sometimes called rubber-modified polystyrene and is normally produced by copolymerization of styrene and a synthetic rubber. (See Wagner, et al., "Polystyrene," The Wiley Encyclopedia of Packaging Technology, Second Edition, 1997, pp. 768-771 (John Wiley & Sons, Inc., New York, New York), which is incorporated in its entirety in this application by this reference.) Examples of HIPS include but are not limited to Impact Polystyrene 825E and Impact Polystyrene 945E, both of which are available from Total Petrochemicals USA, Inc; EB6025 Rubber Modified High Impact Polystyrene, which is available from Chevron Phillips Company (The Woodlands, Texas); and 6210 High Impact Polystyrene, which is available from Ineos Nova LLC (Channahon, Illinois). GPPS is often called crystal polystyrene, as a reference to the clarity of the resin. Examples of GPPS include but are not limited to Crystal Polystyrene 524B and Crystal Polystyrene 525B, both of which are available from Total Petrochemicals USA, Inc. Styrene block copolymers (SBC) include styrene butadiene copolymers (SB). The styrene-butadiene copolymers that are suitable for packaging applications are those resinous block copolymers that typically contain a greater proportion of styrene than butadiene and that are predominantly polymodal with respect to molecular weight distribution. (See Hartsock, "Styrene-Butadiene Copolymers," The Wiley Encyclopedia of Packaging Technology, Second Edition, 1997, pp. 863-864 (John Wiley & Sons, Inc., New York, New York), which is incorporated in its entirety in this application by this reference.) A non-limiting example of SB is DK13 K-Resin® Styrene-Butadiene Copolymer, which is available from Chevron Phillips Chemical Company (The Woodlands, Texas).

- [38] It should be understood that the phrase "tie layer material" may include, but not limited to, unmodified polyolefins such as polyethylenes and ethylene vinyl acetate copolymers, unmodified ester copolymers such as ethylene acrylate copolymers and ethylene methacrylate copolymers and unmodified ethylene acid copolymers such as ethylene acrylic acid copolymers and blends thereof. Tie layer materials may also include modified polyolefins including, but not limited to anhydride modified polyethylenes, maleic anhydride modified ethylene elastomers, anhydride modified ethylene vinyl acetate copolymers, modified ester copolymers such as anhydride modified ethylene acrylate copolymers, modified ethylene acid copolymers such as anhydride modified ethylene acrylic acid copolymers and blends thereof. Tie layer materials may further include a blend of an unmodified polyolefin or unmodified ester copolymer or unmodified ethylene acid copolymer and a modified polyolefin or modified ester copolymer or modified ethylene acid copolymer.
- [39] In one embodiment as depicted in FIG. 3a, thermoformed blister component **11** comprises a multilayer palindromic film **100a** comprising at least a three-layer structure of a first exterior layer **101a**, a central core layer **102a** and a second exterior layer **103a**. In this embodiment, first and second exterior layers **101a** and **103a** comprise the same materials selected from the group consisting of polyvinylchloride (PVC) and polyvinylidene chloride (PVdC). In another embodiment represented in FIG. 3b, thermoformed blister component **11b** comprises a multilayer non-palindromic film **100b** comprising at least a three-layer structure of a first exterior layer **101b**, a central core layer **102b** and a second exterior layer **103b**. The first and second exterior layers **101b** and **103b** comprise different materials where the first exterior layer **101b** comprises a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC), and the second exterior layer **103b** comprises comprising a material selected from the group consisting of cyclic olefin copolymer (COC), polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block

copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA). In these embodiments, the central core layer, **102a** and **102b**, each comprises a blend of a high density polyethylene, a high density polyethylene nucleation additive and/or a hydrocarbon resin (HDPE-Blend) or a high density polyethylene (HDPE) and has a thickness of between 50 μm to 406 μm (2 mil to 16 mil).

[40] These three-layer embodiments described above may include, but are not limited to the following layer sequences and general layer compositions: PVC / HDPE-Blend / PVC; PVC / HDPE / PVC; PVdC / HDPE-Blend / PVdC; PVdC / HDPE / PVdC; PVC / HDPE-Blend / COC; PVC / HDPE-Blend / PP; PVC / HDPE-Blend / HIPS; PVC / HDPE / HIPS; PVdC / HDPE-Blend / HIPS; PVdC / HDPE / PVdC; PVC / HDPE-Blend / GPPS; PVC / HDPE / GPPS; PVdC / HDPE-Blend / GPPS; PVdC / HDPE / GPPS; PVC / HDPE-Blend / SBC; PVC / HDPE / SBC; PVdC / HDPE-Blend / SBC; PVdC / HDPE / SBC; PVC / HDPE-Blend / PET; PVC / HDPE / PET; PVdC / HDPE-Blend / PET; PVdC / HDPE / PET; PVC / HDPE-Blend / OPET; PVC / HDPE / OPET; PVdC / HDPE-Blend / OPET; PVdC / HDPE / OPET; PVC / HDPE-Blend / APET; PVC / HDPE / APET; PVdC / HDPE-Blend / APET; PVdC / HDPE / APET; PVC / HDPE-Blend / PETG; PVC / HDPE-Blend / PLA; PVdC / HDPE-Blend / COC; PVdC / HDPE-Blend / PP; PVdC / HDPE-Blend / PETG; PVdC / HDPE-Blend / PLA; PVdC / HDPE / COC; PVdC / HDPE / PP; PVdC / HDPE / PETG; and PVdC / HDPE / PLA.

[41] In another preferred embodiment, as depicted in FIG. 4a, thermoformed blister component **11** comprises a multilayer palindromic film **200a** comprising a five-layer structure of a first exterior layer **201a**, a central core layer **202a**, a second exterior layer **203a** and two tie layers **204a** and **205a**, each positioned between an exterior layer and the central core layer. In this embodiment, first and second exterior layers **101a** and **103a** comprise the same materials selected from the

group consisting of polyvinylchloride (PVC) and polyvinylidene chloride (PVdC). The central core layer, **202a**, comprises a blend of a high density polyethylene, a high density polyethylene nucleation additive and/or a hydrocarbon resin (HDPE-Blend), or a high density polyethylene (HDPE) and has a thickness of between 50 μm to 406 μm (2 mil to 16 mil). Each tie layer comprises a maleic anhydride modified ethylene elastomer. In another embodiment, thermoformed blister component **11** comprises a multilayer non-palindromic film **200b** illustrated in FIG. 4b. In this embodiment, film **200b** comprises the same film sequence and layer compositions as described for film **200a** in FIG. 4a, except for the second exterior layer **203b** comprises a different material than the first exterior layer which is selected from the group consisting of cyclic olefin copolymer (COC), polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA).

- [42] In another preferred embodiment, as depicted in FIG. 4c, thermoformed blister component **11** comprises a multilayer palindromic film **200c** comprising a five-layer structure of a first exterior layer **201c**, a central core layer **202a**, a second exterior layer **203c** and two interior layers **204c** and **205c**, each positioned between an exterior layer and the central core layer. In this embodiment, first and second exterior layers **201c** and **203c** comprise the same materials selected from the group consisting of polyvinylchloride (PVC) and polyvinylidene chloride (PVdC). The central core layer **202c** may comprise any thermoplastic material and preferably, comprises an ethylene vinyl acetate copolymer. The two interior layers, **204c** and **205c**, each comprises a blend of a high density polyethylene, a high density polyethylene nucleation additive and/or hydrocarbon resin (HDPE-Blend), or a high density polyethylene (HDPE) and has a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil). In another embodiment, thermoformed

blister component **11** comprises a multilayer non-palindromic film **200d** illustrated in FIG. 4d. In this embodiment, film **200d** comprises the same film sequence and layer compositions as described for film **200c** in FIG. 4c, except for the second exterior layer **203d** comprises a different material than the first exterior layer which is selected from the group consisting of cyclic olefin copolymer (COC), polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA).

- [43]** These five-layer embodiments described above may include, but are not limited to the following layer sequences and general layer compositions: PVC / tie / HDPE-Blend / tie / PVC; PVC / tie / HDPE / tie / PVC; PVdC / tie / HDPE-Blend / tie / PVdC; PVdC / tie / HDPE / tie / PVdC; PVC / tie / HDPE-Blend / tie / COC; PVC / tie / HDPE-Blend / tie / PP; PVC / tie / HDPE-Blend / tie / HIPS; PVC / tie / HDPE / tie / HIPS; PVdC / tie / HDPE-Blend / tie / HIPS; PVdC / tie / HDPE / tie / HIPS; PVC / tie / HDPE-Blend / tie / GPPS; PVC / tie / HDPE / tie / GPPS; PVdC / tie / HDPE-Blend / tie / GPPS; PVdC / tie / HDPE / tie / GPPS; PVC / tie / HDPE-Blend / tie / SBC; PVC / tie / HDPE / tie / SBC; PVdC / tie / HDPE-Blend / tie / SBC; PVdC / tie / HDPE / tie / SBC; PVC / tie / HDPE-Blend / tie / PET; PVC / tie / HDPE / tie / PET; PVdC / tie / HDPE-Blend / tie / PET; PVdC / tie / HDPE / tie / PET; PVC / tie / HDPE-Blend / tie / OPET; PVC / tie / HDPE / tie / OPET; PVdC / tie / HDPE-Blend / tie / OPET; PVdC / tie / HDPE / tie / OPET; PVC / tie / HDPE-Blend / tie / APET; PVC / tie / HDPE / tie / APET; PVdC / tie / HDPE-Blend / tie / APET; PVdC / tie / HDPE / tie / APET; PVC / tie / HDPE-Blend / tie / PETG; PVC / tie / HDPE-Blend / tie / PLA; PVdC / tie / HDPE-Blend / tie / COC; PVdC / tie / HDPE-Blend / tie / PP; PVdC / tie / HDPE-Blend / tie / PETG; PVdC / tie / HDPE-Blend / tie / PLA; PVdC / tie / HDPE / tie / COC; PVdC / tie / HDPE / tie / PP; PVdC / tie / HDPE / tie / PETG; and PVdC / tie / HDPE / tie / PLA.

- [44] Those skilled in the art will recognize that a tie layer material may not be needed to bond a cyclic olefin copolymer (COC) to a high density polyethylene. Therefore, while the above examples illustrate symmetrical film structures having at least five layers, a tie layer between cyclic olefin copolymer (COC) and high density polyethylene may be omitted and thus, four-layer film structures can be formed as well.
- [45] In another preferred embodiment, as depicted in FIG. 5a, thermoformed blister component **11** comprises a multilayer palindromic film **300a** comprising a seven-layer structure of a first exterior layer **301a**, a central core layer **302a**, a second exterior layer **303a** and two interior layers **304a** and **305a**, each positioned between an exterior layer and the central core layer, and two tie layers **306a** and **307a**, each positioned between an exterior layer and the central core layer. The two interior layers **304a** and **305a**, each comprises a blend of a high density polyethylene, a high density polyethylene nucleation additive and/or hydrocarbon resin (HDPE-Blend), or a high density polyethylene (HDPE) and has a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil). In this embodiment, first and second exterior layers **301a** and **303a** comprise the same materials selected from the group consisting of polyvinylchloride (PVC) and polyvinylidene chloride (PVdC). The central core layer **302c** comprises any thermoplastic material and preferably, comprises an ethylene vinyl acetate copolymer. Each tie layer comprises a maleic anhydride modified ethylene elastomer. In another embodiment, thermoformed blister component **11** comprises a multilayer non-palindromic film **300b** illustrated in FIG. 5a. In this embodiment, film **300b** comprises the same film sequence and layer compositions as described for film **300a** in FIG. 5a, except for the second exterior layer **303b** comprises a different material than the first exterior layer which is selected from the group consisting of cyclic olefin copolymer (COC), polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET),

amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA).

- [46]** These seven-layer embodiments described above may include, but are not limited to the following layer sequences and general layer compositions: PVC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / PVC; PVC / tie / HDPE / EVA / HDPE / tie / PVC; PVdC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / PVdC; PVdC / tie / HDPE / EVA / HDPE / tie / PVdC; PVC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / COC; PVC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / PP; PVC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / HIPS; PVC / tie / HDPE / EVA / HDPE / tie / HIPS; PVdC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / HIPS; PVdC / tie / HDPE / EVA / HDPE / tie / HIPS; PVC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / GPPS; PVC / tie / HDPE / EVA / HDPE / tie / GPPS; PVdC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / GPPS; PVdC / tie / HDPE / EVA / HDPE / tie / GPPS; PVC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / SBC; PVC / tie / HDPE / EVA / HDPE / tie / SBC; PVdC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / SBC; PVdC / tie / HDPE / EVA / HDPE / tie / SBC; PVC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / PET; PVC / tie / HDPE / EVA / HDPE / tie / PET; PVdC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / PET; PVdC / tie / HDPE / EVA / HDPE / tie / PET; PVC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / OPET; PVC / tie / HDPE / EVA / HDPE / tie / OPET; PVdC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / OPET; PVdC / tie / HDPE / EVA / HDPE / tie / OPET; PVC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / APET; PVC / tie / HDPE / EVA / HDPE / tie / APET; PVdC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / APET; PVdC / tie / HDPE / EVA / HDPE / tie / APET; PVC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / PETG; PVC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / PLA; PVC / tie / HDPE / EVA / HDPE / tie / COC; PVC / tie / HDPE / EVA / HDPE / tie / PP; PVC / tie / HDPE / EVA / HDPE / tie / PETG; PVC / tie / HDPE / EVA / HDPE / tie / PLA; PVdC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / COC; PVdC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / PP; PVdC / tie /

HDPE-Blend / EVA / HDPE-Blend / tie / PETG; PVdC / tie / HDPE-Blend / EVA / HDPE-Blend / tie / PLA; PVdC / tie / HDPE / EVA / HDPE / tie / COC; PVdC / tie / HDPE / EVA / HDPE / tie / PP; PVdC / tie / HDPE / EVA / HDPE / tie / PETG; PVdC / tie / HDPE / EVA / HDPE / tie / PLA.

- [47] It should be understood that in the examples described above, when a layer comprising a blend of a high density polyethylene, a high density polyethylene nucleation additive and/or hydrocarbon resin (HDPE-Blend), or a high density polyethylene (HDPE) is in direct contact with a layer comprising cyclic olefin copolymer (COC), the tie layer may not be required to bond these materials together, and thus structures having fewer tie layers may be created.
- [48] It should be understood that in the above-described generic embodiments, the thermoformed blister component may include additional film layers.
- [49] The total thickness of multilayer films of the thermoformed blister component **11** of the present invention is generally from about 12.7 μm (0.5 mil) to about 508 μm (20 mil), typically from about 50.8 μm (2 mil) to about 254 μm (10 mil), most typically from about 76.2 μm (3 mil) to about 203.2 μm (8 mil).
- [50] In accordance with the practice of the present invention, one embodiment of a lidding component **12** of the present invention is depicted in FIG. 5. In this embodiment, lidding component **12** comprises a laminate **400** having a first exterior layer **401**, and a second exterior layer **402**. Preferably, first exterior layer **401** comprises a metal foil such as aluminum, and second exterior **402** comprises adhesive material such as an acrylic coating which is heat sealable to polyvinylchloride (PVC) and polyvinylidene chloride (PVdC).
- [51] The blister packages of the present invention can be manufactured using methods known in the art. Generally, the blister cavities are thermoformed from the blister components of the present invention in-line just prior to filling the cavities with a product to be packaged. The lidding component is then unwound

from a roll and brought into contact with the formed and filled blister component such that the heat-seal layer of the lidding component contacts the blister component. The lidding and blister components are heat sealed, typically using a heated platen. Some areas of the package may not be sealed to provide a starting point for peeling off the lidding component prior to removing the product. If the lidding component is not pre-printed, printing is generally done just before heat sealing. After heat-sealing, the individual blisters may be perforated using methods known in the art so that they can be removed at point of use.

- [52]** The above description and the following examples illustrate certain embodiments of the present invention and are not to be interpreted as limiting. Selection of particular embodiments, combinations thereof, modifications, and adaptations of the various embodiments, conditions and parameters normally encountered in the art will be apparent to those skilled in the art and are deemed to be within the spirit and scope of the present invention.

What is claimed:

1. A blister component for a blister package, comprising:

a multilayer thermoplastic film comprising:

- i. first exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC);
- ii. a central core layer comprising a blend of a high density polyethylene and a high density polyethylene nucleation additive; and
- iii. a second exterior layer comprising a material selected from the group consisting of polyvinylchloride (PVC), polyvinylidene chloride (PVdC), cyclic olefin copolymer (COC), polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA).

2. A component according to claim 1, wherein the central core layer comprises a hydrocarbon resin.

3. A blister component for a blister package, comprising:

a multilayer thermoplastic film comprising:

- i. a first exterior layer comprising a polyvinylchloride or a polyvinylidene chloride;

- ii. a central core layer comprising a high density polyethylene and has a thickness of between 50 μm to 406 μm (2 mil to 16 mil); and
 - iii. a second exterior layer comprising a material selected from the group consisting of polyvinylchloride (PVC), polyvinylidene chloride (PVdC), cyclic olefin copolymer (COC), polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA).
- 4. A component according to claims 1 to 3, wherein the multilayer thermoplastic film comprises two interior layers each comprising a tie layer material.
 - 5. A component according to claim 4, wherein each of the two interior layers are in direct contact an exterior layer.
 - 6. A component according to claim 4, wherein each of the two interior layers are in direct contact the central core layer.
 - 7. A component according to claim 4, wherein the two interior layers each comprise a maleic anhydride modified ethylene elastomer.

8. A component according to claims 1 to 3, wherein the central core layer has a thickness of at least 40% of the total thickness of the multilayer thermoplastic film
9. A component according to claims 1 to 3, wherein the central core layer has a thickness of at least 45% of the total thickness of the multilayer thermoplastic film.
10. A component according to claims 1 to 3, wherein the central core layer has a thickness of at least 50% of the total thickness of the multilayer thermoplastic film.
11. A component according to claims 1 to 3, wherein the central core layer has a thickness of at least 55% of the total thickness of the multilayer thermoplastic film.
12. A component according to claims 1 to 3, wherein the central core layer has a thickness of at least 60% of the total thickness of the multilayer thermoplastic film.
13. A component according to claims 1 to 3, wherein the central core layer has a thickness of at least 65% of the total thickness of the multilayer thermoplastic film.

14. A component according to claims 1 to 3, wherein the central core layer has a thickness of at least 75% of the total thickness of the multilayer thermoplastic film.
15. A component according to claims 1 to 3, wherein each exterior layer has a thickness of less than 127 μm (5 mil).
16. A component according to claim 15, wherein each exterior layer has a thickness of between 19 μm to 50 μm (0.75 mil to 4 mil).
17. A blister component for a blister package, comprising:
a multilayer thermoplastic film comprising:
 - i. a first exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC); and
 - ii. a first interior layer comprising a blend of a high density polyethylene and a high density polyethylene nucleation additive;
 - iii. a central core layer;
 - iv. a second interior layer comprising a blend of a high density polyethylene and a high density polyethylene nucleation additive; and
 - v. a second exterior layer comprising a material selected from the group consisting of polyvinylchloride (PVC), polyvinylidene chloride (PVdC), cyclic olefin copolymer (COC), polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET),

oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA).

18. A blister component according to claim 17, wherein the first and second interior layer each comprises a hydrocarbon resin.
19. A blister component for a blister package, comprising:
a multilayer thermoplastic film comprising:
 - i. a first exterior layer comprising a polyvinylchloride (PVC) or a polyvinylidene chloride (PVdC);
 - ii. a first interior layer comprising a high density polyethylene and having a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil)
 - iii. a core layer;
 - iv. a second interior layer comprising a high density polyethylene and having a thickness of between 38.1 μm to 190.5 μm (1.5 mil to 7.5 mil); and
 - v. a second exterior layer comprising a material selected from the group consisting of polyvinylchloride (PVC), polyvinylidene chloride (PVdC), cyclic olefin copolymer (COC), polypropylene (PP), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG) and polylactic acid (PLA).

20. A component according to claims 17 to 19, wherein the multilayer thermoplastic film comprises a first tie layer and a second tie layer each comprising a tie layer material; wherein the first tie layer is positioned between the first exterior layer and the first interior layer, and the second tie layer is positioned between the second exterior layer and the second interior layer.
21. A component according to claims 17 to 19, wherein the first exterior layer has a thickness of less than 127 μm (5 mil), and more preferably, between 19 μm to 50 μm (0.75 mil to 4 mil).
22. A component according to claim 21, wherein the first exterior layer has a thickness between 19 μm to 50 μm (0.75 mil to 4 mil).
23. A component according to claim 20, wherein the first tie layer is in direct contact with both the first exterior layer and the first interior layer.
24. A component according to claim 20, wherein the second tie layer is in direct contact with both the second exterior layer and the second interior layer.
25. A component according to claim 20, wherein the first tie layer and the second tie layer each comprise a maleic anhydride modified ethylene elastomer.

26. A component according to claims 1 to 19, wherein the central core layer comprises a high density polyethylene having a density of at least about 0.96 g/cm³.
27. A component according to claims 1 to 19, wherein the cyclic olefin copolymer is formed from norbornene and ethylene monomers.
28. A component according to claims 1 to 19, wherein the cyclic olefin copolymer has a heat deflection temperature under load (0.45 MPa) of about 75° C.
29. A component according to claims 1 to 19, wherein the cyclic olefin copolymer has a heat deflection temperature under load (0.45 MPa) of about 130° C.
30. A component according to claims 1 to 19, wherein the cyclic olefin copolymer has a heat deflection temperature under load (0.45 MPa) of about 150° C.
31. A component according to claims 1 to 19, wherein the cyclic olefin copolymer has a heat deflection temperature under load (0.45 MPa) of about 170° C.
32. A component according to claims 1 to 19, wherein the multilayer thermoplastic film comprises at least 5 layers.

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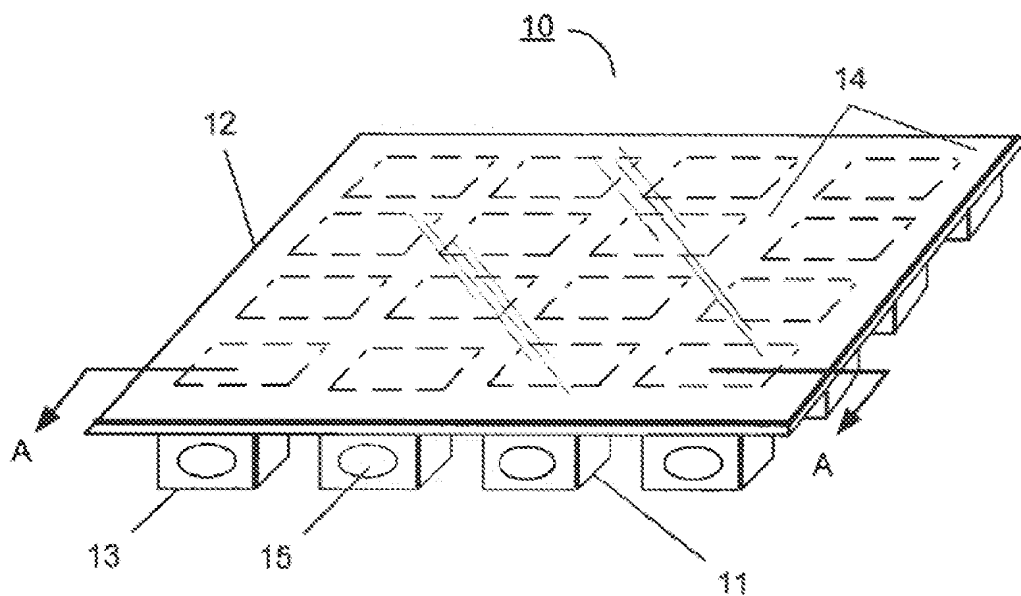
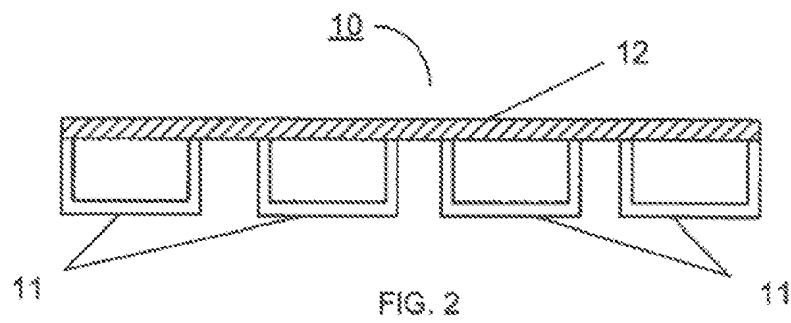


FIG. 1

2/12



3/12

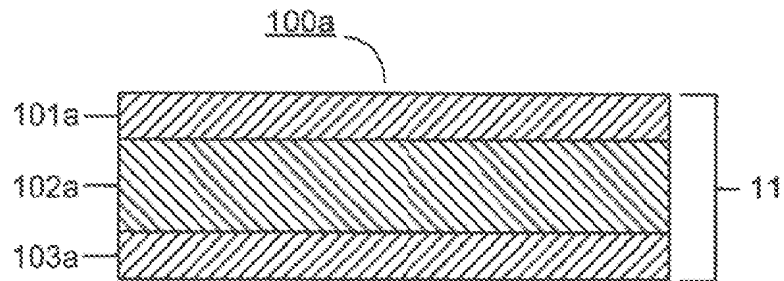


FIG. 3a

4/12

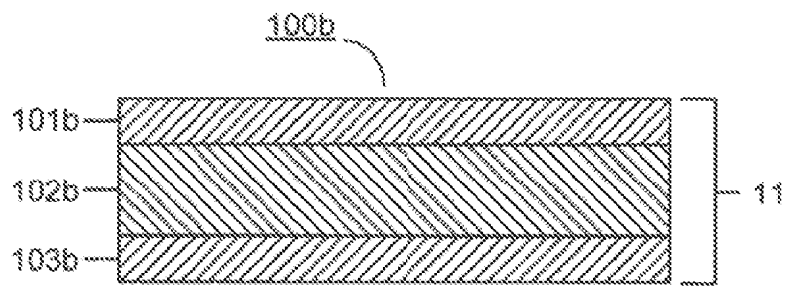


FIG. 3b

5/12

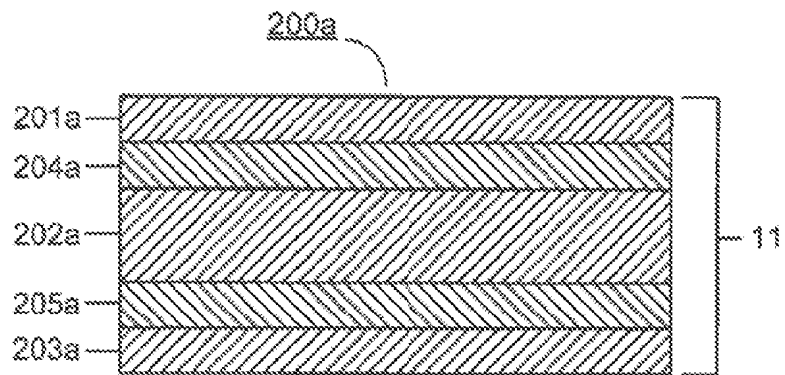


FIG. 4a

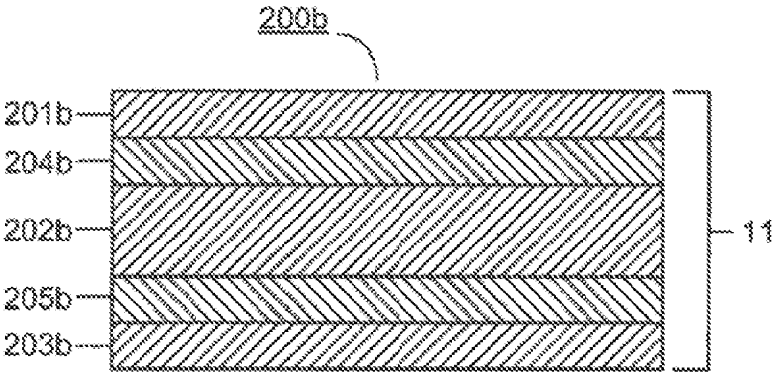


FIG. 4b

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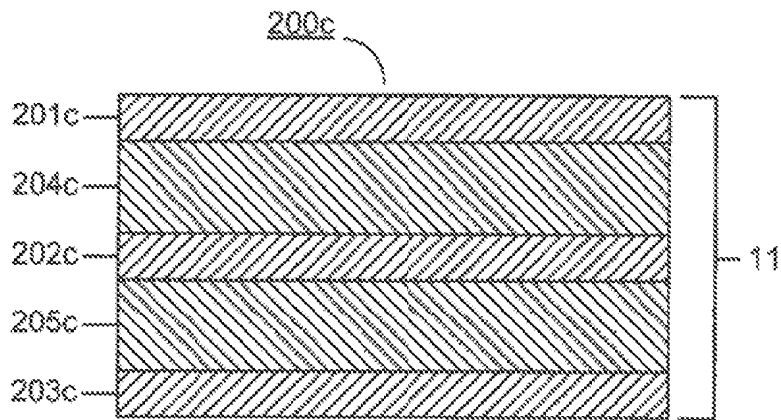


FIG. 4c

8/12

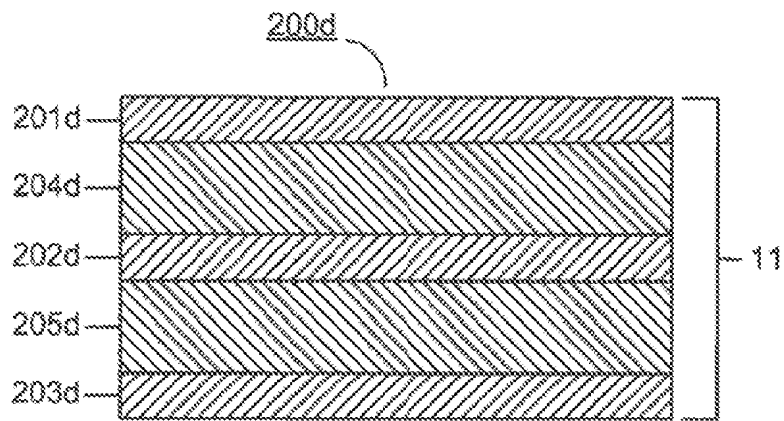


FIG. 4d

9/12

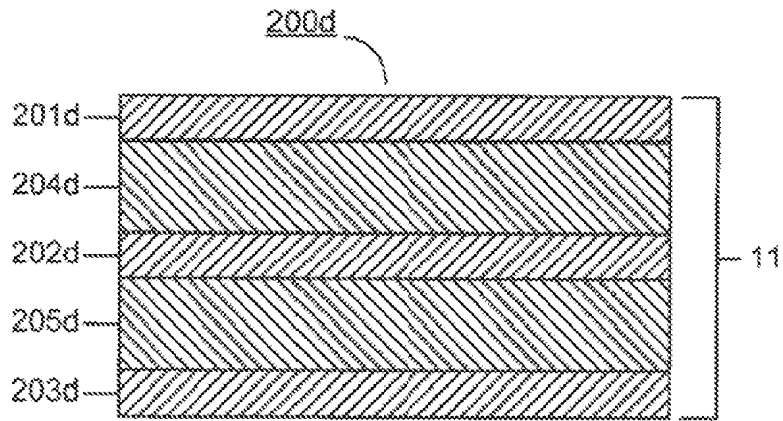


FIG. 4d

10/12

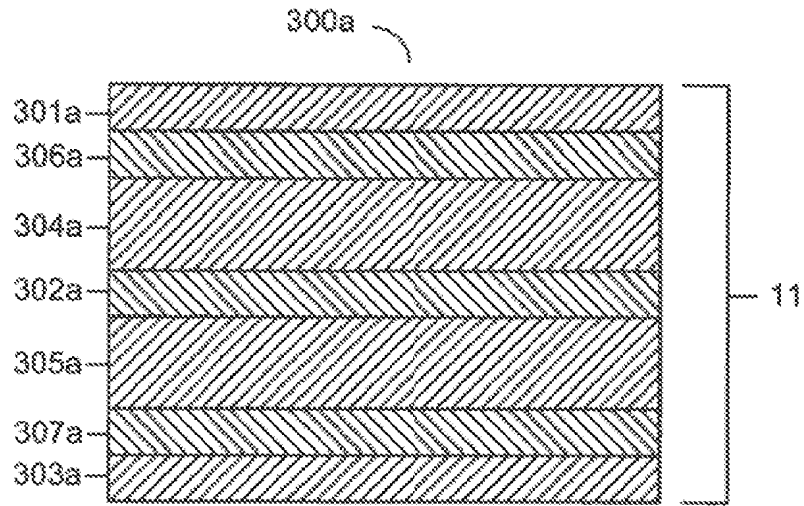


FIG. 5a

11/12

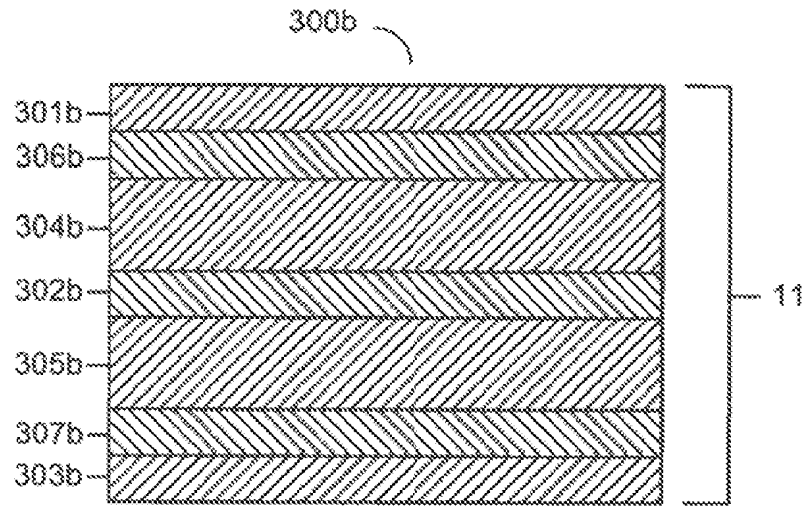


FIG. 5b

12/12

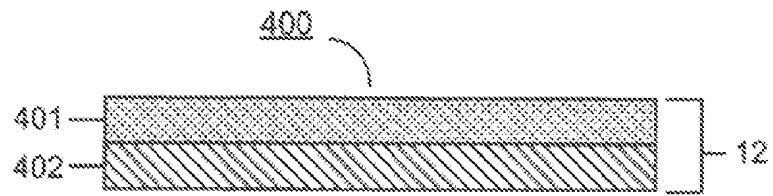


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 14/41260

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - B32B 27/00; B65D 83/04 (2014.01) CPC - B32B 27/32, 15/08 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) CPC: B32B 27/32, 15/08 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC: 206/531; 428/336 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PubWEST (USPT,PGPB,JPAB,EPAB); Google Search Terms: Blister packaging multilayer thermoplastic film exterior inner first polyvinylchloride core layer high density polyethylene nucleation agent polypropylene thickness hydrocarbon resin tie layer		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/0286547 A1 (Hubbard et al.) 20 Nov 2008 (20.11.2008), entire document especially abstract, para [0025], [0029], [0049], [0054]; claims 1 and 15	1-3 and 17-19
Y	US 2011/0049003 A1 (Bellamah et al.) 03 Mar 2011 (03.03.2011), entire document especially abstract, para [0017] and [0055]	1-3 and 17-19
A	US 6,969,740 B2 (Klosiewicz) 29 Nov 2005 (29.11.2005), entire document	1-3 and 17-19
☐ Further documents are listed in the continuation of Box C. ☐		
* 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 14 Sep 2014 (14.09.2014)		Date of mailing of the international search report 28 AUG 2015
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201		Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 14/41260

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-16 and 20-32
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.



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(71) Applicant: **BEMIS COMPANY, INC.** [US/US]; One Neenah Center 4th Floor, 134 E. Wisconsin Avenue, Neenah, WI 54956 (US).

(72) Inventors: **MCMILLAN, Lyndsey, A.**; 885 Maple Street, Neenah, WI 54956 (US). **BERBERT, Miriam, B.**; 1905 Timberline Drive, Oshkosh, WI 54904 (US).

(74) Agent: **HALL, Tom, J.**; Bemis Company, Inc., P.O. Box 669, Neenah, WI 54957 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM,

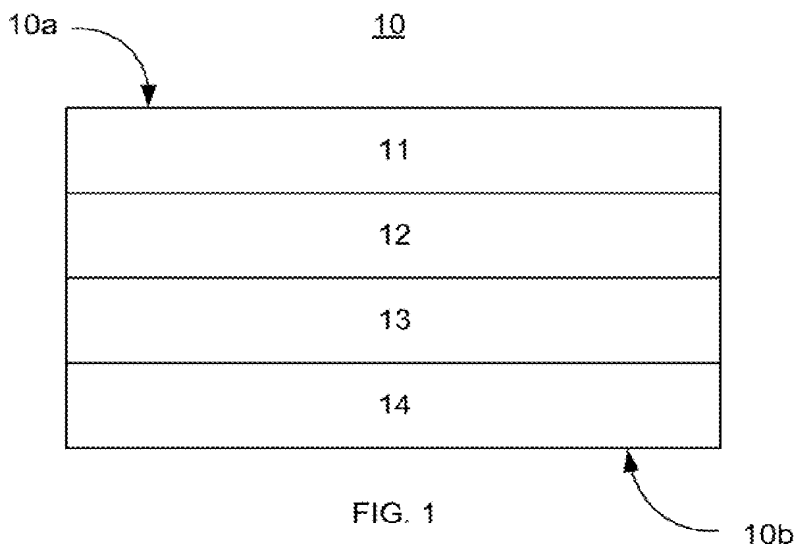
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: CHEMICALLY-RESISTANT BARRIER FILM



(57) Abstract: The present invention is directed to a laminate having a first exterior surface and a second exterior surface, the laminate includes a first layer comprising a heat sealable material, a second layer comprising a cyclic olefin copolymer, a third layer comprising a metallic foil or metallized polymer material, and a fourth layer comprising a thermoplastic film or paper. The laminate provides high oxygen and/or moisture barrier properties and can withstand the corrosive effects of products containing solvents, halogens or strong acids and bases.

CHEMICALLY-RESISTANT BARRIER FILM

BACKGROUND OF THE INVENTION

- [01] The present invention relates generally to primary packaging and more particularly, to multilayer high moisture barrier laminates for use as a chemically-resistant barrier film.
- [02] The food, beverage, and pharmaceutical industries have high demand for packages with characteristic high barrier to gases, water vapor and flavors, while maintaining durability. For this reason, flexible multilayer polymeric film is commonly used in a variety of packages and decorative applications. Regardless of the type of product stored in the package, it is necessary that the package be capable of containing the product without the film degrading due to the type of product. In some instances where metallic foil or metallized film is used as a barrier against air and moisture, it can be difficult to maintain the packaging film's integrity when solvents, halogens or strong acids and bases are present in the product. For example, commonly used topical antiseptic products contain isopropyl or ethyl alcohol, povidone iodine, poloxamer iodine, benzalkonium chloride, benzethonium chloride, or chlorhexidine gluconate as a single agent or in combination with alcohol. Food condiments such as mustard, ketchup, and horseradish typically include acetic, citric and/or formic acid as an ingredient. Those skilled in the art recognize that halogens, acids and bases can slowly destroy the barrier properties of a film by attacking the metal layer directly or by affecting the adhesion of the metal layer to other film layers. As a result, there is a need to develop packaging materials having a layer of metallic foil or metallized film which provides high oxygen and/or moisture barrier properties and which can withstand the corrosive effects of products containing solvents, halogens or acids and bases.

- [03]** Those skilled in the art will recognize that conventional film laminates commonly used in the healthcare packaging industry require multiple layers of biaxially oriented polyethylene terephthalate (OPET) which act as a chemical barrier to aggressive solvents and other chemicals. The metal foil layer and its adjacent layers of such laminates need to be protected against the ingress of these aggressive chemicals which could minimize or destroy the adhesion between these layers and ultimately affect the barrier properties of the laminate. Consequently, the method of making these conventional laminates is complex and costly because the foil layer and each of the OPET layers require a separate lamination operation in order to fabricate the final laminate structure. Therefore, it would be highly desirable to provide high oxygen and/or high moisture barrier film laminates which can withstand the aggressive chemical effects of solvents, halogens or acids and bases without the need for multiple layers of biaxially oriented polyethylene terephthalate (OPET).

SUMMARY OF THE INVENTION

- [04]** The present invention is directed to flexible chemically-resistant barrier laminates for packaging a product. The product may be a foodstuff, a personal health care product, a pharmaceutical product, an industrial product or an agricultural product. The laminate includes a first exterior layer comprising a thermoplastic film or paper, a second exterior layer comprising a heat sealable material, a first interior layer comprising metallic foil or metallized polymer material, and a second interior layer positioned between the first interior layer and the second exterior layer; wherein the second interior layer comprises a cyclic olefin copolymer. An important aspect of the present invention is relative positioning of the cyclic olefin copolymer layer with respect to other film layers of the laminate. The inventors have discovered that the layer of cyclic olefin copolymer can act as a chemical barrier to some substances that may migrate from the product through the film to the metallic foil or metallized film layer and cause undesirable

degradation of the barrier properties of the metallic foil or metallized film and/or undesirable delamination to adjacent layers. This in turn means that the cyclic olefin copolymer layer must be positioned between the sealant layer which is exposed to the product and the layer of metallic foil or metallized film. The cyclic olefin copolymer (COC) may be any copolymer having at least one norbornene structural moiety within the repeating backbone of the polymer. Typical cyclic olefin copolymers include both norbornene and olefin structural moieties. Preferably, the COC is a copolymer of ethylene and 2-norbornene. Suitable COCs for use in the present invention may have a heat deflection temperature under load (0.45 MPa) of about 75° C, or 130° C, or 150° C, or 170° C. Exemplary of commercially available cyclic olefin copolymers include, but are not limited to, the TOPAS® family of resins which is supplied by TOPAS Advanced Polymers, Inc. (Florence, KY, USA).

- [05] Another important aspect of the present invention is that the laminates have sufficient flexibility to permit the fabrication of flexible pouches, bags and the like on conventional packaging equipment such as for example, but not limited to vertical form-fill-seal or horizontal form-fill-seal manufacturing equipment. A precondition for such flexibility is that the laminates should exhibit a bending resistance (or stiffness) of between 51.4 and 177 Gurley Units (0.50 and 1.74 mNewton) in either the machine and/or transverse direction. Industry standards for measuring the bending resistance (or stiffness) adopted by the Technical Association of the Pulp and Paper Industry (TAPPI) can be used to characterize the bending resistance of the laminates of the present invention. Bending resistance can be measured in accordance with T 543 TAPPI test method. For example, the Gurley Stiffness value can be measured via a Gurley Stiffness Tester, manufactured by Gurley Precision Instruments of Troy, N.Y. The Gurley Stiffness Tester measures the externally applied moment required to produce a given deflection of a strip of material of specific dimensions fixed at one end and having a concentrated load applied to the other end. The results are obtained as

"Gurley Stiffness Units", which can be readily converted into force units, mNewton (mN) by multiplying the "Gurley Stiffness Units" by 9.807×10^{-3} .

- [06]** Still another important aspect of the present invention is that the laminates provide a barrier to the outside environment for products packaged within these laminates. The term "barrier" refers to laminates having an oxygen gas transmission rate of between 0 to 10.0 cm³/100 in²/24 hours (0 to 155 cm³/m²/24 hours) at 73° F (23° C) and 0% relative humidity and/or a water vapor transmission rate of between 0 to 0.1 g/100 in²/24 hours (0 to 1.55 g/m²/24 hours) at 100° F (38° C) and 90% relative humidity.

BRIEF DESCRIPTION OF THE DRAWINGS

- [07]** Further features and advantages of the present invention will become apparent from the following detailed description, taken in combination with the appended drawings, in which:
- [08]** FIG. 1 illustrates a schematic view of one preferred embodiment of a laminate according to the present invention.
- [09]** FIG. 2 illustrates a schematic view of another preferred embodiment of a laminate according to the present invention.
- [10]** FIG. 3 illustrates a schematic view of another embodiment of a laminate according to the present invention.
- [11]** FIG. 4 illustrates a schematic view of still another embodiment of a laminate according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

- [12]** Referring now more particularly to FIG. 1 of the drawings, a preferred embodiment of laminate **10** embodying the present invention is shown having at

least four layers. The laminate **10** has a first exterior surface **10a** and a second exterior surface **10b**, and comprises a first layer **11** comprising a heat sealable material, a second layer **12** comprising a cyclic olefin copolymer, a third layer **13** comprising metallic foil or metallized polymer material, and a fourth layer **14** comprising a thermoplastic film or paper. As can be seen, the first layer **11** forms the first exterior surface **10a** and the fourth layer **14** forms the second exterior surface **10b** of laminate **10**. Second layer **12** is positioned between first layer **11** and third layer **13**. In this embodiment, laminate **10** may include more layers than depicted and may include any number of film layers and film layer compositions depending upon both functional and aesthetic requirements of the laminate. For example, the thermoplastic film of fourth layer **14** may itself be a multilayer film having 2, 3, 4, 5, 6, 7 or more layers. Alternatively, the first layer **11** may include a multilayer film with the proviso that there is a second layer **12** containing a cyclic olefin copolymer disposed between it and the metallic foil or metallized polymer film of third layer **13**.

- [13] First layer **11** comprising a heat sealable material may be any thermoplastic material which forms a fusion or peelable fusion seal to itself or a similar material under pressure and heat. Such material may include, but is not limited to, homopolymers and copolymers of polyethylene such as low density polyethylene (LDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), ultra-low density polyethylene (ULDPE), ionomers and blends thereof. First layer **11** may also include copolymers of ethylene with one or more comonomers selected from C₃ to C₁₀ alpha-olefins such as propene, butene-1, hexene-1, octene-1, etc. in which the molecules of the copolymers comprise long polymer chains with relatively few side chain branches arising from the alpha-olefin which was reacted with ethylene. Heat sealable materials may also include ethylene vinyl acetate copolymers, ethylene acrylic acid copolymers, ethylene methacrylic acid, ethylene methacrylate copolymers and blends thereof. Heat sealable materials may even further include certain grades of cyclic olefin

copolymers. In one preferred embodiment, first layer **11** has a total thickness of at least 25.4 μm (1 mil). In another preferred embodiment, first layer **11** has a total thickness of about 50.8 μm (2 mil).

- [14] The second layer **12** comprises a cyclic olefin copolymer. Ethylene/norbornene copolymers are known commercially as cyclic olefin copolymers, "COC," with one or more different cyclic olefin units randomly or alternately attached to the ethylene polymer backbone. In general, COCs exhibit a high glass transition temperature (greater than 50° C), optical clarity, low heat shrinkage, low moisture absorption and low birefringence. These materials have been produced by a number of polymerization techniques which include chain polymerization of cyclic monomers such as 8, 9, 10-trinorborn-2-ene (norbornene) of 1, 2, 3, 4, 4a, 5, 8, 8a-octa-hydro-1, 4:5, 8-dimethanonaphthalene (tetracyclododecene) with ethane; or ring-opening metathesis of various cyclic monomers followed by hydrogenation. It is also contemplated that second layer **12** may comprise a blend of COC and another thermoplastic material such as, but not limited to homopolymers and copolymers of polyethylene.
- [15] Third layer **13** may comprise any metallic foil such as, but not limited to, aluminum, tin, copper and the like. These materials are well known in the art. Alternatively, third layer **13** may include a metallized polymer layer. Any conventional metallization technique known to those skilled in the art can be used to form a metallized polymer layer. An especially preferred metallization technique is vacuum deposition wherein the metal is vacuum evaporated and then deposited onto the polymer layer. (See, William Goldie in *Metallic Coating of Plastics*, Vol. 1, Electrochemical Publications Limited, Chap. 12 (1968), the disclosure of which is incorporated herein by reference in its entirety.) A metal may be preferably deposited onto a polymer layer by vapor deposition techniques, typically by applying the molten metal under vacuum by such techniques as electron beam evaporation, sputtering, induction heating, or

thermal evaporation. A particularly specific technique for metallization is by electron beam vacuum evaporation deposition methods. Preferred values for the average thickness of the metal are within the range of about 1.0 to 100 nanometers, with the preferred average thickness being within the range of about 3 to 25 nanometers. (1 micron equals 10^{-7} meters, and 1 nanometer equals 10^{-8} meters.) Regardless, the metal coating preferably has a thickness less than the polymer substrate on which it is deposited, preferably substantially less than said substrate. It is contemplated that the metallized polymer layer can also include a metal oxide such as but not limited to aluminum oxide.

- [16] The thermoplastic film of fourth layer 14 may include, but is not limited to, aromatic polyesters such as, but not limited to, polyethylene terephthalate (PET), oriented polyethylene terephthalate (OPET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG), aliphatic polyesters such as, but not limited to, polylactic acid (PLA); polyhydroxyalkonates including but not limited to polyhydroxypropionate, poly(3-hydroxybutyrate) (PH3B), poly(3-hydroxyvalerate) (PH3V), poly(4-hydroxybutyrate) (PH4B), poly(4-hydroxyvalerate) (PH4V), poly(5-hydroxyvalerate) (PH5V), poly(6-hydroxydodecanoate) (PH6D); or polyamides such as, but not limited to, oriented and unoriented nylon 6, nylon 66, nylon 6/66 and blends thereof, polystyrenes such as, but not limited to, high impact polystyrene (HIPS), general purpose polystyrene (GPPS), and styrene block copolymer (SBC). HIPS is sometimes called rubber-modified polystyrene and is normally produced by copolymerization of styrene and a synthetic rubber. (See Wagner, et al., "Polystyrene," The Wiley Encyclopedia of Packaging Technology, Second Edition, 1997, pp. 768-771 (John Wiley & Sons, Inc., New York, New York), which is incorporated in its entirety in this application by this reference.) Examples of HIPS include but are not limited to Impact Polystyrene 825E and Impact Polystyrene 945E, both of which are available from Total Petrochemicals USA, Inc.; EB6025 Rubber Modified High Impact Polystyrene, which is available

from Chevron Phillips Company (The Woodlands, Texas); and 6210 High Impact Polystyrene, which is available from Ineos Nova LLC (Channahon, Illinois). Alternatively, the thermoplastic film may comprise a polyolefin such as polyethylene including, but not limited to, high density polyethylene (HDPE), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), ultra-low density polyethylene (ULDPE) and blends thereof, or polypropylene and blends thereof. A non-limiting example of high density polyethylene includes Alathon® M6020 from Equistar Chemicals LP (Houston, Tex.). Other specific non-limiting examples of HDPE include Alathon® M6020 available from Equistar Chemicals LP (Houston, Tex.); Alathon® L5885 available from Equistar Chemicals LP (Houston, Tex.); ExxonMobil™ HDPE HD 7925.30 available from ExxonMobil Chemical Company (Houston, Tex.); and ExxonMobil™ HDPE HD 7845.30 available from ExxonMobil Chemical Company (Houston, Tex.). In one preferred embodiment, the thermoplastic film is uniaxially oriented. In another preferred embodiment, the thermoplastic film is biaxially oriented.

- [17] In contrast to a thermoplastic film, fourth layer 14 may alternatively comprise paper. Those skilled in the art can differentiate paper from paperboard based on a variety of different characteristics. For example, generally paper is composed of a single layer and has an area weight of less than 224 g/m^2 , preferably less than 224 g/m^2 , more preferably, less than 100 g/m^2 , and most preferably, less than 50 g/m^2 . In contrast to paper, paperboard usually consists of two or three layers and has an area weight of 224 g/m^2 or more. Typically, most papers have a thickness of between 2.54 and $254 \text{ }\mu\text{m}$ (0.1 and 10 mil), while paperboard is generally thicker than paper having a thickness of at least $305 \text{ }\mu\text{m}$ (12 mil). Suitable papers for use in the present invention include, but are not limited to Kraft paper, medical grade paper, bleached paper, vegetable parchment, water, grease and oil-resistant paper, waxed paper, specialty-treated paper, wet-strength paper, absorbent paper, tissue paper and coated paper. (See Brody, et

al., "Paper" and "Paperboard", The Wiley Encyclopedia of Packaging Technology, Second Edition, 1997, pp. 714-723 (John Wiley & Sons, Inc., New York, New York), which is incorporated in its entirety in this application by this reference.) Specific non-limiting examples of commercially available papers for use in the present invention include Duncote II HG high gloss calendared family of paper manufactured by Dunn Corporation (Port Huron, MI).

- [18]** Referring now to FIG. 2, there is shown a preferred embodiment of a six-layer laminate **20** which has the same layer compositions described above for laminate **10** and illustrated in FIG. 1, but also includes a fifth layer **15** a sixth layer **16**. Layers **15** and **16** are positioned on either side of the third layer **13** and adheres the foil or metallized polymer layer within the laminate structure. Accordingly, each of layers **15** and **16** may comprise an adhesive material or an extrusion lamination material such as, but not limited to ethylene acrylic acid copolymer, a polyurethane adhesive, and polyethylene including low density polyethylene and linear low density polyethylene or blends thereof.
- [19]** As shown in FIG. 3, there is illustrated a seven-layer preferred embodiment of a laminate **30** of the present invention. Laminate **30** includes the same layer compositions described above for laminate **20** and illustrated in FIG. 2, but further includes a seventh layer **17**. As depicted, seventh layer **17** is disposed between fourth layer **14** and sixth layer **16**. Layer **17** may include a polyethylene such as, but not limited to as low density polyethylene (LDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), ultra-low density polyethylene (ULDPE) and blends thereof.
- [20]** Alternatively, the laminate of the present invention may include an eight-layer structure **40** as illustrated in FIG. 4. This embodiment includes the same layer sequence having the same layer compositions as described above for laminate **30**, but further includes an eighth layer **18** positioned between the sixth layer **16**

and fourth layer **14**. Layer **18** may comprise a homopolymer or copolymer of polyethylene, an ethylene acrylic acid copolymer or blends thereof.

WORKING EXAMPLE

- [21] In the following example, laminate structure **30** was produced using tandem extrusion lamination apparatuses, and methods which are well known to those skilled in the art. Prior to lamination, a unitary film composed of layers **11** and **12** was fabricated by blown film co-extrusion film apparatus and methods which are also well known in the art. The unitary film and the remaining layers were fabricated into a laminate using a tandem laminator.

Example 1

- [22] Example 1 is one embodiment of laminate **30** of the present invention having a layer sequence (in the order as shown below) and layer compositions as described below and as illustrated in FIG. 3. Reported below is the layer composition relative to the total weight of the layer.

Layer 11 (Sealant): 82.3 wt.-% of a linear low density polyethylene (LLDPE)-DOWLEX™ 2045G (The Dow Chemical Company, Midland, MI, USA), 15 wt.-% of a low density polyethylene (LDPE)-Petrothene® NA952000 (Equistar Chemicals, LP, Houston, TX, USA) and 2.7 wt.-% of a polyethylene masterbatch comprising processing additives.

Layer 12: 100 wt.-% of a cyclic olefin copolymer (COC)-TOPAS® 8007F-400 (TOPAS Advanced Polymers, Inc., Florence, KY, USA).

Layer 15: 100 wt.-% of a polyurethane adhesive-Liofol® 3649/ Liofol® 6255 (Liofol Company, Cary, NC, USA).

Layer 13: 100 wt.-% of a 35 gauge aluminum foil-(Jiangsu Zhongji Lamination Materials Co., Ltd., Jiangyin City, Jiangsu Province, P.R.C.).

- Layer 16: 100 wt.-% of an ethylene acrylic acid copolymer (EAA)-Primacor[®] 3440 (The Dow Chemical Company, Midland, MI, USA).
- Layer 17: 100 wt.-% of a low density polyethylene (LDPE)-Petrothene[®] NA216000 (Equistar Chemicals, LP, Houston, TX, USA).
- Layer 14: 100 wt.-% of a 48 gauge biaxially oriented polyethylene terephthalate (OPET)-Skyrol[®] SP65 (SKC, Inc., Covington, GA, USA).

[23] In the following example, laminate structure **40** illustrated in FIG. 4 was produced using tandem extrusion lamination apparatuses, and methods which are well known to those skilled in the art. Prior to lamination, a unitary film composed of layer **11** was fabricated by blown film co-extrusion film apparatus and methods which are also well known in the art. The unitary film and the remaining layers were fabricated into a laminate by a tandem laminator.

Example 2

[24] Example 2 is one embodiment of laminate **40** of the present invention which was produced using tandem extrusion lamination apparatuses, and methods which are well known to those skilled in the art. Prior to lamination, a unitary film composed of layer **11** was fabricated by blown film co-extrusion film apparatus and methods which are also well known in the art. The unitary film and the remaining layers were fabricated into a laminate using a tandem laminator.

Layer 11 (Sealant): 82.3 wt.-% of a linear low density polyethylene (LLDPE)-DOWLEX[™] 2045G (The Dow Chemical Company, Midland, MI, USA), 15 wt.-% of a low density polyethylene (LDPE)- Petrothene[®] NA952000 (Equistar Chemicals, LP, Houston, TX, USA) and 2.7 wt.-% of a polyethylene masterbatch comprising processing additives.

- Layer 18: 100 wt.-% of a low density polyethylene (LDPE)-DOW™ LDPE 4012 (The Dow Chemical Company, Midland, MI, USA).
- Layer 12: 100 wt.-% of a cyclic olefin copolymer (COC)-TOPAS® 8007F-400 (TOPAS Advanced Polymers, Inc., Florence, KY, USA).
- Layer 15: 100 wt.-% of an ethylene acrylic acid copolymer (EAA)-Primacor® 3440 (The Dow Chemical Company, Midland, MI, USA).
- Layer 13: 100 wt.-% of a 35 gauge aluminum foil-(Jiangsu Zhongji Lamination Materials Co., Ltd., Jiangyin City, Jiangsu Province, P.R.C.).
- Layer 16: 100 wt.-% of an ethylene acrylic acid copolymer (EAA)-Primacor® 3440 (The Dow Chemical Company, Midland, MI, USA).
- Layer 17: 100 wt.-% of a low density polyethylene (LDPE)-Petrothene® NA216000 (Equistar Chemicals, LP, Houston, TX, USA).
- Layer 14: 100 wt.-% of a 48 gauge biaxially oriented polyethylene terephthalate (OPET)-Skyrol® SP65 (SKC, Inc., Covington, GA, USA).

[23] In the following comparative example, a laminate was produced using tandem extrusion lamination apparatuses, and methods which are well known to those skilled in the art. Prior to lamination, a primary unitary film composed of layer **11** was fabricated by blown film co-extrusion film apparatus and methods which are also well known in the art. Then this primary unitary film was laminated together with layers **18** and **12** to form a three-layer secondary unitary film. Subsequently, this secondary unitary film and the remaining layers were fabricated into a laminate using a tandem laminator.

Comparative Example 1

- [24]** Comparative Example 1 is a laminate having the layer sequence (in the order as shown below) as illustrated in FIG. 4, but with different layer compositions as described above for laminate **40**. Those skilled in the art will recognize that Comparative Example 1 is a conventional film laminate commonly used in the health and food packaging industry. Reported below is the layer composition relative to the total weight of the layer.

Layer 11 (Sealant): 100 wt.-% of a linear low density polyethylene (LLDPE)-DOWLEX™ 2045G (The Dow Chemical Company, Midland, MI, USA).

Layer 18: 100 wt.-% of a polyurethane adhesive-Liofol® 3649/ Liofol® 6255 (Liofol Company, Cary, NC, USA).

Layer 12: 100 wt.-% of a 36-48 gauge biaxially oriented polyethylene terephthalate (OPET)-Skyrol® SP65 (SKC, Inc., Covington, GA, USA).

Layer 15: 100 wt.-% of a polyurethane adhesive-Liofol® 3649/ Liofol® 6255 (Liofol Company, Cary, NC, USA).

Layer 13: 100 wt.-% of a 35 gauge aluminum foil-(Jiangsu Zhongji Lamination Materials Co., Ltd., Jiangyin City, Jiangsu Province, P.R.C.).

Layer 16: 100 wt.-% of an ethylene acrylic acid copolymer (EAA)-Primacor® 3440 (The Dow Chemical Company, Midland, MI, USA).

Layer 17: 100 wt.-% of a low density polyethylene (LDPE)-DOW™ LDPE 4012 (The Dow Chemical Company, Midland, MI, USA).

Layer 14: 100 wt.-% of a 48 gauge biaxially oriented polyethylene terephthalate (OPET)-Skyrol® SP65 (SKC, Inc., Covington, GA, USA).

- [25] The bending resistance of Example 2 was measured on a Gurley-type tester. This measurement substantially followed the test procedure in accordance with TAPPI Test Method T 543 "Bending Resistance of Paper (Gurley-Type Tester)". The results are reported below in TABLE 1.

TABLE 1-Gurley Stiffness		
	Example 2	
Gurley Stiffness (Gurley units)	MD	TD
Average	57.2	64.8
Std. Dev.	4.21	2.66
Max	73.7	72.3
Min	51.4	61.2
n=	24	25

- [26] The chemical resistance of Example 2 and Comparative Example 1 to various liquid substances was determined by folding a film specimen in half to form a 3 inch x 3 inch area pouch having two 0.375 in. side heat seals. Into each pouch there was placed a 10 mL aliquot of a liquid substance, the pouch was sealed with a third 0.375 in. side heat seal and then was laid flat for a number of days

under accelerated aging conditions in an aging chamber (50° C and 10% relative humidity). After 1, 5, 12, 22 and 32 days in the aging chamber, the pouch was opened, the liquid removed and the pouch was dried. A positive test result was indicated (“+”) when no discernable delamination of the foil layer to its adjacent layers or corrosion of the foil was observed. A negative test result was indicated (“-”) when delamination between the foil layer and its adjacent layers and/or corrosion of the foil was observed. The results for Example 2 and Comparative Example 1 are reported below in TABLES 2 and 3, respectively.

TABLE 2-Example 1 Chemical Resistance					
	Day 1	Day 5	Day 12	Day 22	Day 32
Iodine	+	+	+	+	+
Bleach	+	+	+	+	+
Tabasco	+	+	+	+	+
Ketchup	+	+	+	+	+
Propylene Glycol	+	+	+	+	+
Ammonia	+	+	+	+	+

Acetic Acid	+	+	+	+	+
Isopropanol	+	+	+	+	+
Water	+	+	+	+	+

TABLE 3-Comparative Example 1 Chemical Resistance					
	Day 1	Day 5	Day 12	Day 22	Day 32
Iodine	+	+	+	+	+
Bleach	+	+	+	+	+
Tabasco	+	+	+	-	-
Ketchup	+	+	+	+	-
Propylene Glycol	+	+	+	+	+
Ammonia	+	+	+	-	-

Acetic Acid	+	+	+	-	-
Isopropanol	+	+	+	+	+
Water	+	+	+	+	+

- [27] These accelerated aging test results indicate that the laminates of the present invention having a single layer of cyclic olefin copolymer (COC) between the sealant layer and the metal foil layer performed as well as or better than a conventional laminate structure having multiple layers of biaxially oriented polyethylene terephthalate (OPET).
- [28] The above description and examples illustrate certain embodiments of the present invention and are not to be interpreted as limiting. Selection of particular embodiments, combinations thereof, modifications, and adaptations of the various embodiments, conditions and parameters normally encountered in the art will be apparent to those skilled in the art and are deemed to be within the spirit and scope of the present invention.

What is claimed:

1. A flexible chemically-resistant barrier laminate for packaging a product, the laminate having a first exterior surface and a second exterior surface, the laminate comprising:

a first layer comprising a heat sealable material; wherein the first layer forms the first exterior surface of the laminate;

a second layer comprising a cyclic olefin copolymer;

a third layer comprising metallic foil or metallized polymer material; wherein the second layer is positioned between the first and third layers;

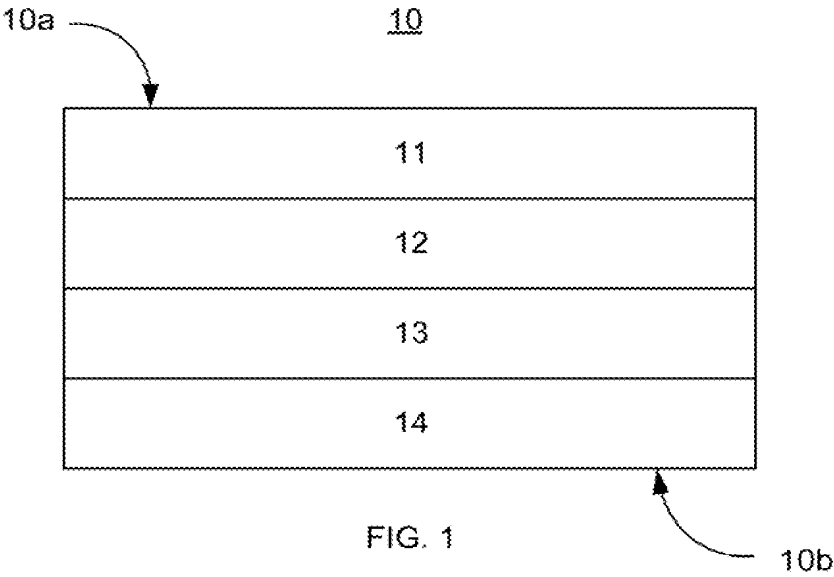
a fourth layer comprising a thermoplastic film or paper; wherein the fourth layer forms the second exterior surface of the laminate; and

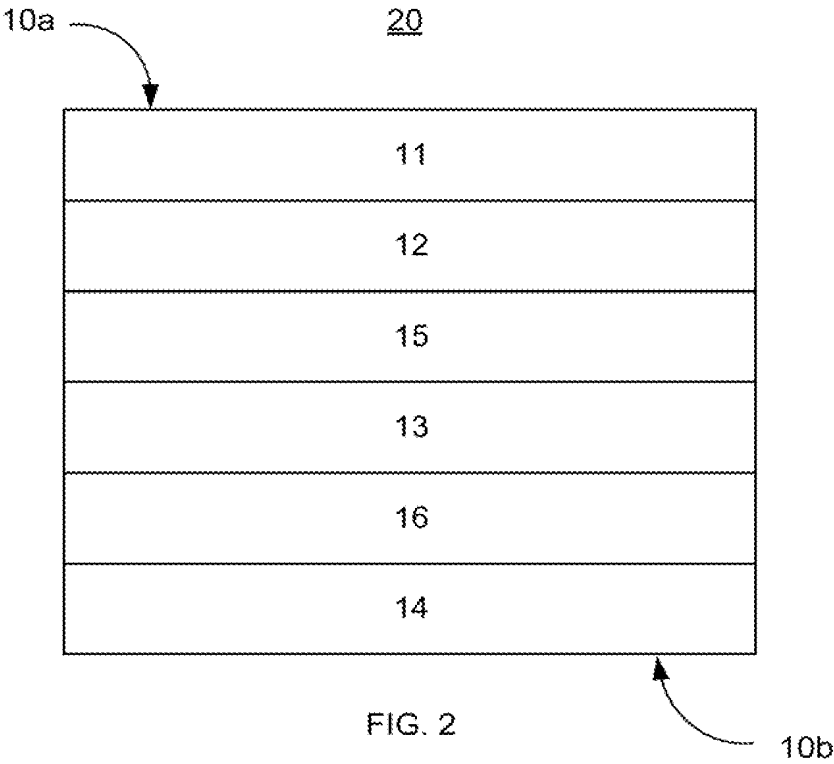
wherein the laminate has a bending resistance of between 51.4 and 177 Gurley Units (0.50 and 1.74 mNewton) in either the machine or transverse direction.
2. A laminate according to claim 1, wherein the paper has a thickness of between 25.4 and 305 μm (1 and 12 mil).
3. A laminate according to claim 1, wherein the paper has a basis weight of between 1 and 224 g/m^2 .
4. A laminate according to claim 3, wherein the paper has a basis weight of between 1 and 160 g/m^2 .

5. A laminate according to claim 4, wherein the paper has a basis weight of between 1 and 100 g/m².
6. A laminate according to claim 5, wherein the paper has a basis weight of between 1 and 50 g/m².
7. A laminate according to claim 1, wherein the thermoplastic film comprises a material selected from the group consisting of polyethylene terephthalate (PET), polypropylene (PP), polyamide (PA), high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC), high density polyethylene (HDPE), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), ultra-low density polyethylene (ULDPE) and blends thereof.
8. A laminate according to claim 7, wherein the thermoplastic film is oriented.
9. A laminate according to claim 1, wherein the laminate comprises a fifth layer and a sixth layer; wherein both the fifth and sixth layers comprise at least one of an ethylene acrylic acid copolymer and a polyurethane adhesive.
10. A laminate according to claim 9, wherein third layer is in direct contact with both the fifth and sixth layers.

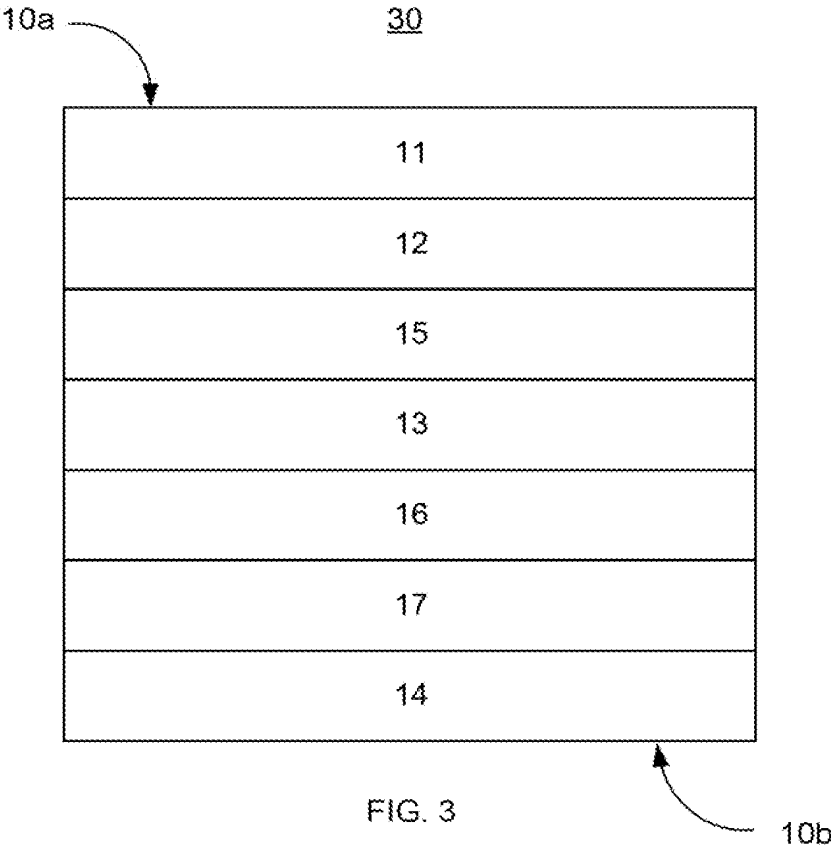
11. A laminate according to claim 11, wherein the laminate comprises a seventh layer disposed between the fourth layer and the sixth layer.
12. A laminate according to claim 11, wherein the seventh layer comprises a low density polyethylene.
13. A laminate according to claim 11, wherein the laminate comprises an eighth layer disposed between the first layer and the second layer.
14. A laminate according to claim 13, wherein the eighth layer comprises a low density polyethylene or a polyurethane adhesive.
15. A laminate according to claim 1, wherein the heat sealable material comprises a polyolefin.
16. A laminate according to claim 16, wherein the polyolefin comprises a polyethylene.
17. A laminate according to claim 17, wherein the polyethylene comprises a linear low density polyethylene.
18. A laminate according to claim 1, wherein the first layer has a total thickness of at least 25.4 μm (1 mil).

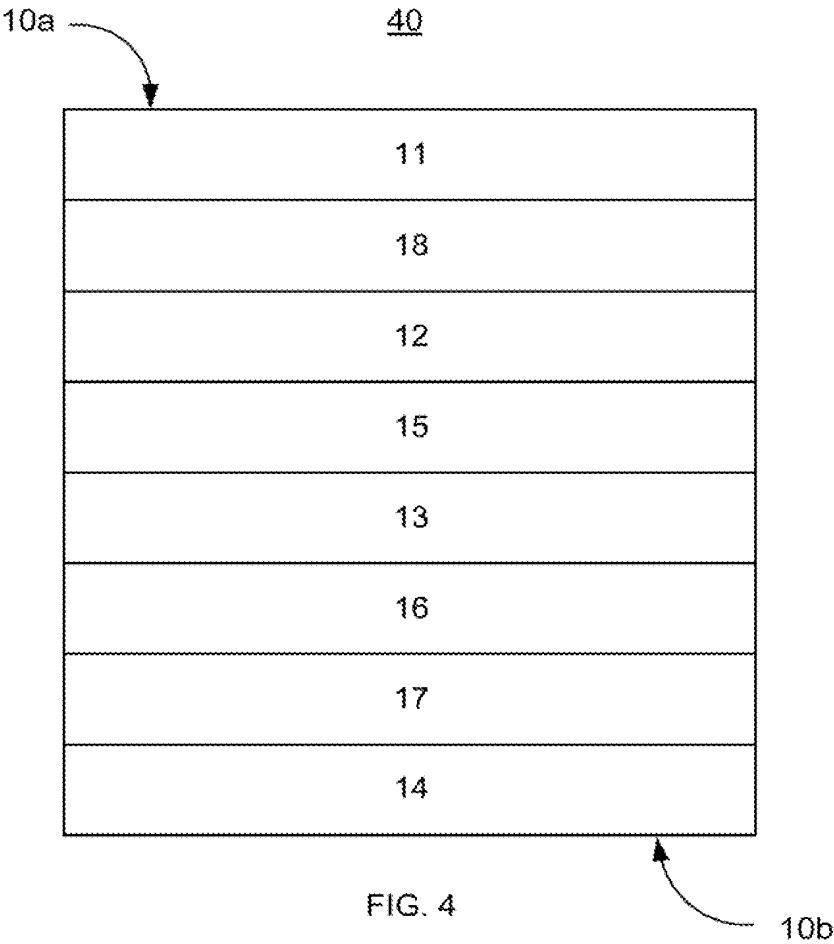
19. A laminate according to claim 17, wherein the first layer has a total thickness of about 50.8 μm (2 mil).
20. A laminate according to claim 1, wherein the cyclic olefin copolymer is an ethylene 2-norbornene copolymer.
21. A laminate according to claim 1, wherein the product is a foodstuff, a personal health care product, pharmaceutical product, industrial product or agricultural product.





3/4





INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 14/65133

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B32B 25/10 (2014.01)

CPC - C08J 5/24; B32B 25/02; B32B 27/12

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)

CPC (C08J5/24; B32B25/02; B32B27/12; B32B27/34; B32B27/06; B32B27/08; B32B27/36; B32B27/28; B32B15/08; B32B15/20; B32B27/32; B65D31/02; B31B37/00; B65D33/18; B31B2237/10; B31B23/00; B31B2237/05; C08J5/18; C08J2323/16; C08L23/0815; C08

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

USPC (428/297.1; 428/301.4; 383/106; 383/109; 383/121; 383/113; 383/123; 525/211; 428/220; 428/518; 428/41.8; 428/517; 428/519; 428/354; 428/41.3; 428/516; 428/520; 426/129; 428/318.6; 428/317.7; 156/244.19; 428/316.6; 428/308.4; 428/218; 206/497; 156/244.11;

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatBase, Google Patents/Scholar - Terms: flexible laminate packaging multilayer chemically resistant heat-sealable cyclic olefin polymer metal bending resistance Gurley thermoplastic paper micro-Newton polyurethane adhesive basis-weight thickness norbornene thermal insulating isolating foil wrap box container bag flexural strength ring stiffness te

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2010/100490 A1 (FORSYTH) 10 Sep 2010 (10.09.2010) pg 3, para 3 and 7; pg 4, para 1-3; pg 5, para 3; abstract; figures 1 and 2	1-21
Y	US 2007/0047853 A1 (SHARP et al.) 1 March 2007 (01.03.2007) para [0008], [0012], [0059], [0066], [0067]; table 4; figure 21	1-21
Y	US 6,111,019 A (ARJUNAN et al.) 31 March 1997 (31.03.1997) abstract; col 2, ln 33-59	1-21
Y	WO 2013/086950 A1 (REN et al.) 20 June 2013 (20.06.2013) pg 9, para 3	2-6
A	US 2008/0050651 A1 (WAKAI et al.) 28 Feb 2008 (28.02.2008) -- the entire patent	1

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

* 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

02 January 2015 (02.01.2015)

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(71) Applicant: **POLYONE CORPORATION** [US/US];
33587 Walker Road, Avon Lake, Ohio 44012 (US).(72) Inventors: **DUAN, Yannan**; 1510 Crossings Parkway,
Westlake, Ohio 44145 (US). **AVAKIAN, Roger W.**; 6611
Duneden Avenue, Solon, Ohio 44139-4047 (US).(74) Agents: **HORNICKEL, John H.** et al.; Polyone Corpora-
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DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
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TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*
- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*

(54) Title: CHEMICALLY RESISTANT AND TOUGH CYCLIC OLEFIN COPOLYMER COMPOUNDS

(57) Abstract: Cyclic olefin copolymer (COC) has its impact toughness and its resistance to UV absorbers and fatty acid derivatives enhanced to commercially acceptable levels by the addition of an impact modifying polymer selected from the group consisting of styrenic block copolymers and olefinic block copolymers and combinations thereof; and a linear or branched polyolefin, respectively.



WO 2016/164794 A1

Chemically Resistant and Tough Cyclic Olefin Copolymer Compounds

CROSS-REFERENCE

[0001] This application claims the benefit of the filing date under 35 U.S.C. § 119 to U.S. provisional patent application Serial No. 62/146,036 filed April 10, 2015 and entitled “Chemically Resistant and Tough Cyclic Olefin Copolymer Compounds,” and to U.S. provisional patent application Serial No. 62/209,332 filed August 24, 2015 and entitled “Chemically Resistant and Tough Cyclic Olefin Copolymer Compounds,” the disclosures of which are incorporated by reference in their entireties for all purposes.

FIELD

[0002] The disclosure relates generally to polymers having chemical resistance and impact toughness to cyclic olefin copolymer. More particularly, various embodiments related to combinations of cyclic olefin copolymers with impact modifying polymers and polyolefins.

BACKGROUND

[0003] Cyclic olefin copolymer (COC) is an amorphous, transparent copolymer based on polymerization of a combination of cyclic olefins and linear olefins. COC has high transparency, low water absorption, variable heat deflection temperature up to 170°C and good resistance to acids and alkalis.

[0004] But COC also is known to have poor resistance to certain other chemicals with considerable chemical reactivity. Often, one common consumer product, sunscreen lotions which contain ultraviolet absorbers and fatty acid derivatives, serves as a litmus test of chemical resistance for polymers to be used in consumer products. The lack of chemical resistance of COC to sunscreen lotions hinders its use in consumer products. The ultraviolet absorbers and fatty acid derivatives in sunscreen make that lotion, when contact with a polymer compound, relentless in reactivity with COC.

[0005] Also COC is not tough enough to be suitable for metal replacement in many consumer products. COC needs impact strength.

[0006] As replacement of metal with polymers is considered for many consumer products from automobile parts to handheld electronic devices, COC has not been chosen because of its lack of chemical resistance and lack of toughness.

SUMMARY

[0007] What the art needs is a chemically resistant, tough COC to become a candidate for metal replacement in consumer products.

[0008] It has been found, unexpectedly, that a combination of two other polymer types can provide both chemical resistance and impact toughness, particularly in balance, to be suitable for any consumer product as a metal replacement initiative.

[0009] One aspect of the disclosure is directed to a cyclic olefin copolymer compound comprising (a) cyclic olefin copolymer; (b) an impact modifying polymer selected from the group consisting of styrenic block copolymers and olefinic block copolymers and combinations thereof; and (c) a linear polyolefin, wherein the linear polyolefin resists chemical attack against the cyclic olefin copolymer by ultraviolet light absorbers.

[00010] Another aspect of the disclosure is directed to a cyclic olefin copolymer compound comprising (a) cyclic olefin copolymer; (b) an impact modifying polymer selected from the group consisting of styrenic block copolymers and olefinic block copolymers and combinations thereof; and (c) a branched polyolefin, wherein the branched polyolefin resists chemical attack against the cyclic olefin copolymer by ultraviolet light absorbers.

[00011] Another aspect of the disclosure is directed to any polymeric article made from either cyclic olefin copolymer compound identified above.

[00012] Embodiments of the disclosure explain the establishment of chemical resistance and impact strength in COC-based polymer compounds.

DETAILED DESCRIPTION

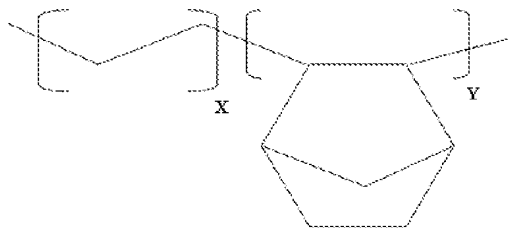
[00013] It should be understood that the following descriptions are not intended to limit the embodiments to any particular embodiment. To the contrary, it is intended to cover alternatives, modifications, and equivalents as can be included within the spirit and scope of the described embodiments as defined by the appended claims.

[00014] Embodiments of this disclosure are directed to a cyclic olefin copolymer compound comprising (a) cyclic olefin copolymer; (b) an impact modifying polymer selected from the group consisting of styrenic block copolymers and olefinic block copolymers and combinations thereof; and (c) a polyolefins, including linear polyolefins and branched polyolefins, which resist chemical attack against the cyclic olefin copolymer by ultraviolet light absorbers. These cyclic olefin copolymer compounds may further comprise one or more optional additives.

Cyclic Olefin Copolymer (COC)

[00015] Cyclic olefin copolymer (COC) can refer to copolymers of cyclic olefin monomers, such as norbornene or tetracyclododecene, with ethene or other alkenes. For example, in some embodiments, the COC may be an alkylene-tetracyclododecene copolymer, such as ethylene-tetracyclododecene copolymer or propylene-tetracyclododecene copolymer. In other embodiments, the COC may be an alkylene-norbornene copolymer, such as ethylene-norbornene copolymer or propylene-norbornene copolymer.

[00016] In some instances, the COC is ethylene-norbornene copolymer which has a CAS No. of 26007-43-2. Ethylene-norbornene copolymer may have the following structure:



wherein X ranges from about 40 wt.% to about 20 wt.%, such as from about 25 wt.% to about 18 wt.% and wherein Y ranges from about 60 wt.% to about 80 wt.% and such as from about 75 wt.% to about 82 wt.%. In some embodiments, X may range from about 40 wt.% to about 20 wt.%, such as from about 25 wt.% to about 18 wt.%. In other embodiments, X may be at least about 18 wt.% of the COC. In other embodiments, X may be at least about 20 wt.% of the COC. In other embodiments, X may be less than about 40 wt.% of the COC. In other embodiments, X may be less than about 25 wt.% of the COC. In some embodiments, Y may range from about 60 wt.% to about 80 wt.% and such as from about 75 wt.% to about 82 wt.%. In other embodiments, Y may be at least about 60 wt.% of the COC. In other embodiments, Y may be at least about 75 wt.% of the COC. In other embodiments, Y may be less than about 82 wt.% of the COC. In other embodiments, Y may be less than about 80 wt.% of the COC.

[00017] Any COC is a candidate for use in the disclosure to have its chemical resistance and impact toughness enhanced.

[00018] COC should have a weight average molecular weight (Mw) ranging from about 40,000 to about 130,000, such as from about 93,000 to about 125,000.

[00019] In some embodiments, COC can have a Mw of at least about 40,000. In other embodiments, COC can have a Mw of at least about 93,000. In yet other embodiments, COC can have a Mw of less than about 130,000. In still other embodiments, COC can have Mw of less than about 125,000.

[00020] COC can have a heat deflection temperature ranging from about 30°C to about 170°C, such as from about 75°C to about 170°C at 0.45 MPa (66 psi load).

[00021] In some embodiments, COC can have a heat deflection temperature of at least about 30°C. In other embodiments, COC can have a heat deflection temperature of at least about 75°C. In yet other embodiments, COC can have a heat deflection temperature of less than about 170°C. In still other embodiments, COC can have a heat deflection temperature of less than about 170°. In various embodiments, the heat deflection temperatures can be measured at a pressure of about 0.45 MPa (66 psi load).

[00022] Commercially available COC is sold by TOPAS Advanced Polymers using the TOPAS® brand. Of the commercial grades available, TOPAS® 6017S-04 COC, an injection molding grade, and TOPAS® 6013S-04, a general purpose injection molding grade may be selected because they have heat deflection temperatures within the TOPAS product family.

[00023] TOPAS® 6017S-04 COC has a Vicat softening temperature B50 (50°C/h 50N) is 178°C as tested using the procedure of ISO 306. Also, its degree of light transmission is 91% as tested using the procedure of ISO 13468-2. Its tensile modulus (1mm/min) is 3000 MPa as tested using the procedure of ISO 527-2/1A.

[00024] TOPAS® 6013S-04 COC has a Vicat softening temperature B50 (50°C/h 50N) of 137°C as tested using the procedure of ISO 306. Also, its degree of light transmission is 91% as tested using the procedure of ISO 13468-2. Its tensile modulus (1mm/min) is 2900 MPa as tested using the procedure of ISO 527-2/1A.

[00025] In some variations, the COC can be a polymer with low amounts of oligomers. The COC can volatilize or plasticize other polymers it may contact. In some variations, the COC is non-polar polymer such that the COC compound has very little adhesive attraction to polar polymer compounds.

Impact Modifiers

[00026] A polymer can be blended with COC to enhance impact toughness. Any well-known polymer known for providing impact strength to a polymer such COC can be used.

[00027] In some variations, the polymer includes an styrenic block copolymer (SBC). SBCs are block copolymers with at least one hard block of styrene monomer and one soft block of olefin monomer. Of the SBCs commercially available, styrene-butadiene-styrene (SBS), styrene-ethylene-butylene-styrene (SEBS), and styrene-ethylene-propylene-styrene (SEPS) are the leading SBCs used. Kraton LLC sells many different grades and combinations of these SBCs. Without wishing to be limited to a particular mechanism or mode of action, the styrenic block copolymers (SBCs) can provide elastomeric properties to a non-elastomeric polymer resin.

[00028] In some embodiments, the SBC may be selected from styrene-butadiene-styrene (SBS), styrene-ethylene-butylene-styrene (SEBS), styrene-ethylene-propylene-styrene (SEPS), styrene-isobutylene-styrene (SIBS), and combinations thereof. In some embodiments, the SBC is styrene-butadiene-styrene (SBS). In some embodiments, the SBC is styrene-ethylene-butylene-styrene (SEBS). In some embodiments, the SBC is styrene-ethylene-propylene-styrene (SEPS). In some embodiments, the SBC is styrene-isobutylene-styrene (SIBS).

[00029] In some variations, the impact modifier is an olefin block copolymer (OBC). OBCs are block copolymers with at least one hard block of polyethylene and one soft block of α -olefin ethylene copolymer. Dow Chemical sells many different grades and combinations of these OBCs. Without wishing to be limited to a particular mechanism or mode of action, OBCs may also provide elastomeric properties to a non-elastomeric polymer resin.

Chemical Resistance Polymer

[00030] Polyolefins can provide chemical resistance against sunscreen lotion without unduly affecting the basic properties of COC. Further, the polyolefin can provide chemical resistance without unduly affecting the enhanced toughness provided by the impact modifier.

[00031] Any polyolefin can be used as a chemical resister to UV absorbers in sunscreen lotion. What is surprising is that the COC itself is olefinic but includes a linear polyolefins to provide the chemical resistance.

[00032] In some embodiments, the polyolefin is a polyalkylene. Non-limiting examples of suitable polyolefins include both polyethylenes (such as high density polyethylene (HDPE) and linear low density polyethylenes (LLDPE)) and linear and branched polypropylenes. These olefins can be acquired commercially from a large number of suppliers in a variety of grades and combinations.

Optional Additives

[00033] The compound of the present disclosure can include conventional plastics additives in an amount that is sufficient to obtain a desired processing or performance property for the compound. The amount should not be wasteful of the additive or detrimental to the processing or performance of the compound. Those skilled in the art of thermoplastics compounding, without undue experimentation but with reference to such treatises as Plastics Additives Database (2004) from Plastics Design Library (elsevier.com), can select from many different types of additives for inclusion into the compounds of the present disclosure.

[00034] Non-limiting examples of optional additives include adhesion promoters; biocides; antibacterials; fungicides; mildewcides; anti-fogging agents; anti-static agents; bonding, blowing agents; foaming agents; dispersants; fillers; extenders; fire retardants; flame retardants; flow modifiers; smoke suppressants; impact modifiers; initiators; lubricants; micas; pigments, colorants

and dyes; plasticizers; processing aids; release agents; silanes, titanates and zirconates; slip agents; anti-blocking agents; stabilizers; stearates; ultraviolet light absorbers; viscosity regulators; waxes; and combinations of them.

[00035] In some embodiments, the optional additive is titanate comprising titanium dioxide. In some embodiments, the optional additive is a polyhedral oligomeric silsesquioxane (POSS), such as trisilanol-isobutyl POSS® or octaisobutyl POSS®. In some embodiments, the optional additive is a highly branched polyester dendrimer. In some embodiments, the optional additive is an antioxidant chosen from a phenolic primary antioxidant (such as Irganox™ 1010) or a phosphite antioxidant (such as Songnox™ 1680).

[00036] In some embodiments, the optional additives are melt-mix additives, which may not chemically react with the other cyclic copolymer compound constituents. When added, these optional additive may be solid ingredient additives to a melted copolymer compound.

[00037] Table 1 shows ranges of ingredients in polymeric articles containing thermally conductive, electrically insulative additives, all expressed in weight percent (wt. %) of the entire compound. The compound can comprise, consist essentially of, or consist of these ingredients. Any number between the ends of the ranges is also contemplated as an end of a range, such that all possible combinations are contemplated within the possibilities of Table 1 as candidate compounds for use in this disclosure.

Table 1			
	Broad	Intermediate	Narrow
COC	40-75	49-67	48-57
SBC or OBC Impact Modifier	10-30	15-25	23-26
Olefin Chemical Resistance Polymer	15-30	18-26	20-26
Optional Additives	0-7	0-5	0-5

[00038] In some variations, the cyclic olefin copolymer compound disclosed herein may have a notched Izod measurement ranging between about 10.4 ft.lb/in to about 13.4 ft.lb/in (between about 718 J/m and about 556 J/m), such as between about 10.4 ft.lb/in to about 11 ft.lb/in, between about 11 ft.lb/in to about 12 ft.lb/in, or between about 12 ft.lb/in to about 13 ft.lb/in. In some embodiments, the cyclic olefin copolymer compound may have a notched Izod measurement of at least about 10.4 ft.lb/in (556 J/m). In other embodiments, the cyclic olefin copolymer compound may have a notched Izod measurement of less than about 13.4 ft.lb/in (718 J/m).

[00039] In other variations, the cyclic olefin copolymer compounds disclosed herein may have a tensile strength ranging between about 2940 psi and about 3710 psi, such as between about 2940 psi and about 3000 psi, between about 3000 psi and about 3100 psi, between about 3100 psi and about 3200 psi, between about 3200 psi and about 3300 psi, between about 3300 psi and about 3400 psi, between about 3400 psi and about 3500 psi, between about 3500 psi and about 3600 psi, and between about 3600 psi and about 3700 psi. In some embodiments, the cyclic olefin copolymer compound may have a tensile strength of at least about 2940 psi. In some embodiments, the cyclic olefin copolymer compound may have a tensile strength of less than about 3710 psi.

[00040] In other variations, the cyclic olefin copolymer compounds disclosed herein may have an elongation percentage ranging between about 36% to about 96%, such as between about 36% and about 40%, between about 40% and about 45%, between about 45% and about 50%, between about 50% and about 55%, between about 55% and about 60%, between about 60% and about 65%, between about 65% and about 70%, between about 70% and about 75%, between about 75% and about 80%, between about 80% and about 85%, between about 85% and about 90%, or between about 90% and about 95%. In some embodiments, the cyclic olefin copolymer compound may have an elongation percentage of at least 36%. In some embodiments, the cyclic olefin

copolymer compound may have an elongation percentage of less than about 96%.

[00041] In other variations, the cyclic olefin copolymer compounds disclosed herein may have a tensile modulus ranging between about 113 ksi and about 166 ksi, such as between about 113 ksi and about 115 ksi, between about 115 ksi and about 120 ksi, between about 120 ksi and about 125 ksi, between about 125 ksi and about 130 ksi, between about 130 ksi and about 135 ksi, between about 135 ksi and about 140 ksi, between about 140 ksi and about 145 ksi, between about 145 ksi and about 150 ksi, between about 150 ksi and about 155 ksi, between about 155 ksi and about 160 ksi, or between about 160 ksi and about 165 ksi. In some embodiments, the cyclic olefin copolymer compound may have a tensile modulus of at least about 113 ksi. In some embodiments, the cyclic olefin copolymer compound may have a tensile modulus of less than about 165 ksi.

[00042] In other variations, the cyclic olefin copolymer compounds disclosed herein may have a flex strength ranging between about 3905 psi and about 5967 psi, such as between about 3905 psi and about 4000 psi, between about 4000 psi and about 4500 psi, between about 4500 psi and about 5000 psi, between about 5000 psi and about 5500 psi, or between about 5500 psi and about 5900 psi. In some embodiments, the cyclic olefin copolymer compound may have a flex strength of at least about 3905 psi. In some embodiments, the cyclic olefin copolymer compound may have a flex strength of less than about 5900 psi.

[00043] In other variations, the cyclic olefin copolymer compounds disclosed herein may have a flex modulus ranging between about 106 ksi and about 167 ksi, such as between about 106 ksi and about 110 ksi, as between about 110 ksi and about 120 ksi, as between about 120 ksi and about 130 ksi, as between about 130 ksi and about 140 ksi, as between about 140 ksi and about 150 ksi, as between about 150 ksi and about 160 ksi, or as between about 160 ksi and about 167 ksi. In some embodiments, the cyclic olefin copolymer

compound may have a flex modulus of at least about 106 ksi. In some embodiments, the cyclic olefin copolymer compound may have a flex modulus of less than about 167 ksi.

Processing

[00044] Mixing in a continuous process typically occurs in an extruder that is elevated to a temperature that is sufficient to melt the polymer matrix with addition either at the head of the extruder or downstream in the extruder of the solid ingredient additives. Extruder speeds can range from about 50 to about 500 revolutions per minute (rpm), such as from about 100 to about 300 rpm. Typically, the output from the extruder is pelletized for later extrusion or molding into polymeric articles.

[00045] Mixing in a batch process typically occurs in a Banbury mixer that is also elevated to a temperature that is sufficient to melt the polymer matrix to permit addition of the solid ingredient additives. The mixing speeds range from 60 to 1000 rpm and temperature of mixing can be ambient. In some embodiments, the mixing speeds may be at least about 60 rpm. In other embodiments, the mixing speeds may be less than about 1000 rpm. Also, the output from the mixer may be chopped into smaller sizes for later extrusion or molding into polymeric articles.

[00046] Subsequent extrusion or molding techniques are well known to those skilled in the art of thermoplastics polymer engineering. Without undue experimentation but with such references as “Extrusion, The Definitive Processing Guide and Handbook”; “Handbook of Molded Part Shrinkage and Warpage”; “Specialized Molding Techniques”; “Rotational Molding Technology”; and “Handbook of Mold, Tool and Die Repair Welding”, all published by Plastics Design Library (elsevier.com), one can make articles of any conceivable shape and appearance using compounds of the present disclosure.

[00047] If COC polymer compounds can be formulated to be both tough and impact resistant, then compounds of the present disclosure can be made into any extruded, molded, calendered, thermoformed, or 3D-printed article. Candidate end uses for such thermoplastic articles are listed in summary fashion below.

[00048] Appliances: Refrigerators, freezers, washers, dryers, toasters, blenders, vacuum cleaners, coffee makers, and mixers;

[00049] Building and Construction: Fences, decks and rails, floors, floor covering, pipes and fittings, siding, trim, windows, doors, molding, and wall coverings;

[00050] Consumer Goods: Power hand tools, rakes, shovels, lawn mowers, shoes, boots, golf clubs, fishing poles, and watercraft;

[00051] Electrical/Electronic Devices: Printers, computers, business equipment, LCD projectors, mobile phones and other handheld electronic devices, connectors, chip trays, circuit breakers, and plugs;

[00052] Healthcare: Wheelchairs, beds, testing equipment, analyzers, labware, ostomy, IV sets, wound care, drug delivery, inhalers, and packaging;

[00053] Industrial Products: Containers, bottles, drums, material handling, gears, bearings, gaskets and seals, valves, wind turbines, and safety equipment;

[00054] Consumer Packaging: Food and beverage, cosmetic, detergents and cleaners, personal care, pharmaceutical and wellness containers;

[00055] Transportation: Automotive aftermarket parts, bumpers, window seals, instrument panels, consoles, under hood electrical, and engine covers; and

[00056] Wire and Cable: Cars and trucks, airplanes, aerospace, construction, military, telecommunication, utility power, alternative energy, and electronics.

[00057] The copolymer compounds and embodiments as described herein can be included in various electronic devices. Such electronic devices can be any electronic devices known in the art. For example, the device can be a

telephone, such as a mobile phone, and a land-line phone, or any communication device, such as a smart phone, including, for example an iPhone®, and an electronic email sending/receiving device. The alloys can be used in electric interconnects in a display, such as a digital display, a TV monitor, an electronic-book reader, a portable web-browser (e.g., iPad®), watch (e.g., AppleWatch), or computer monitor. Devices can also be entertainment devices, including a portable DVD player, conventional DVD player, Blue-Ray disk player, video game console, music player, such as a portable music player (e.g., iPod®), etc. Devices include control devices, such as those that control the streaming of images, videos, sounds (e.g., Apple TV®), or a remote control for a separate electronic device. The device can be a part of a computer or its accessories, laptop keyboard, laptop track pad, desktop keyboard, mouse, and speaker.

EXAMPLES

Comparative Examples A-K and Examples 1-22

[00058] Five series of experiments have been performed.

[00059] The First Series, Comparative Examples A-E showed COC formulations containing only impact modifier and pigments could not survive the Sunscreen Exposure Test identified below. All of Comparative Examples A-E showed stress cracking when undergoing the Sunscreen Exposure Test.

[00060] The Second Series, Comparative Examples F-K and Examples 1-3 showed the chemical resistance of COC under stress to sunscreen lotions can be significantly improved by blending with different polyolefins and different amounts of polyolefins. Some of the Examples showed very high notched Izod impact strength, close to 500 J/m. Most importantly, the distinctions between the successful Examples 1-3 and the unsuccessful Examples F-K demonstrate the unpredictability of how the addition of polyolefins counteracts the aggressiveness of sunscreen upon COC.

[00061] The Third Series, Examples 4-8 showed that formulations can be constructed to balance well both high notched Izod impact strength and sunscreen resistance of modified COC under the strain of the Sunscreen Exposure Test.

[00062] The Fourth Series, Examples 9-18 showed how the successful formulations of the Second and Third Series can have the flowability of COC blends improved by use of flow enhancers and selection of resin grades with different melt flow indices.

[00063] The Fifth Series, Examples 19-22 showed how use of linear and branched polypropylenes could also yield acceptable embodiments of the disclosure.

Test Methods

[00064] Tensile Test, Rigid ASTM D-638

[00065] Flexural Properties ASTM D-790

[00066] IZOD Impact (notched) ASTM D-256

[00067] Dielectric constant and dissipation factor, ASTM D150

[00068] Sunscreen Exposure Test, explained below

[00069] Xenon Arc Weathering, ASTM D-4459 with insulated black panel to monitor the temperature.

Sunscreen Exposure Test

[00070] The purpose of the test is to assess chemical resistance of COC formulations to sunscreen lotions while under strain.

[00071] Sample Preparation: The formulations are molded into ASTM D-638 Type I Tensile Bars and then fixed into a constant radius jig to induce 2.0% strain.

[00072] Sunscreen Lotion tested: Identified in the Tables 5-8

[00073] Test Procedures:

- [00074] Apply 1 ml of Lotion on the neck region (or extensometer region) of the Tensile Bar specimens and spread the Lotion to cover at least 1 cm² area.
- [00075] Gently wipe off any excess amount of Lotion using a clean, dry cloth but at least leave a layer of Lotion on surface of the Tensile Bar specimen.
- [00076] Repeat application of Lotion every 2 hrs for the first 8 hours and four times a day at 2 hour intervals for four days thereafter.
- [00077] Leave Tensile Bar specimens exposed to Lotion at room temperature (about 23°C) for 5 days.
- [00078] Wipe Tensile Bar specimens with a clean, dry cloth (no additional cleaning agents).
- [00079] Examine specimens for any crazing/cracking/breakage.

Formulations and Test Results

[00080] Table 2 shows the list of ingredients. Table 3 shows the extrusion conditions. Table 4 shows the molding conditions. Tables 5-10 show the recipes and the test results.

Table 2		
Brand Name	Ingredient and Purpose	Commercial Source
SCLAIR® 2907	HDPE (high density polyethylene)	NOVA Chemicals
Novapol® GF-0218	LLDPE (linear low density polyethylene)	NOVA Chemicals
Pro-Fax® 6331	PP (linear polypropylene)	Basell Polyolefins
Pro-Fax® HP403G	PP (linear polypropylene)	Basell Polyolefins
Inspire® 114	PP (branched polypropylene)	Braskem (formerly Dow)
SibStar® 102T	SIBS(Styrene Iso- Butylene Styrene, styrenic block copolymer)	Kaneka

Table 2		
Brand Name	Ingredient and Purpose	Commercial Source
Topas® 6017S	COC (cyclic olefin copolymer)	TOPAS Advanced Polymers, Inc.
Topas® 6013S	COC (cyclic olefin copolymer)	TOPAS Advanced Polymers, Inc.
Kraton® G1651	SEBS polymer	Kraton Performance Polymers, Inc.
TIONA® RCL 4	TiO ₂	Cristal Global
NOVAPOL® PI-2024-A	LLDPE (linear low density polyethylene)	NOVA Chemicals
SO1450	Trisilanol-isobutyl POSS®	Hybrid Plastics
MS0825	OctaIsobutyl POSS®	Hybrid Plastics
Boltron™ H20	Highly branched polyester dendrimer	Perstorp
Irganox™ 1010	Phenolic Primary Antioxidant	BASF
Songnox™ 1680	Phosphite Antioxidant	Songwon

Table 3	
Extruder Conditions	
All Comparative Examples and Examples	
Extruder Type	Prism 16mm TSE (40 L/D) screw extruder
Order of Addition	All ingredients mixed together and fed into the extruder hopper.
Zone 1	280 °C
Zone 2	280 °C
Zone 3	280 °C
Zone 4	280 °C
Zone 5	280 °C
Zone 6	280 °C

Table 3 Extruder Conditions All Comparative Examples and Examples	
Zone 7	280 °C
Zone 8	280 °C
Zone 9	280 °C
Die	280 °C
Revolution speed	300 rpm

Table 4 Molding Conditions All Comparative Examples and Examples	
Nissei 88 molding machine	
Drying Conditions before Molding:	
Temperature (°C)	80°C
Time (h)	16 hrs for First – Third, Fifth Series; 4 hrs for Fourth Series
Temperatures:	
Nozzle (°C)	260
Zone 1 (°C)	254
Zone 2 (°C)	249
Zone 3 (°C)	243
Mold (°C)	145 for First – Third, Fifth Series; 62 for Fourth Series
Oil Temp (°C)	43
Speeds:	
Screw RPM (%)	60
% Shot - Inj Vel Stg 1	50
% Shot - Inj Vel Stg 2	40
% Shot - Inj Vel Stg 3	30
% Shot - Inj Vel Stg 4	20
% Shot - Inj Vel Stg 5	10
Pressures:	
Hold Stg 1 (mPa) - Time(sec)	6
Hold Stg 2 (mPa) - Time(sec)	No stg 2
Timers:	
Injection Hold (sec)	7

Table 4	
Molding Conditions	
All Comparative Examples and Examples	
Nissei 88 molding machine	
Cooling Time (sec)	20
Operation Settings:	
Shot Size (mm)	44
Cushion (mm)	2.5 for First – Third Series; 3.2 for Fourth Series

First Series – Table 5					
Example	Comp. A	Comp. B	Comp. C	Comp. D	Comp. E
Kraton® G1651 SEBS	10.00		10.00	20.00	15.00
Topas® 6013S COC	88.00				
Topas® 6017S COC		98.00	88.00	78.00	83.00
TIONA® RCL 4 TiO ₂	2.00	2.00	2.00	2.00	2.00
Total (%)	100.0	100.0	100.0	100.0	100.0
Sunscreen Exposure Test Result (Three sunscreen lotions for First-series: Hawaiian Tropic® SPF 50, Coppertone® SPF 30, and Banana Boat® SPF 30)	—	Broke	Broke	Broke	Broke
Notched Izod (ft.lb/in)	—	0.22	1.12	3.29	2.67
Stdev (ft.lb/in)	—	0.01	0.09	0.17	0.10
Notched Izod (J/m)	—	11.40	60.10	176.00	143.00
Stdev (J/m)	—	0.25	4.85	8.82	5.32
Tensile strength (psi)	—	7511	7296.3	5641.4	6360.60
Stdev (psi)	—	662.5	140.7	49.4	37.70
Elongation%	—	2.054	5.67	15.539	7.44
Stdev (%)	—	0.243	0.649	1.765	2.32
Tensile modulus (ksi)	—	424.00	348.36	280.76	318.48
Stdev (ksi)	—	3.31	3.92	3.03	2.30
Flex strength (psi)	—	12988.6	13189.2	10094.9	11976.3

First Series – Table 5					
Example	Comp. A	Comp. B	Comp. C	Comp. D	Comp. E
Stdev (psi)	—	384.0	279.2	292.8	202.50
Flex modulus (ksi)	—	440.00	365.00	285.00	337.00
Stdev (ksi)	—	5.00	10.00	8.00	5.00
Xenon Arc Weathering (Hrs. according to Comp. Example)	CIE 94 Delta E				
A&E:145; B-D:142	0.10	0.66	0.57	0.75	0.20
A&E:315; B-D:311	0.20	0.67	0.51	0.55	1.16
A&E:482; B-D:479	0.38	1.52	1.06	0.84	2.38
A&E:650; B-D:642	0.89	3.28	2.46	2.04	3.88
A&E:818; B-D:813	1.78	4.96	4.29	3.48	5.43
A&E:983; B-D:983	1.85	5.74	5.35	4.75	6.74
B-D:1150		5.65	5.21	4.97	

Second Series – Table 6										
Example	Comp. F	1	Comp. G	2	Comp. H	3	Comp. I	Comp. J	Comp. K	
Topas® 6017S COC	60.00	54.00	60.00	54.00	60.00	54.00	40.00		80.00	80.00
Topas® 6013S COC								80.00		
Kraton® G1651 SEBS		20.00		20.00		20.00		20.00		
SCLAIR® 2907 HDPE	40.00	26.00					60.00			
Novapol® GF-0218 LLDPE			40.00	26.00						
Pro-Fax® 6331 PP					40.00	26.00				
SibStar® 102T SIBS									20.00	
Total (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Sunscreen Exposure Test Result (One sunscreen for Second Series: Banana Boat® SPF 30)	OK	OK	OK	OK	Broken	OK	OK	Broken	Broken	
Notched Izod (ft.lb/in)	0.34	4.98	0.56	9.27	0.26	1.21	0.54	8.14	0.41	
Stdev (ft.lb/in)	0.01	0.71	0.24	0.35	0.07	0.07	0.4	0.8	0.05	
Notched Izod (J/m)	17.9	266	30.1	495.5	13.7	64.9	28.9	435	21.9	
Stdev (J/m)	0.74	38.2	12.7	18.6	4.07	3.57	21.5	43	2.54	
Tensile strength (psi)	5485.7	4755	5038.2	4083.5	5430.2	4687.1	4046.2	5309.9	6290.8	

Second Series – Table 6										
Example	Comp. F	1	Comp. G	2	Comp. H	3	Comp. I	Comp. J	Comp. K	
Stdev (psi)	73.9	32.4	68.7	14.1	628.7	25	404.1	99.7	49.4	
Elongation%	3.392	22.891	9.25	27.909	2.776	6.354	6.409	13.721	3.434	
Stdev (%)	0.227	5.022	1.339	4.389	0.21	1.727	0.973	7.967	0.351	
Tensile modulus (ksi)	314.17	225.2	232.2	184.9	325.7	242.2	242.7	269.7	308.4	
stdev	1.7	1.3	2.4	1.9	20.2	3.3	9.4	3.8	10.5	
Flex strength (psi)	10457.8	8380.2	8810.9	7274.4	11086	8881.5	7770.3	10107.6	11607.5	
Stdev (psi)	86.7	63.9	88.5	73.3	1361.5	120.3	642.1	385.8	111.9	
Flex modulus (ksi)	336	238	246	202	332	263	265	295	325	
Stdev (ksi)	3	4	2	3	43	8	11	8	2	
Xenon Arc Weathering (Hrs.)	CIE 94 Delta E									
218	0.72	1.53	2.5	2.72	1.71	1.61	0.48	1.48	1.62	
330	1.43	1.86	2.57	2.48	1.19	1.09	1.89	1.52	4.37	
386	1.8	2.24	2.42	2.28	0.61	1.09	2.36	1.45	1.45	
551	3.35	3.19	1.38	1.63	0.76	1.16	3.99	1.46	1.66	

Third Series – Table 7					
Example	4	5	6	7	8
Kraton® G1651 SEBS	20.00	20.00	23.00	23.00	23.00
Topas® 6013S COC				35.00	24.00
Topas® 6017S COC	53.00	52.00	49.00	14.000	25.00
TIONA® RCL 4 TiO ₂	1.00	2.00	2.00	2.00	2.00
Novapol® GF-0218 LLDPE	26.00	26.00	26.00	26.00	26.00
Total (%)	100.0	100.0	100.0	100.0	100.0
Sunscreen Exposure Test Result (One sunscreen for Third Series: Banana Boat® SPF 30)	OK	OK	OK	OK	OK
Notched Izod (ft.lb/in)	9.74	9.82	10.8	12.1	11.6
Stdev (ft.lb/in)	0.38	0.44	0.52	0.51	0.48
Notched Izod (J/m)	521	525	578	649	622
Stdev (J/m)	19.1	23.7	27.2	26.6	25.5
Tensile strength (psi)	3959.9	3958.4	3663.3	3490.1	3592.4
Stdev (psi)	110.5	61.9	46.9	40.1	26
Elongation%	26.61	30.676	46.85	63.606	54.271
Stdev (%)	9.679	3.451	6.729	6.839	5.818
Tensile modulus (ksi)	176.61	177.95	162.48	161.88	163.82
Stdev (ksi)	4.77	2.46	2.18	1.71	1.49
Flex strength (psi)	6735.5	6581.9	5959.2	5739.1	5929.5
Stdev (psi)	183.3	181.8	121.9	57.1	55.7
Flex modulus (ksi)	179	173	156	153	157
Stdev (ksi)	8	5	4	3	2
Xenon Arc Weathering (Hrs.)	CIE 94 Delta E				
164	1.4	1.1	0.96	0.84	0.97
333	1.5	0.9	0.87	0.76	0.9

Fourth Series --Table 8										
Example	9	10	11	12	13	14	15	16	17	18
Kraton G1651 SEBS	20.00	23.000	23.00	23.00	23.00	23.00	23.00	23.00	23.00	23.00
Topas 6013S COC	52.00	49.00	35.00	34.00	32.00	34.00	30.00	34.00	30.00	35.00
Topas 6017S COC				14.00	14.00	14.00	14.00	14.00	14.00	14.00
TIONA® RCL 4 TiO ₂	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Novapol® GF-0218 LLDPE	26.00	26.00	40.00	26.00	26.00	26.00	26.00	26.00	26.00	
Boltron™ H20 Polyester Dendrimer				1.00	3.00					
SO1450 Trisilanol-Isobutyl POSS®						1.00	5.00			
MS0825 - Octa-Isobutyl POSS®								1.00	5.00	
NOVAPOL® PI-2024 LLDPE										26.00
Total (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Sunscreen Exposure Test Result (One sunscreen for Fourth- Series: Banana Boat® SPF 30)	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
Notched Izod (ft.lb/in)	13.0	13.4	12.5	12.8	12.7	12.9	12.3	13.1	13.0	10.4
Stdev (ft.lb/in)	0.2	0.27	0.24	0.16	0.24	0.39	0.21	0.26	0.23	0.35

Fourth Series --Table 8										
Example	9	10	11	12	13	14	15	16	17	18
Notched Izod (J/m)	693	718	666	684	679	688	660	697	692	556
Stdev (J/m)	10.6	14.3	12.2	9.31	11.9	21.1	11.2	13.7	12.9	18.6
Tensile strength (psi)	3710.7	3470.2	2935.9	3602.3	3504.5	3518.1	3185.8	3574.3	3249.6	3520.9
Stdev (psi)	57.5	27.7	26.4	57.5	68.3	23.1	39.1	58.2	19.4	54.3
Elongation%	37.211	66.074	96.426	43.905	44.997	42.336	57.626	56.897	55.426	36.376
Stdev (%)	15.136	10.442	4.85	7.152	10.354	8.047	14.412	9.681	17.092	2.982
Tensile modulus (ksi)	166.37	154.81	112.74	159.27	151.66	156.92	139.2	129.76	144.5	164.25
Stdev (ksi)	2.46	1.46	1.67	1.46	1.14	1.33	3.06	58.969	1.65	2.51
Flex strength (psi)	5967.2	5623.7	3904.3	5574.2	5554.9	5556.5	4892.7	5409.9	5001.8	5619
Stdev (psi)	27.1	74.9	21.5	58.3	112.9	25.8	38.4	38.8	21.8	41.4
Flex modulus (ksi)	167	156	106	152	149	151	134	148	141	158
Stdev (ksi)	2	2	1	1	3	2	1	1	1	1
Xenon Arc Weathering (Hrs.)	CIE 94 Delta E									
168	0.90	0.85	0.87	1.73	1.39	0.52	0.60	0.80	1.18	0.92

Fifth Series – Table 9				
Example	19	20	21	22
Kraton® G1651 SEBS	22.98	22.98	23	23
Topas® 6013S COC	34.91	34.91	35	35
Topas® 6017S COC	13.97	13.97	14	14
Inspire® 114 PP (0.5 melt flow rate ¹)	25.94		26	
Pro-Fax® HP403G (1.5 melt flow rate)		25.94		26
(Irganox 1010)	0.1	0.1	0	0
(Add ingredient here Songnox 1680)	0.1	0.1	0	0
TIONA® RCL 4 TiO ₂	2	2	2	2
Total (%)	100.0	100.0	100.0	100.0
Sunscreen Exposure Test Result (Banana Boat® SPF 30)	OK	OK	OK	OK
Notched Izod (ft.lb/in) ASTM D256	1.45	1.3	4.55	2.58
Stdev (ft.lb/in)	0.2	0.2	0.41	0.11
Notched Izod (J/m)	77.40	69.39		
Stdev (J/m)	10.7	10.7		
Tensile strength (psi) ASTM D-638	2290	4038	4003	4173
Stdev (psi)	45	29	65	17
Elongation% ASTM D-638	29	25	39	29
Stdev (%)	10.2	11.4	4.9	2.5
Tensile modulus (ksi) ASTM D-638	183.18	211.79	211.6	223.2
Stdev (ksi)	2.3	1.8	3.0	0.1
Flex strength (psi)	6678	7547		
Stdev (psi)	20.1	22.1		
Flex modulus (ksi)	202.20	217.30		
Stdev (ksi)	2.1	1.9		
Shore A Hardness ASTM D-2240 Instant			72.4	73.8
Shore A Hardness ASTM D-2240 15 second delay			67.9	69.3
Mean Brittle Failure Energy (MBFE) (in·lb) ASTM D-4226			240	257.3

Fifth Series – Table 9				
Example	19	20	21	22
MBFE stdev			3.6	3.3
MBFE/thickness (in·lb/mil)			1.94	2.1
Xenon Arc Weathering (Hrs. according to Comp. Example) ASTM D-2565	CIE 94 Delta E			
t=168h			0.77	0.87
t= 333h			0.64	0.68
t= 502h			0.48	0.54

¹ g/10 min (230°C/ 2.16 kg)

Table 10					
Frequency (Hz)	1 MHz	10MHz	100MHz	500MHz	1GHz
Comp. Example E					
Dielectric Constant	2.37	2.38	2.37	2.37	2.36
Dissipation Factor	8.84 $\times 10^{-3}$	3.62 $\times 10^{-3}$	0.63 $\times 10^{-3}$	0.10 $\times 10^{-3}$	0.00 $\times 10^{-3}$
Example 6					
Dielectric Constant	2.39	2.40	2.40	2.40	2.40
Dissipation Factor	2.09 $\times 10^{-3}$	3.02 $\times 10^{-3}$	2.70 $\times 10^{-3}$	0.00 $\times 10^{-3}$	0.13 $\times 10^{-3}$

[00081] Comparative Examples B-E all failed because none had any chemical resistance polymer added. Comparative Example A is expected to also fail, if it had been tested. Also Comparative Example B, which had no impact modifier either, had a very poor Notched Izod value, compared with Comparative Examples C-E which did have impact modifier.

[00082] Comparative Examples F, G, H, and I contained no impact modifier but did contain polyolefin chemical resistance modifier. While the results were acceptable against chemical resistance, the Notched Izod impact results were totally unacceptable. To be acceptable, one must have at least about 53 Joules/meter toughness (1.0 ft.lb/in) in the Notched Izod test. Desirably, the toughness is at least 265 J/m (5 ft.lb/in.), such as at least

530 J/m (10 ft.lb/in.) and has been found in one Example to be as much as 649 J/m (12.1 ft.lb/in.).

[00083] Comparative Examples J and K contained no polyolefin chemical resistance modifier. While the Notched Izod impact results were acceptable, the breakage failures of the Sunscreen Exposure Test were totally unacceptable.

[00084] This Second Series of tests confirms that the well-balanced COC polymer compound uses all three polymers: COC, impact modifier such as SBC, and chemical resistance modifier such as linear PP or PE to solve the deficiencies of COC respecting toughness and chemical resistance to sunscreen.

[00085] However, what distinguishes Examples 1-3 from Comparative Examples A-K is the presence of both impact modifier and chemical resistance modifier. Acceptable chemical resistance is achieved whether the polyolefin is HDPE, LLDPE, or linear PP (Examples 1, 2 or 3, respectively).

[00086] The success of Examples 1-3 provided the basis for the Third and Fourth Series experiments which further refined embodiments of the disclosure. The Third Series explored the grades of COC to benefit from the disclosure, and some variation in impact modifier content. The Fourth Series continued that exploration along with consideration of flow modifiers. The test results indicated that the COC polymer compound can produce intricate, thin-walled parts by injection molding without defects by use of a variety of flow modifiers. We have observed improvement of surface visually of molded parts (1/8 inch ASTM bars). The surface tends to be smoother.

[00087] The Fifth Series experiments showed that use of either linear polypropylene or branched polypropylene as an Olefin Chemical Resistance Polymer resulted in acceptable chemical resistance and physical properties. It was also noted that the titanium dioxide for coloration also provided increased apparent hardness of the polymer compound when molded. Examples 19 and 20 differed from Examples 21 and 22 based on the use of minor amounts of anti-oxidants, further indicating to a person having ordinary skill in the art how properties of the desired polymer compound are affected by optional additives. Nonetheless, the chemical resistance and physical properties were acceptable with or without such antioxidants, regardless whether a linear or a branched polypropylene was used.

[00088] Xenon Arc Weathering data demonstrated that for the First Series, all formulations showed very low delta E under the Xenon Arc weathering test. The CIE 94 Delta E is less than 2 after 300 hours. For the Second Series, the CIE 94 delta E varies in the

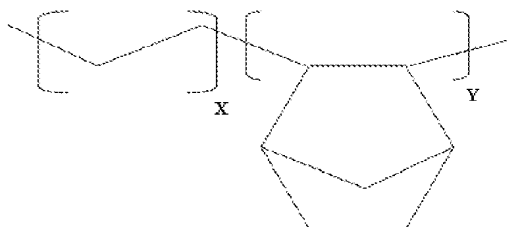
range of 1-5 after 300 hours depending on which olefin chemical resistance polymer is used. For the Third Series, the CIE 94 Delta E is less than 2 after 300 hours. For the Fourth Series, the CIE 94 Delta E is also less than 2 after 168 hours.

[00089] Table 10 shows a comparison for Dielectric Constant and Dissipation Factor between a formulation which had not Chemical Resistance Polymer (Comp. Ex. E) and which did (Example 6). The results showed that these formulations have low dielectric constant and low dissipation factor, which are key factors for many electronic applications. The addition of olefin chemical resistance polymer, SBC or OBC impact modifier or other additives did not alter the low dielectric constant and low dissipation factor up to 1 GHz. The dielectric constant of Topas® COC is around 2.35, which is typical of the values obtained with olefinic materials. It stays constant in the high frequency area up to 20 GHz.

[00090] The foregoing description, for purposes of explanation, used specific nomenclature to provide a thorough understanding of the described embodiments. However, it will be apparent to one skilled in the art that the specific details are not required in order to practice the described embodiments. Thus, the foregoing descriptions of the specific embodiments described herein are presented for purposes of illustration and description. They are not target to be exhaustive or to limit the embodiments to the precise forms disclosed. It will be apparent to one of ordinary skill in the art that many modifications and variations are possible in view of the above teachings.

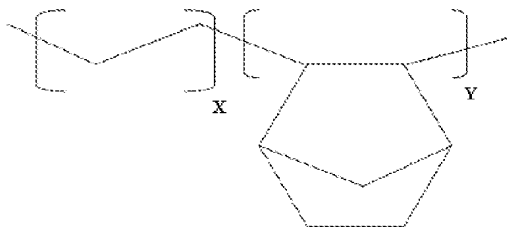
What is claimed is:

1. A cyclic olefin copolymer compound, comprising:
 - (a) cyclic olefin copolymer;
 - (b) an impact modifying polymer selected from the group consisting of styrenic block copolymers and olefinic block copolymers and combinations thereof; and
 - (c) a linear polyolefin,wherein the linear polyolefin resists chemical attack against the cyclic olefin copolymer by ultraviolet light absorbers and fatty acid derivatives.
2. A cyclic olefin copolymer compound, comprising:
 - (a) cyclic olefin copolymer;
 - (b) an impact modifying polymer selected from the group consisting of styrenic block copolymers and olefinic block copolymers and combinations thereof; and
 - (c) a branched polyolefin,wherein the branched polyolefin resists chemical attack against the cyclic olefin copolymer by ultraviolet light absorbers and fatty acid derivatives.
3. The compound of Claim 1 or Claim 2, wherein the cyclic olefin copolymer (COC) is a copolymer of cyclic olefin monomers with alkenes.
4. The compound of Claim 3, wherein the cyclic olefin copolymer is ethylene-norbornene copolymer which has a CAS No. of 26007-43-2.
5. The compound of Claim 4, wherein the ethylene-norbornene copolymer has the following structure:



wherein X ranges from about 40 wt.% to about 20 wt.% and wherein Y ranges from about 60 wt. % to about 80 wt. %.

6. The compound of Claim 4, wherein the ethylene-norbornene copolymer has the following structure:



wherein X ranges from about 25 wt.% to about 18 wt. % and wherein Y ranges from about 75 wt. % to about 82 wt. %.

7. The compound of Claim 4, wherein the cyclic olefin copolymer has a weight average molecular weight (Mw) ranging from about 40,000 to about 130,000, and a heat deflection temperature ranging from about 30°C to about 170°C at 0.45 MPa (66 psi load).

8. The compound of Claim 1, wherein the impact modifying polymer is styrene-ethylene-butylene-styrene and wherein the linear polyolefin is selected from the group consisting of high density polyethylene, linear low density polyethylene, linear polypropylene, and combinations thereof.

9. The compound of Claim 2, wherein the polyolefin is branched polypropylene.

10. The compound of any one of Claims 1-9, wherein the support material further comprises one or more optional additives selected from the group consisting of adhesion promoters, biocides, antibacterials, fungicides, mildewcides, anti-fogging agents, anti-static agents, bonding agents, blowing agents, foaming agents, dispersants, fillers, extenders, fire retardants, flame retardants, smoke suppressants, impact modifiers, initiators, lubricants, micas, pigments, colorants, dyes, plasticizers, processing aids, release agents, silanes, titanates, zirconates, slip agents, anti-blocking agents, stabilizers, stearates, viscosity regulators, waxes, and combinations of them.

11. A polymer article comprising the compound of any one of Claims 1-10.

12. The polymer article of Claim 11, wherein the polymer article is in a shape resulting from any extruding, molding, calendering, thermoforming, or 3D-printing process.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/026749**A. CLASSIFICATION OF SUBJECT MATTER****C08L 45/00(2006.01)i, C08L 25/10(2006.01)i, C08L 23/00(2006.01)i, C08K 5/01(2006.01)i, C08J 3/20(2006.01)i, C08F 232/02(2006.01)i, C08F 212/08(2006.01)i, C08F 210/00(2006.01)i**

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08L 45/00; B32B 7/02; B29C 47/14; C08L 23/10; C08L 25/10; C08L 23/00; C08K 5/01; C08J 3/20; C08F 232/02; C08F 212/08; C08F 210/00

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: cyclic olefin copolymer (COC), ethylene, norbornene, branched polypropylene, linear low density polyethylene, SEBS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DORIGATO, A. et al. `Linear low density polyethylene/cycloolefin copolymer blends.` eXPRESS Polymer Letters. 2011, Vol. 5, Issue 1, pages 23-37. See page 23, left column; page 24, left column, first and second paragraphs.	1-9
A	STRICKER, F. et al. `Rubber-toughened cycloolefin copolymers.` Die Angewandte Makromolekulare Chemie. 1998, Vol. 256, Issue 1, pages 101-104. See summary; page 102, left column; Figure 1.	1-9
A	KHONAKDAR, H. A. et al. `Miscibility analysis, viscoelastic properties and morphology of cyclic olefin copolymer/polyolefin elastomer (COC/POE) blends.` Composites: Part B. 2015, Vol. 69, pages 111-119 (Available online 2 October 2014) See page 111.	1-9
A	WO 96-11983 A1 (EXXON CHEMICAL PATENTS INC.) 25 April 1996 See claims 1-5.	1-9
A	US 2011-0256373 A1 (TATARKA, P. D. et al.) 20 October 2011 See claims 1-7.	1-9

☐ 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

"I" 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

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Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

Facsimile No. +82-42-481-8578

Authorized officer

KIM, Dong Seok

Telephone No. +82-42-481-5405



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/026749

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 12
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 12 refers to claim 11 which does not comply with PCT Rule 6.4(a).
3. ☒ Claims Nos.: 10, 11
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/026749

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 96-11983 A1	25/04/1996	CA 2202403 A1 DE 69518250 D1 DE 69518250 T2 EP 0680491 A1 EP 0785969 A1 EP 0785969 B1 ES 2149381 T3 JP 08-505898 A JP 10-507478 A JP 3793881 B2 US 5723545 A US 5763532 A US 5837787 A US 6121383 A WO 94-17113 A1 WO 96-11983 A1	25/04/1996 07/09/2000 01/02/2001 02/05/1997 27/10/1999 02/08/2000 01/11/2000 25/06/1996 21/07/1998 05/07/2006 03/03/1998 09/06/1998 17/11/1998 19/09/2000 04/08/1994 25/04/1996
US 2011-0256373 A1	20/10/2011	WO 2011-129869 A1	20/10/2011

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(19) 世界知的所有権機関
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2016 年 12 月 1 日(01.12.2016)

(10) 国際公開番号
WO 2016/190081 A1

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C08L 45/00 (2006.01) C08L 65/00 (2006.01)
C08L 53/02 (2006.01)
- (21) 国際出願番号: PCT/JP2016/063847
- (22) 国際出願日: 2016 年 5 月 10 日(10.05.2016)
- (25) 国際出願の言語: 日本語
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- (30) 優先権データ:
特願 2015-108605 2015 年 5 月 28 日(28.05.2015) JP
特願 2016-089840 2016 年 4 月 27 日(27.04.2016) JP
- (71) 出願人: デクセリアルズ株式会社 (DEXERIALS CORPORATION) [JP/JP]; 〒1410032 東京都品川区大崎 1 丁目 1 番 2 号 ゲートシティ大崎イーストタワー 8 階 Tokyo (JP).
- (72) 発明者: 細谷 健 (HOSOYA, Ken); 〒1410032 東京都品川区大崎 1 丁目 1 番 2 号 ゲートシティ大崎イーストタワー 8 階 デクセリアルズ株式会社内 Tokyo (JP). 堀井 明宏 (HORII, Akihiro); 〒1410032 東京都品川区大崎 1 丁目 1 番 2 号 ゲートシティ大崎イーストタワー 8 階 デクセリアルズ株式会社内 Tokyo (JP). 沼倉 新一 (NUMAKURA, Shinichi); 〒1410032 東京都品川区大崎

1 丁目 1 番 2 号 ゲートシティ大崎イーストタワー 8 階 デクセリアルズ株式会社内 Tokyo (JP). 高橋 康弘 (TAKAHASHI, Yasuhiro); 〒1410032 東京都品川区大崎 1 丁目 1 番 2 号 ゲートシティ大崎イーストタワー 8 階 デクセリアルズ株式会社内 Tokyo (JP). 佐竹 由貴 (SATAKE, Yutaka); 〒1410032 東京都品川区大崎 1 丁目 1 番 2 号 ゲートシティ大崎イーストタワー 8 階 デクセリアルズ株式会社内 Tokyo (JP). 小幡 慶 (OBATA, Kei); 〒1410032 東京都品川区大崎 1 丁目 1 番 2 号 ゲートシティ大崎イーストタワー 8 階 デクセリアルズ株式会社内 Tokyo (JP). 前川 欣之 (MAEKAWA, Yoshiyuki); 〒1410032 東京都品川区大崎 1 丁目 1 番 2 号 ゲートシティ大崎イーストタワー 8 階 デクセリアルズ株式会社内 Tokyo (JP). 石森 拓 (ISHIMORI, Taku); 〒1410032 東京都品川区大崎 1 丁目 1 番 2 号 ゲートシティ大崎イーストタワー 8 階 デクセリアルズ株式会社内 Tokyo (JP).

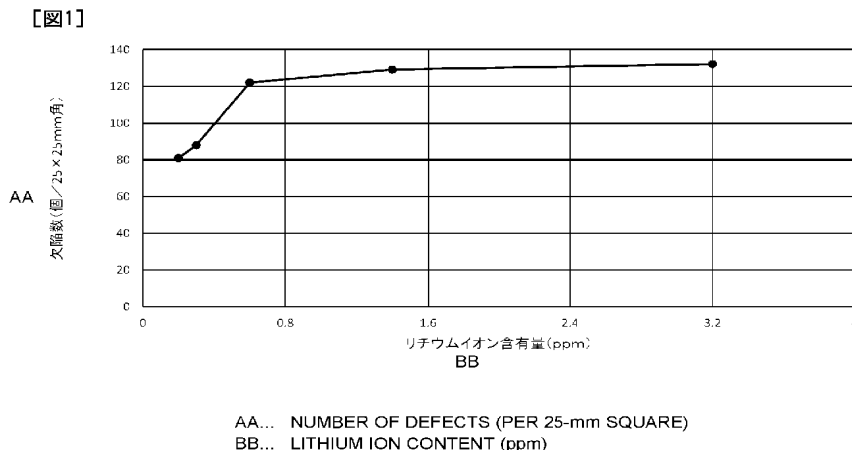
(74) 代理人: 野口 信博 (NOGUUCHI, Nobuhiro); 〒1010054 東京都千代田区神田錦町 3-16-1 エルヴァージュ神田錦町 2 階 Tokyo (JP).

(81) 指定国 (表示のない限り、全ての種類の国内保護が可能): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN,

[続表有]

(54) Title: FILM OF CYCLOOLEFIN-BASED RESIN COMPOSITION

(54) 発明の名称: 環状オレフィン系樹脂組成物フィルム



(57) Abstract: Provided is a film of a cycloolefin-based resin composition, the film having few defects. The film of a cycloolefin-based resin composition comprises a cycloolefin-based resin and an antioxidant, the antioxidant satisfying at least one of the following requirements (1) to (3). (1) To have a lithium ion content of 0.4 ppm or less. (2) To have a cation content of 0.9 ppm or less. (3) To have a chloride ion content of 0.1 ppm or less.

(57) 要約: 欠陥が少ない環状オレフィン系樹脂組成物フィルムを提供する。環状オレフィン系樹脂組成物フィルムは、環状オレフィン系樹脂と酸化防止剤とを含有し、上記酸化防止剤が以下の(1)~(3)の条件の少なくとも1つを満たす。(1) 上記酸化防止剤に含まれるリチウムイオンの含有量が0.4 ppm以下である。(2) 上記酸化防止剤に含まれる陽イオンの含有量が0.9 ppm以下である。(3) 上記酸化防止剤に含まれる塩化物イオンの含有量が0.1 ppm以下である。



CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) 指定国 (表示のない限り、全ての種類の広域保護が可能): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), ユー

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添付公開書類:

- 国際調査報告 (条約第 21 条(3))

明 細 書

発明の名称：環状オレフィン系樹脂組成物フィルム

技術分野

[0001] 本発明は、環状オレフィン系樹脂と酸化防止剤とを含有する環状オレフィン系樹脂組成物フィルムに関する。本出願は、日本国において2015年5月28日に出願された日本出願番号特願2015-108605、及び日本国において2016年4月27日に出願された日本出願番号特願2016-89840を基礎として優先権を主張するものであり、これらの出願は参照されることにより、本出願に援用される。

背景技術

[0002] 環状オレフィン系樹脂は、その主鎖に環状のオレフィン骨格を持った非晶性で熱可塑性のオレフィン系樹脂であり、優れた光学特性（透明性、低複屈折性）を持ち、低吸水性とそれに基づく寸法安定性、高防湿性といった、優れた性能を有している（例えば、特許文献1～5を参照）。そのため環状オレフィン系樹脂からなるフィルムもしくはシートは、各種光学用途、例えば位相差フィルム、偏光板保護フィルム、光拡散板等や、防湿包装用途、例えば医薬品包装、食品包装等への展開が期待されている。

先行技術文献

特許文献

[0003] 特許文献1：特開2001-139756号公報
特許文献2：特開2009-234982号公報
特許文献3：特開2004-156048号公報
特許文献4：特開2004-359819号公報
特許文献5：特開2000-86870号公報

発明の概要

発明が解決しようとする課題

[0004] 環状オレフィン系樹脂は、高ガラス転移点により、より高い温度で成形、

加工することが必要となる。このような高温条件下で成形加工を行うと、得られる成形品が着色されて無色透明性が損なわれたり、上記成形品が樹脂（環状ポリオレフィン系樹脂）及び／又は添加剤（含有成分）の熱分解に起因する焼け（黒状）が生じたりする問題がある。

[0005] 例えば、環状オレフィン系樹脂を用いてフィルムを溶融成形する場合、樹脂間のせん断によるゲルが発生しやすく、成形温度を高くする（例えば280～360℃）ことが必要であり、焼け（黒状）が発生することがある。透明導電性フィルムの基材のような薄膜品においては、僅かな焼けでも品質上問題となる。

[0006] そこで、環状ポリオレフィン系樹脂が有する優れた光学特性（レタデーション、ヘイズ）と靱性を保持しつつ、高温条件下で成形加工して得られる成形品に欠陥（例えば、酸化劣化による着色や、熱分解による焼け（黒状）など）を発生させないことが求められている。

[0007] 本発明は、このような従来の実情の鑑みてなされたものであり、欠陥が少ない環状オレフィン系樹脂組成物フィルムを提供する。

課題を解決するための手段

[0008] 本願発明者らは、鋭意検討の結果、酸化防止剤に含まれる特定イオンの含有量を所定値以下とすることにより、上記課題を解決できることを見出した。

[0009] すなわち、本発明に係る環状オレフィン系樹脂組成物フィルムは、環状オレフィン系樹脂と酸化防止剤とを含有し、上記酸化防止剤が以下の（１）～（３）の条件の少なくとも１つを満たす。

（１）上記酸化防止剤に含まれるリチウムイオンの含有量が0.4 ppm以下である。

（２）上記酸化防止剤に含まれる陽イオンの含有量が0.9 ppm以下である。

（３）上記酸化防止剤に含まれる塩化物イオンの含有量が0.1 ppm以下である。

発明の効果

[0010] 本発明によれば、酸化防止剤が上記（１）～（３）の条件の少なくとも１つを満たすことにより、環状オレフィン樹脂組成物フィルムの欠陥を抑制することができる。

図面の簡単な説明

[0011] [図1]図１は、酸化防止剤に含まれるリチウムイオンの含有量と欠陥数との関係を示すグラフである。

[図2]図２は、酸化防止剤に含まれる陽イオンの含有量と欠陥数との関係を示すグラフである。

[図3]図３は、酸化防止剤に含まれる塩化物イオンの含有量と欠陥数との関係を示すグラフである。

発明を実施するための形態

[0012] 以下、本発明の実施の形態について、図面を参照しながら下記順序にて詳細に説明する。

- １．環状オレフィン系樹脂組成物フィルム
- ２．実施例

[0013] ＜１．環状オレフィン系樹脂組成物フィルム＞

本実施の形態に係る環状オレフィン系樹脂組成物フィルムは、環状オレフィン系樹脂と酸化防止剤とを含有し、酸化防止剤が以下の（１）～（３）の条件の少なくとも１つを満たす。

（１）酸化防止剤に含まれるリチウムイオンの含有量が０．４ppm以下である。

（２）酸化防止剤に含まれる陽イオンの含有量が０．９ppm以下である。

（３）酸化防止剤に含まれる塩化物イオンの含有量が０．１ppm以下である。

[0014] 本実施の形態に係る環状オレフィン系樹脂組成物フィルムによれば、欠陥を抑制することができる。また、光学特性（レタデーション、ヘイズ）と靱性を良好にすることができる。

[0015] 環状オレフィン系樹脂組成物フィルムに用いられる環状オレフィン系樹脂組成物中において、酸化防止剤に含まれる上記各イオンが、酸化防止剤の近傍に過剰に存在していると、上記各イオンが酸化防止剤に作用して酸化防止剤の機能を低下させやすい。その結果、環状オレフィン系樹脂組成物を用いてフィルムを溶融成形する際に、欠陥が発生しやすくなる傾向にある。酸化防止剤に含まれる上記各イオンとしては、酸化防止剤の製造過程に起因するものが挙げられる。例えば、リチウム触媒を用いて得られるフェノール系酸化防止剤を用いる場合、酸化防止剤にはリチウムが過剰に含まれやすい。

[0016] 一方、環状オレフィン系樹脂組成物中において、環状オレフィン樹脂に由来する上記各イオンは、酸化防止剤の近傍には存在しにくいいため、酸化防止剤の機能の低下には寄与しにくいと考えられる。

[0017] 本実施の形態に係る環状オレフィン系樹脂組成物フィルムは、フィルム又はシート状である。環状オレフィン系樹脂組成物フィルムは、厚みが0.1 μm ~ 2 mmであることが好ましく、1 μm ~ 1 mmであることがより好ましい。以下、環状オレフィン系樹脂組成物フィルムに用いられる環状オレフィン系樹脂、酸化防止剤等について、詳細に説明する。

[0018] [環状オレフィン系樹脂]

環状オレフィン系樹脂は、主鎖が炭素-炭素結合からなり、主鎖の少なくとも一部に環状炭化水素構造を有する高分子化合物である。この環状炭化水素構造は、ノルボルネンやテトラシクロドデセンに代表されるような、環状炭化水素構造中に少なくとも一つのオレフィン性二重結合を有する化合物（環状オレフィン）を単量体として用いることで導入される。

[0019] 環状オレフィン系樹脂は、環状オレフィンの付加（共）重合体又はその水素添加物（A）、環状オレフィンと α -オレフィンの付加共重合体又はその水素添加物（B）、環状オレフィンの開環（共）重合体又はその水素添加物（C）に分類される。

[0020] 環状オレフィンの具体例としては、シクロペンテン、シクロヘキセン、シクロオクテン；シクロペンタジエン、1, 3-シクロヘキサジエン等の1環

の環状オレフィン；ビシクロ〔2. 2. 1〕ヘプター2-エン（慣用名：ノルボルネン）、5-メチルビシクロ〔2. 2. 1〕ヘプター2-エン、5-ジメチルビシクロ〔2. 2. 1〕ヘプター2-エン、5-エチルビシクロ〔2. 2. 1〕ヘプター2-エン、5-ブチルビシクロ〔2. 2. 1〕ヘプター2-エン、5-エチリデンビシクロ〔2. 2. 1〕ヘプター2-エン、5-ヘキシルビシクロ〔2. 2. 1〕ヘプター2-エン、5-オクチルビシクロ〔2. 2. 1〕ヘプター2-エン、5-オクタデシルビシクロ〔2. 2. 1〕ヘプター2-エン、5-メチリデンビシクロ〔2. 2. 1〕ヘプター2-エン、5-ビニルビシクロ〔2. 2. 1〕ヘプター2-エン、5-プロペニルビシクロ〔2. 2. 1〕ヘプター2-エン等の2環の環状オレフィン；

[0021] トリシクロ〔4. 3. 0. 1^{2, 5}〕デカー3, 7-ジエン（慣用名：ジシクロペンタジエン）、トリシクロ〔4. 3. 0. 1^{2, 5}〕デカー3-エン；トリシクロ〔4. 4. 0. 1^{2, 5}〕ウンデカー3, 7-ジエン若しくはトリシクロ〔4. 4. 0. 1^{2, 5}〕ウンデカー3, 8-ジエン又はこれらの部分水素添加物（又はシクロペンタジエンとシクロヘキセンの付加物）であるトリシクロ〔4. 4. 0. 1^{2, 5}〕ウンデカー3-エン；

5-シクロペンチルビシクロ〔2. 2. 1〕ヘプター2-エン、5-シクロヘキシルビシクロ〔2. 2. 1〕ヘプター2-エン、5-シクロヘキセニルビシクロ〔2. 2. 1〕ヘプター2-エン、5-フェニルビシクロ〔2. 2. 1〕ヘプター2-エンといった3環の環状オレフィン；

[0022] テトラシクロ〔4. 4. 0. 1^{2, 5}. 1^{7, 10}〕ドデカー3-エン（単にテトラシクロドデセンともいう）、8-メチルテトラシクロ〔4. 4. 0. 1^{2, 5}. 1^{7, 10}〕ドデカー3-エン、8-エチルテトラシクロ〔4. 4. 0. 1^{2, 5}. 1^{7, 10}〕ドデカー3-エン、8-メチリデンテトラシクロ〔4. 4. 0. 1^{2, 5}. 1^{7, 10}〕ドデカー3-エン、8-エチリデンテトラシクロ〔4. 4. 0. 1^{2, 5}. 1^{7, 10}〕ドデカー3-エン、8-ビニルテトラシクロ〔4. 4. 0. 1^{2, 5}. 1^{7, 10}〕ドデカー3-エン、8-プロペニルテトラ

シクロ [4. 4. 0. 1^{2, 5}. 1^{7, 10}] ドデカー 3-エンといった 4 環の環状オレフィン；

[0023] 8-シクロペンチル-テトラシクロ [4. 4. 0. 1^{2, 5}. 1^{7, 10}] ドデカー 3-エン、8-シクロヘキシル-テトラシクロ [4. 4. 0. 1^{2, 5}. 1^{7, 10}] ドデカー 3-エン、8-シクロヘキセニル-テトラシクロ [4. 4. 0. 1^{2, 5}. 1^{7, 10}] ドデカー 3-エン、8-フェニル-シクロペンチル-テトラシクロ [4. 4. 0. 1^{2, 5}. 1^{7, 10}] ドデカー 3-エン；テトラシクロ [7. 4. 1^{3, 6}. 0^{1, 9}. 0^{2, 7}] テトラデカー 4, 9, 11, 13-テトラエン (1, 4-メタノー 1, 4, 4a, 9a-テトラヒドロフルオレンともいう)、テトラシクロ [8. 4. 1^{4, 7}. 0^{1, 10}. 0^{3, 8}] ペンタデカー 5, 10, 12, 14-テトラエン (1, 4-メタノー 1, 4, 4a, 5, 10, 10a-ヘキサヒドロアントラセンともいう)；ペンタシクロ [6. 6. 1. 1^{3, 6}. 0^{2, 7}. 0^{9, 14}] -4-ヘキサデセン、ペンタシクロ [6. 5. 1. 1^{3, 6}. 0^{2, 7}. 0^{9, 13}] -4-ペンタデセン、ペンタシクロ [7. 4. 0. 0^{2, 7}. 1^{3, 6}. 1^{10, 13}] -4-ペンタデセン；ヘプタシクロ [8. 7. 0. 1^{2, 9}. 1^{4, 7}. 1^{11, 17}. 0^{3, 8}. 0^{12, 16}] -5-エイコセン、ヘプタシクロ [8. 7. 0. 1^{2, 9}. 0^{3, 8}. 1^{4, 7}. 0^{12, 17}. 1^{13, 16}] -14-エイコセン；シクロペンタジエンの 4 量体などの多環の環状オレフィンが挙げられる。これらの環状オレフィン、それぞれ単独であるいは 2 種以上組み合わせて用いることができる。

[0024] 環状オレフィンと共重合可能な α -オレフィンの具体例としては、エチレン、プロピレン、1-ブテン、1-ペンテン、1-ヘキセン、3-メチル-1-ブテン、3-メチル-1-ペンテン、3-エチル-1-ペンテン、4-メチル-1-ペンテン、4-メチル-1-ヘキセン、4, 4-ジメチル-1-ヘキセン、4, 4-ジメチル-1-ペンテン、4-エチル-1-ヘキセン、3-エチル-1-ヘキセン、1-オクテン、1-デセン、1-ドデセン、1-テトラデセン、1-ヘキサデセン、1-オクタデセン、1-エイコセンなどの炭素数 2～20、好ましくは炭素数 2～8 の α -オレフィンなどが挙

げられる。これらの α -オレフィンは、それぞれ単独で、あるいは2種以上を組み合わせで使用することができる。これらの α -オレフィン、環状ポリオレフィンに対して、5～200%の範囲で含有されたものを使用することができる。

[0025] 環状オレフィン又は環状オレフィンと α -オレフィンとの重合方法及び得られた重合体の水素添加方法に、格別な制限はなく、公知の方法に従って行うことができる。

[0026] 環状オレフィン系樹脂として、本実施の形態では、エチレンとノルボルネンの付加共重合体が好ましく用いられる。

[0027] 環状オレフィン系樹脂の構造には、特に制限はなく、鎖状でも、分岐状でも、架橋状でもよいが、好ましくは直鎖状である。

[0028] 環状オレフィン系樹脂の分子量は、GPC法による数平均分子量が5000～30万、好ましくは1万～15万、さらに好ましくは1.5万～10万である。数平均分子量が低すぎると機械的強度が低下し、大きすぎると成形性が悪くなる。

[0029] また、環状オレフィン系樹脂には、前述の環状オレフィン系樹脂(A)～(C)に極性基(例えば、カルボキシル基、酸無水物基、エポキシ基、アミド基、エステル基、ヒドロキシル基など)を有する不飽和化合物(u)をグラフト及び／又は共重合したもの(D)を含めることができる。上記環状オレフィン系樹脂(A)～(D)は、二種以上混合して使用してもよい。

[0030] 上記不飽和化合物(u)としては、(メタ)アクリル酸、マレイン酸、無水マレイン酸、無水イタコン酸、グリシジル(メタ)アクリレート、(メタ)アクリル酸アルキル(炭素数1～10)エステル、マレイン酸アルキル(炭素数1～10)エステル、(メタ)アクリルアミド、(メタ)アクリル酸-2-ヒドロキシエチル等が挙げられる。

[0031] 極性基を有する不飽和化合物(u)をグラフト及び／又は共重合した変性環状オレフィン系樹脂(D)を用いることにより金属や極性樹脂との親和性を高めることができるので、蒸着、スパッタ、コーティング、接着等、各種

二次加工の強度を高めることができ、二次加工が必要な場合に好適である。しかし、極性基の存在は環状オレフィン系樹脂の吸水率を高めてしまう欠点がある。そのため極性基（例えば、カルボキシル基、酸無水物基、エポキシ基、アミド基、エステル基、ヒドロキシル基など）の含有量は、環状オレフィン系樹脂 1 k g 当り 0 ~ 1 m o l / k g であることが好ましい。

[0032] [酸化防止剤]

酸化防止剤は、樹脂材料又はゴム材料の分野において通常使用されるものであり、上述した（１）～（３）の条件、すなわちイオン含有量の条件の少なくとも１つを満たす。

[0033] （１）酸化防止剤に含まれるリチウムイオンの含有量は、0.4 p p m 以下であり、0.3 p p m 以下であることが好ましく、0.2 p p m 以下であることがより好ましい。リチウムイオンの含有量が0.4 p p m を超えると、酸化防止剤による効果（熱安定性改良効果）が小さくなってしまう結果、欠陥を抑制することが困難となる。

[0034] （２）酸化防止剤に含まれる陽イオンの含有量は、0.9 p p m 以下であり、0.7 p p m 以下であることが好ましく、0.6 p p m 以下であることがより好ましい。陽イオンの含有量には、上記リチウムイオンの含有量が含まれる。陽イオンの含有量が0.9 p p m を超えると、酸化防止剤による効果（熱安定性改良効果）が小さくなってしまう結果、欠陥を抑制することが困難となる。

[0035] （３）酸化防止剤に含まれる塩化物イオンの含有量は、0.1 p p m 以下であり、0.095 p p m 以下であることが好ましく、0.080 p p m 以下であることがより好ましく、0.050 p p m 以下であることがさらに好ましい。塩化物イオンの含有量が0.1 p p m を超えると、酸化防止剤による効果（熱安定性改良効果）が小さくなってしまう結果、欠陥を抑制することが困難となる。

[0036] 特に、酸化防止剤は、少なくとも上記（１）又は（３）の条件、すなわち、酸化防止剤に含まれるリチウムイオンの含有量が0.4 p p m 以下である

こと、及び、酸化防止剤に含まれる塩化物イオンの含有量が0.1 ppm以下であることのいずれか一方を満たすことが好ましく、上記(1)～(3)の条件を全て満たすことがより好ましい。

[0037] 上記各イオンの含有量と熱安定性の作用機構は定かではないが、例えば組成物中に過剰にリチウムイオンが存在すると、押出加工時にリチウムイオンが酸化防止剤に作用し、酸化防止剤の効果を抑制してしまうと考えられる。特に、環状オレフィン系樹脂は、溶融温度が高いため、酸化防止剤の効果の抑制が顕著となる。

[0038] 酸化防止剤の具体例としては、フェノール系酸化防止剤、リン系酸化防止剤等が挙げられ、欠陥数をより効果的に抑制する観点から、フェノール系酸化防止剤が好ましい。フェノール系酸化防止剤の具体例としては、ビタミンE、テトラキスー(メチレンー3-(3', 5'-ジ-tert-ブチル-4'-ヒドロキシフェニル)プロピオネート)メタン、2, 5'-ジ-tert-ブチルハイドロキノン、2, 6'-ジ-tert-ブチル-p-クレゾール、4, 4'-チオビスー(6-tert-ブチルフェノール)、2, 2'-メチレンビスー(4-メチル-6-tert-ブチルフェノール)、オクタデシルー3-(3', 5'-ジ-tert-ブチル-4'-ヒドロキシフェニル)プロピオネート、4, 4'-チオビスー(6-tert-ブチルフェノール)、2-tert-ブチル-6-(3-tert-ブチル-2-ヒドロキシ-5-メチルベンジル)-4-メチルフェニルアクリレート、ペンタエリスリトールテトラキス(3-ラウリルチオプロピオネート)、ペンタエリスリトールテトラキス[3-(3, 5'-ジ-tert-ブチル-4-ヒドロキシフェニル)プロピオネート]、2, 6'-ジ-(tert-ブチル)-4-メチルフェノール、2, 2'-メチレンビスー(6-tert-ブチル-p-クレゾール)、1, 3, 5-トリス(3, 5-tert-ブチル-4-ヒドロキシベンジル)-1, 3, 5-トリアジン-2, 4, 6-(1H, 3H, 5H)-トリオン、2, 6'-ジ-tert-ブチル-4-(4, 6-ビス(オクチルチオ)-1, 3, 5-トリアジン-2-イルアミノ)フェノール等を挙げることができる。フェノール系酸化防止剤の市販品としては、IRGANO

X1010 (BASF ジャパン (株) 社製)、アデカスタブAO-60 ((株) ADEKA 社製) 等を用いることができる。

[0039] リン系酸化防止剤の具体例としては、2, 2'-メチレンビス(4, 6-ジ-tert-ブチルフェニル)オクチルホスファイト、トリス(2, 4-ジ-tert-ブチルフェニル)ホスファイト、トリフェニルホスファイト、トリス(ノニルフェニル)ホスファイト、トリス(2-エチルヘキシル)ホスファイト、トリスデシルホスファイト、トリス(トリデシル)ホスファイト、ジフェニルモノ(2-エチルヘキシル)ホスファイト、ジフェニルモノデシルホスファイト、ジデシルモノフェニルホスファイト、ジフェニルモノ(トリデシル)ホスファイト、ジラウリルハイドロジェンホスファイト、ジフェニルハイドロゲンホスファイト、テトラフェニルジプロピレングリコールジホスファイト、テトラフェニルテトラ(トリデシル)ペンタエリスリトールテトラホスファイト、テトラ(トリデシル)-4, 4'-イソプロピリデンジフェニルジホスファイト、ビス(ノニルフェニル)ペンタエリスリトールジホスファイト、ジステアリルペンタエリスリトールジホスファイト、水添ビスフェノールA・ペンタエリスリトールホスファイトポリマー、ビス(2, 4-ジ-tert-ブチルフェニル)ペンタエリスリトールジホスファイト、ビス(2, 4-ジ-tert-ブチル-3-メチルフェニル)ペンタエリスリトールジホスファイト等が挙げられる。

[0040] 酸化防止剤の含有量は、環状オレフィン系樹脂及びエラストマーの合計100質量部に対し、通常、0.05~5質量部が好ましく、0.1~3質量部がより好ましい。酸化防止剤の含有量を0.05質量部以上とすることにより、酸化防止剤の機能(酸化防止効果)をより効果的に奏することができる。また、酸化防止剤の含有量を5質量部以下とすることにより、環状オレフィン系樹脂組成物の機械的強度やガラス転移温度などの品質の低下や、環状オレフィン系樹脂組成物の揮発時における揮発成分の増加をより効果的に抑制することができる。酸化防止剤は、単独で使用しても、2種以上を組み合わせ使用してもよい。2種以上の酸化防止剤を用いる場合、その合計量

が上記数値範囲を満たすことが好ましい。

[0041] 環状オレフィン系樹脂組成物フィルムは、その特性を損なわない範囲で、必要に応じて各種配合剤を含有していてもよい。各種配合剤としては、熱可塑性樹脂組成物で通常用いられているものであれば格別な制限はなく、例えば、エラストマー、紫外線吸収剤、光安定剤、可塑剤、滑剤、帯電防止剤、難燃剤、染料や顔料などの着色剤、近赤外線吸収剤、蛍光増白剤などの配合剤、充填剤等が挙げられる。

[0042] エラストマーとしては、スチレン系エラストマーが好ましい。スチレン系エラストマーを含有することにより、フィルムの靱性をより向上させることができる。以下、スチレン系エラストマーについて説明する。

[0043] [スチレン系エラストマー]

スチレン系エラストマーは、スチレンとブタジエンもしくはイソプレン等の共役ジエンの共重合体、及び／又は、その水素添加物である。スチレン系エラストマーは、スチレンをハードセグメント、共役ジエンをソフトセグメントとしたブロック共重合体であり、加硫工程が不要であり、好適に用いられる。また、水素添加をしたものの方が、熱安定性が高く、さらに好適である。

[0044] スチレン系エラストマーの例としては、スチレン／ブタジエン／スチレンブロック共重合体、スチレン／イソプレン／スチレンブロック共重合体、スチレン／エチレン／ブチレン／スチレンブロック共重合体、スチレン／エチレン／プロピレン／スチレンブロック共重合体、スチレン／ブタジエンブロック共重合体などが挙げられる。

[0045] また、水素添加により共役ジエン成分の二重結合をなくした、スチレン／エチレン／ブチレン／スチレンブロック共重合体、スチレン／エチレン／プロピレン／スチレンブロック共重合体、スチレン／ブタジエンブロック共重合体（水素添加されたスチレン系エラストマーともいう。）などを用いてもよい。水素添加されたスチレン系エラストマーは、高い引裂き強度と環境保存後のヘイズ上昇が小さいため好ましい。

[0046] スチレン系エラストマーの分子量は、GPC法による数平均分子量が50000～30万、好ましくは1万～15万、さらに好ましくは2万～10万である。数平均分子量が低すぎると機械的強度が低下し、大きすぎると成形性が悪くなる。

[0047] スチレン系エラストマーを含有する場合、環状オレフィン樹脂とスチレン系エラストマーとの重量比（環状オレフィン樹脂：スチレン系エラストマー）は、60：40～95：5であることが好ましく、85：15～95：5であることがより好ましい。このような範囲とすることにより、得られるフィルムの靱性をより向上させることができる。

[0048] [環状オレフィン系樹脂組成物フィルムの特性]

環状オレフィン系樹脂組成物フィルムは、リタレーションが10.0nm以下であることが好ましく、7.0nm以下であることがより好ましく、5.0nm以下であることがさらに好ましい。リタレーションの値は、フィルムの面内リタレーションROについて、光学材料検査装置（大塚電子株式会社製、商品名：RETS-100）を用いて測定した値をいう。リタレーションが上記範囲を満たすことにより、目的とする光学特性をより満足しやすくなる。

[0049] 環状オレフィン系樹脂組成物フィルムは、ヘイズが2.0%以下であることが好ましく、1.5%以下であることがより好ましい。ヘイズの値は、厚み50 μ mのフィルムについて、ヘイズメーター（製品名：HM150、（株）村上色彩技術研究所製）を用いて測定した値をいう。ヘイズの値が上記範囲を満たすことにより、使用上、初期設定からの特性を維持し、目的とする光学特性をより満足しやすくなる。

[0050] 環状オレフィン系樹脂組成物フィルムは、引裂き強度が50N/mm以上であることが好ましく、60N/mm以上であることがより好ましく、70N/mm以上であることがさらに好ましい。引裂き強度が上記範囲を満たすことにより、製造時や使用時におけるフィルムの破壊をより効果的に防ぐことができる。

[0051] <環状オレフィン系樹脂組成物フィルムの製造方法>

環状オレフィン系樹脂組成物フィルムは、上述した環状オレフィン系樹脂と酸化防止剤とを含有する環状オレフィン系樹脂組成物を用いて形成することができる。例えば、上記環状オレフィン系樹脂組成物を210～300℃の範囲の温度で熔融し、熔融された環状オレフィン系樹脂組成物をフィルム状に押出すことにより得ることができる。環状オレフィン系樹脂組成物フィルムは、無延伸のものでも、一軸延伸のものでも、二軸延伸のものでもよい。フィルムの製法は、特に限定されず、押出法が好ましい。

[0052] 環状オレフィン系樹脂組成物フィルムは、各種光学用途、例えば位相差フィルム、偏光板保護フィルム、光拡散板等、特にプリズムシート、液晶セル基板の用途に好適である。

実施例

[0053] <3. 実施例>

以下、本発明の実施例について説明する。本実施例では、環状オレフィン系樹脂組成物フィルムを作製し、得られたフィルムの欠陥数、リタデーションRO、引き裂き強度及びヘイズを評価した。なお、本発明はこれらの実施例に限定されるものではない。

[0054] [欠陥数]

25mm角のフィルムについて、目視と光学顕微鏡（500倍）にて、大きさが5μm以上の欠陥（酸化劣化による着色、熱分解による焼け（黒状））の数をカウントした。欠陥数が100個以下のものを「○」と評価し、欠陥数が100個を超えるものを「×」と評価した。欠陥数が100個以下であることにより、実際の製造ラインにおいて発生する欠陥数を大きく削減することができる。

[0055] [リタデーション]

リタデーションの測定は、フィルムの面内リタデーションROについて、光学材料検査装置（大塚電子株式会社製、商品名：RETS-100）を用いて測定した。

[0056] [引裂き強度（直角形引き裂き）]

引裂き強度は、厚み $50\mu\text{m}$ のフィルムをJISK7128に従い測定した。試験片として3号形試験片を用い、引張試験機（AG-X、島津製作所（株）製）を用いて試験速度 $200\text{mm}/\text{分}$ で測定した。

[0057] [ヘイズ]

ヘイズは、厚み $50\mu\text{m}$ のフィルムについて、ヘイズメーター（製品名：HM150、（株）村上色彩技術研究所製）を用いて測定した。

[0058] [環状オレフィン系樹脂]

環状オレフィン系樹脂としては、TOPAS6013-S04（ポリプラスチック（株）製、化学名：エチレンとノルボルネンの付加共重合体）を用いた。

[0059] [スチレン系エラストマー]

スチレン系エラストマーとしては、タフテックH1041（スチレン／エチレン／ブチレン／スチレンブロック共重合体、旭化成ケミカルズ（株）製）を用いた。

[0060] [酸化防止剤]

以下の酸化防止剤A～Fのいずれかを用いた。以下の各イオン濃度は、イオンクロマトグラム（DIONEX製、製品名：DX-320）で分析、測定を行った。GI-1000約 0.2g を 10mL の超純水とともにPP容器（ 50mL ）に入れ、 100°C オーブンに10時間放置し測定試料とした。

[0061] <酸化防止剤A>

IRGANOX1010（BASFジャパン（株）社製、ロット番号A1、陽イオン含有量： 0.5ppm 、リチウムイオン含有量： 0.2ppm 、塩化物イオン含有量： 0.048ppm ）

[0062] <酸化防止剤B>

IRGANOX1010（BASFジャパン（株）社製、ロット番号B1、陽イオン含有量： 0.6ppm 、リチウムイオン含有量： 0.3ppm 、

塩化物イオン含有量：0.075 ppm)

[0063] <酸化防止剤C>

IRGANOX 1010 (BASFジャパン(株)社製、ロット番号C1、陽イオン含有量：1.3 ppm、リチウムイオン含有量：0.6 ppm、塩化物イオン含有量：0.105 ppm)

[0064] <酸化防止剤D>

アデカスタブAO-60 ((株)ADEKA社製、ロット番号D1、陽イオン含有量：1.9 ppm、リチウムイオン含有量：1.4 ppm、塩化物イオン含有量：0.117 ppm)

[0065] <酸化防止剤E>

IRGANOX 1010 (BASFジャパン(株)社製、ロット番号E1、陽イオン含有量：4.2 ppm、リチウムイオン含有量：3.2 ppm、塩化物イオン含有量：0.142 ppm)

[0066] [実施例1]

環状オレフィン系樹脂100質量部と、酸化防止剤Aを0.2質量部とを配合した。上記配合物を、先端にダイを取り付けた二軸押出機(仕様：直径25mm、長さ：26D、Tダイ幅：160mm)を用いて、210～300℃の温度範囲の所定温度で混練した後、環状オレフィン系樹脂組成物を250g/minの速さで押し出し、厚さが50mmのフィルムをロールに巻き取った。表1に示すように、得られたフィルムの欠陥数は81個/25mm角であった。また、得られたフィルムのリタデーションROは0.4nmであり、引裂き強度は55N/mmであり、ヘイズは0.2%であった。

[0067] [実施例2]

環状オレフィン系樹脂90質量部と、スチレン系エラストマー10質量部とを配合し、この配合物に酸化防止剤Aを0.2質量部配合し、二軸押出機を用いて混練したこと以外は、実施例1と同様にしてフィルムを作製した。表1に示すように、得られたフィルムの欠陥数は81個/25mm角であった。また、得られたフィルムのリタデーションROは2.0nmであり、引

裂き強度は90N/mmであり、ヘイズは1.4%であった。

[0068] [実施例3]

環状オレフィン系樹脂90質量部と、スチレン系エラストマー10質量部とを配合し、この配合物に酸化防止剤Bを0.2質量部配合し、二軸押出機を用いて混練したこと以外は、実施例1と同様にしてフィルムを作製した。表1に示すように、得られたフィルムの欠陥数は88個/25mm角であった。また、得られたフィルムのリタデーションROは2.0nmであり、引裂き強度は90N/mmであり、ヘイズは1.4%であった。

[0069] [比較例1]

環状オレフィン系樹脂90質量部と、スチレン系エラストマー10質量部とを配合し、この配合物に酸化防止剤Cを0.2質量部配合し、二軸押出機を用いて混練したこと以外は、実施例1と同様にしてフィルムを作製した。表1に示すように、得られたフィルムの欠陥数は122個/25mm角であった。また、得られたフィルムのリタデーションROは2.0nmであり、引裂き強度は90N/mmであり、ヘイズは1.4%であった。

[0070] [比較例2]

環状オレフィン系樹脂90質量部と、スチレン系エラストマー10質量部とを配合し、この配合物に酸化防止剤Dを0.2質量部配合し、二軸押出機を用いて混練したこと以外は、実施例1と同様にしてフィルムを作製した。表1に示すように、得られたフィルムの欠陥数は129個/25mm角であった。また、得られたフィルムのリタデーションROは2.0nmであり、引裂き強度は90N/mmであり、ヘイズは1.4%であった。

[0071] [比較例3]

環状オレフィン系樹脂90質量部と、スチレン系エラストマー10質量部とを配合し、この配合物に酸化防止剤Eを0.2質量部配合し、二軸押出機を用いて混練したこと以外は、実施例1と同様にしてフィルムを作製した。表1に示すように、得られたフィルムの欠陥数は132個/25mm角であった。また、得られたフィルムのリタデーションROは2.0nmであり、

引裂き強度は 90 N/mm であり、ヘイズは 1.4% であった。

[0072]

〔表1〕

	スチレン系 エラストマー	酸化防止剤						欠陥数 (個/25×25mm角)	リタデーションRO (nm)	引裂き強度 (N/mm)	ヘイズ (%)
		種類	品名	ロット	陽イオン 含有量 (ppm)	リチウムイオン 含有量 (ppm)	塩化物イオン 含有量 (ppm)				
実施例1	—	酸化防止剤A	IRGANOX1010	A1	0.5	0.2	0.048	81(O)	0.4	55	0.2
実施例2	タフテックH1041	酸化防止剤A	IRGANOX1010	A1	0.5	0.2	0.048	81(O)	2.0	90	1.4
実施例3	タフテックH1041	酸化防止剤B	IRGANOX1010	B1	0.6	0.3	0.075	88(O)	2.0	90	1.4
比較例1	タフテックH1041	酸化防止剤C	IRGANOX1010	C1	1.3	0.6	0.105	122(×)	2.0	90	1.4
比較例2	タフテックH1041	酸化防止剤D	AO-60	D1	1.9	1.4	0.117	129(×)	2.0	90	1.4
比較例3	タフテックH1041	酸化防止剤E	IRGANOX1010	E1	4.2	3.2	0.142	132(×)	2.0	90	1.4

[0073] 図1は、酸化防止剤に含まれるリチウムイオンの含有量と欠陥数との関係を示すグラフである。図2は、酸化防止剤に含まれる陽イオンの含有量と欠陥数との関係を示すグラフである。図3は、酸化防止剤に含まれる塩化物イオンの含有量と欠陥数との関係を示すグラフである。図1～図3に示すように、リチウムイオンの含有量、陽イオンの含有量又は塩化物イオンの含有量に比例して、欠陥数が増加する傾向にあることが分かった。

[0074] 実施例1～3のように、酸化防止剤が上述した(1)～(3)の条件、すなわち、酸化防止剤に含まれるリチウムイオンの含有量が0.4ppm以下である、酸化防止剤に含まれる陽イオンの含有量が0.9ppm以下である、及び、酸化防止剤に含まれる塩化物イオンの含有量が0.1ppm以下であることの少なくとも1つを満たす環状オレフィン系樹脂組成物フィルムは、欠陥が抑制されていることが分かった。

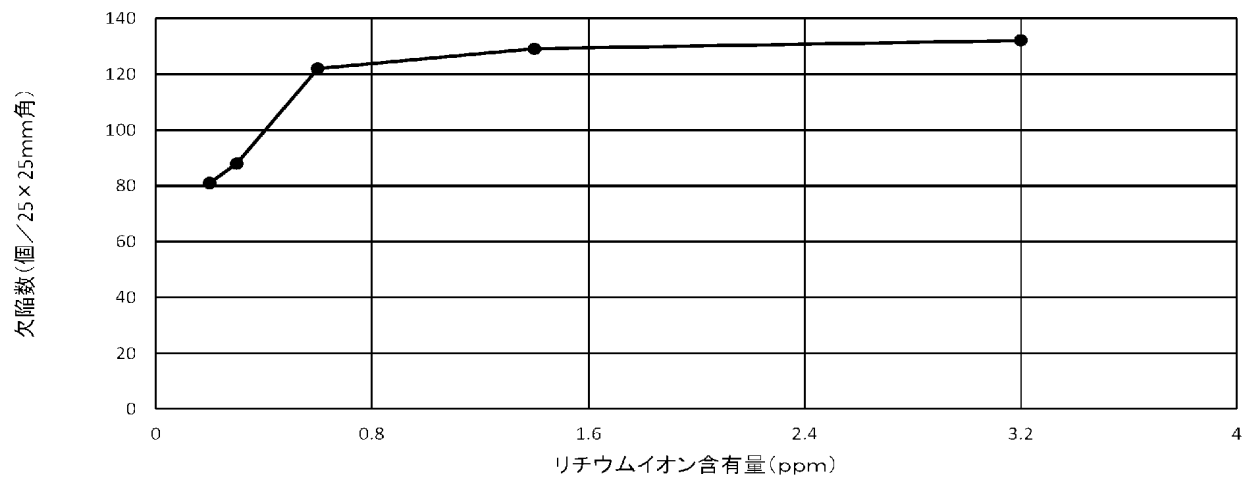
[0075] 特に、酸化防止剤が上述した(1)～(3)の条件をすべて満たす環状オレフィン系樹脂組成物フィルムは、欠陥がより効果的に抑制されていることが分かった。また、実施例2、3のように、スチレン系エラストマーを含有する環状オレフィン系樹脂組成物フィルムは、光学特性（リタデーション、ヘイズ）と靱性（引裂き強度）がより良好であることが分かった。

[0076] 一方、比較例1～3のように、酸化防止剤が上述した(1)～(3)の条件のいずれも満たさない環状オレフィン系樹脂組成物フィルムは、欠陥を抑制するのが困難であることが分かった。

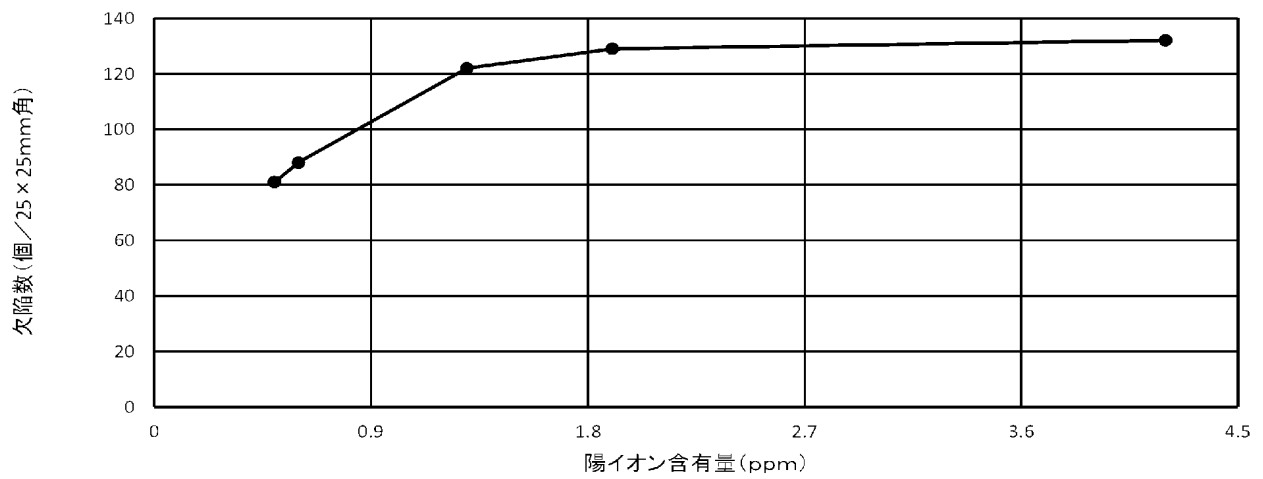
請求の範囲

- [請求項1] 環状オレフィン系樹脂と酸化防止剤とを含有し、上記酸化防止剤が以下の（１）～（３）の条件の少なくとも１つを満たす、環状オレフィン系樹脂組成物フィルム。
- （１）上記酸化防止剤に含まれるリチウムイオンの含有量が０．４ ppm以下である。
- （２）上記酸化防止剤に含まれる陽イオンの含有量が０．９ ppm以下である。
- （３）上記酸化防止剤に含まれる塩化物イオンの含有量が０．１ ppm以下である。
- [請求項2] 上記（１）の条件を少なくとも満たす、請求項１記載の環状オレフィン系樹脂組成物フィルム。
- [請求項3] 上記（３）の条件を少なくとも満たす、請求項１記載の環状オレフィン系樹脂組成物フィルム。
- [請求項4] 上記（１）～（３）の条件を全て満たす、請求項１記載の環状オレフィン系樹脂組成物フィルム。
- [請求項5] 上記酸化防止剤がフェノール系酸化防止剤である、請求項１乃至４のいずれか１項に記載の環状オレフィン系樹脂組成物フィルム。
- [請求項6] スチレン系エラストマーをさらに含有する、請求項１乃至５のいずれか１項に記載の環状オレフィン系樹脂組成物フィルム。
- [請求項7] 上記環状オレフィン系樹脂が、エチレンとノルボルネンの付加共重合体である、請求項１乃至６のいずれか１項に記載の環状オレフィン系樹脂組成物フィルム。

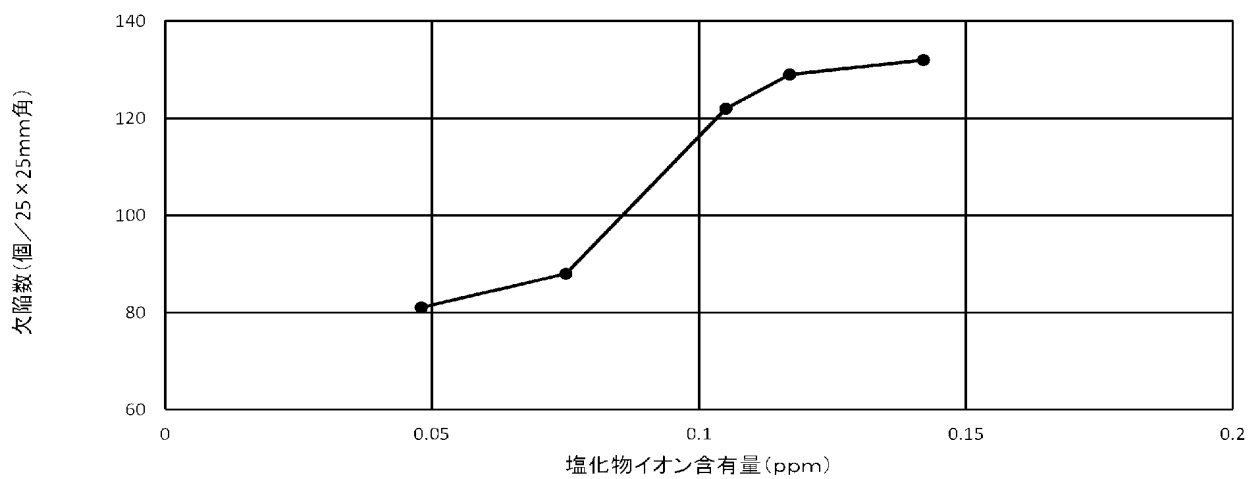
[図1]



[図2]



[図3]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/063847

A. CLASSIFICATION OF SUBJECT MATTER

C08L45/00(2006.01)i, C08L53/02(2006.01)i, C08L65/00(2006.01)i

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)

C08L1/00-101/14

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2016
Kokai Jitsuyo Shinan Koho	1971-2016	Toroku Jitsuyo Shinan Koho	1994-2016

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAplus (STN), REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2001-294615 A (Fuji Electric Co., Ltd.), 23 October 2001 (23.10.2001), claims 1 to 10; paragraphs [0085] to [0109] & US 2001/0056051 A1 claims 1 to 22; paragraphs [0090] to [0106] & US 2003/0204048 A1 & US 2003/0208017 A1	1-7
A	WO 2007/034653 A1 (Nippon Zeon Co., Ltd.), 29 March 2007 (29.03.2007), claims 1 to 18; paragraphs [0056], [0057] & US 2009/0269601 A1 claims 1 to 18; paragraphs [0098], [0100]	1-7

☒ 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

05 July 2016 (05.07.16)

Date of mailing of the international search report

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Name and mailing address of the ISA/

Japan Patent Office

3-4-3, Kasumigaseki, Chiyoda-ku,

Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/063847

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2005-145855 A (Mitsui Chemicals, Inc.), 09 June 2005 (09.06.2005), claims 1 to 11; paragraphs [0057] to [0059] & US 2005/0131182 A1 claims 1 to 6; paragraph [0082]	1-7
A	US 6436476 B1 (Owens Corning Fiberglas Technology, Inc.), 20 August 2002 (20.08.2002), claims 1 to 25; column 12, line 40 to column 15, line 26 & WO 2001/060903 A1	1-7

A. 発明の属する分野の分類（国際特許分類（I P C）） Int.Cl. C08L45/00(2006.01)i, C08L53/02(2006.01)i, C08L65/00(2006.01)i			
B. 調査を行った分野 調査を行った最小限資料（国際特許分類（I P C）） Int.Cl. C08L 1/00-101/14			
最小限資料以外の資料で調査を行った分野に含まれるもの 日本国実用新案公報 1922-1996年 日本国公開実用新案公報 1971-2016年 日本国実用新案登録公報 1996-2016年 日本国登録実用新案公報 1994-2016年			
国際調査で使用した電子データベース（データベースの名称、調査に使用した用語） CAplus (STN), REGISTRY (STN)			
C. 関連すると認められる文献			
引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求項の番号	
X	JP 2001-294615 A（富士電機株式会社） 2001.10.23, 請求項1-10, [0085]-[0109] & US 2001/0056051 A1, 請求の範囲1-22, [0090]-[0106] & US 2003/0204048 A1 & US 2003/0208017 A1	1-7	
A	WO 2007/034653 A1（日本ゼオン株式会社） 2007.03.29, 請求の範囲1-18, [0056], [0057] & US 2009/0269601 A1, 請求の範囲1-18, [0098], [0100]	1-7	
☒ C 欄の続きにも文献が列挙されている。 ☒ パテントファミリーに関する別紙を参照。			
* 引用文献のカテゴリー 「A」特に関連のある文献ではなく、一般的技术水準を示すもの 「E」国際出願日前の出願または特許であるが、国際出願日以後に公表されたもの 「L」優先権主張に疑義を提起する文献又は他の文献の発行日若しくは他の特別な理由を確立するために引用する文献（理由を付す） 「O」口頭による開示、使用、展示等に言及する文献 「P」国際出願日前で、かつ優先権の主張の基礎となる出願日の後に公表された文献 「T」国際出願日又は優先日後に公表された文献であって出願と矛盾するものではなく、発明の原理又は理論の理解のために引用するもの 「X」特に関連のある文献であって、当該文献のみで発明の新規性又は進歩性がないと考えられるもの 「Y」特に関連のある文献であって、当該文献と他の1以上の文献との、当業者にとって自明である組合せによって進歩性がないと考えられるもの 「&」同一パテントファミリー文献			
国際調査を完了した日 05.07.2016		国際調査報告の発送日 12.07.2016	
国際調査機関の名称及びあて先 日本国特許庁（I S A/J P） 郵便番号100-8915 東京都千代田区霞が関三丁目4番3号		特許庁審査官（権限のある職員） 久保田 英樹 電話番号 03-3581-1101 内線 3457	4 J 3776

C (続き) . 関連すると認められる文献		
引用文献の カテゴリ*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求項の番号
A	JP 2005-145855 A (三井化学株式会社) 2005.06.09, 請求項 1 - 1 1, [0 0 5 7] - [0 0 5 9] & US 2005/0131182 A1, 請求の範囲 1-6, [0082]	1-7
A	US 6436476 B1 (Owens Corning Fiberglas Technology, Inc.) 2002.08.20, 請求の範囲 1 - 2 5, 第 1 2 欄第 4 0 行 - 第 1 5 欄第 2 6 行 & WO 2001/060903 A1	1-7

(12) 特許協力条約に基づいて公開された国際出願

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- (25) 国際出願の言語: 日本語
- (26) 国際公開の言語: 日本語
- (30) 優先権データ:
特願 2015-113259 2015 年 6 月 3 日(03.06.2015) JP
- (71) 出願人: ポリプラスチック株式会社(POLY-PLASTICS CO., LTD.) [JP/JP]; 〒1088280 東京都港区港南二丁目 1 8 番 1 号 Tokyo (JP).
- (72) 発明者: 大川 秀俊(OKAWA, Hidetoshi); 〒1088280 東京都港区港南二丁目 1 8 番 1 号 ポリプラスチック株式会社内 Tokyo (JP).
- (74) 代理人: 正林 真之, 外(SHOBAYASHI, Masayuki et al.); 〒1000005 東京都千代田区丸の内 1-7-12 サピアタワー Tokyo (JP).
- (81) 指定国 (表示のない限り、全ての種類の国内保護が可能): AE, AG, AL, AM, AO, AT, AU, AZ, BA,

BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) 指定国 (表示のない限り、全ての種類の広域保護が可能): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), ユーラシア (AM, AZ, BY, KG, KZ, RU, TJ, TM), ヨーロッパ (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

添付公開書類:

- 国際調査報告 (条約第 21 条(3))

(54) Title: LOW-ABSORPTION PACKAGING BAG

(54) 発明の名称: 低吸着性包装袋

(57) Abstract: Provided is a low-absorption packaging bag equipped with a sealant layer that satisfies all of the following: heat-sealability, low absorption, cuttability, and water-vapor barrier properties. A low-absorption packaging bag for storing contents containing a low-molecular-weight volatile compound, wherein a layered body provided with a substrate layer comprising one or more layers and a sealant layer containing a cyclic olefin resin having a glass transition temperature of 50-190°C, inclusive, is formed as a result of heat-sealing with the sealant layer side as the inside surface thereof.

(57) 要約: ヒートシール性、低吸着性、易カット性、水蒸気バリア性のすべてを満足するシーラント層を備える低吸着性包装袋を提供すること。揮発性の低分子化合物を含有する内容物を収容するための包装袋であって、一又は複数の層からなる基材層と、ガラス転移点が 50°C 以上 190°C 以下の環状オレフィン系樹脂を含むシーラント層と、を備える積層体が、シーラント層側を内面としてヒートシールによって形成されている低吸着性包装袋である。



WO 2016/194555 A1

明 細 書

発明の名称：低吸着性包装袋

技術分野

[0001] 本発明は、内容物面側のシーラント層が、医薬品、食品、化粧品等の内容物由来の揮発性低分子化合物の低吸着性（非吸着性）に優れる、低吸着性包装袋に関する。

背景技術

[0002] 環状オレフィン系樹脂とは、主鎖に環状オレフィンの骨格を有する樹脂であり、高透明性、高熱変形温度、低複屈折性、耐加水分解性等、多くの特徴をもつ樹脂である。このため、環状オレフィン系樹脂は、これらの特徴が必要とされる多種多様な分野に用いられている。

[0003] 例えば、下記の特許文献1には、包装用フィルムとして、 T_g が 30°C ～ 55°C の環状オレフィン系樹脂を含む層をシーラント層とする包装用フィルムが開示されている。当該フィルムによれば、非常に低温でのヒートシールが可能となる。

[0004] 一方、包装体の内容物の中には、医薬品、食品、化粧品等の内容物由来の揮発性低分子化合物が存在するものがあり、これらは、包装袋のシーラント層に吸着され易い化合物である。このため、揮発性低分子化合物の低吸着性シーラントとして、EVOH（エチレンービニルアルコール共重合体）、PAN（ポリアクリロニトリル）、PET-G（ジメタノールーポリエチレンテレフタレート）等が主に検討されてきた。

先行技術文献

特許文献

[0005] 特許文献1：特表2007-515511号公報

発明の概要

発明が解決しようとする課題

[0006] 上記のように、従来の低吸着性シーラントであるEVOH、PAN、PE

T-G等は、低吸着性に優れるものの、包装材料としての他の物性である、易カット性、水蒸気バリア性等の点で劣る場合があり、またヒートシール性についても満足できるものではなかった。このため、ヒートシール性、低吸着性、易カット性、水蒸気バリア性のすべてを満足するシーラントフィルム（シーラント層）を備える低吸着性包装袋が要望されていた。

[0007] 本発明は、上記の課題を解決するためになされたものであり、その目的は、ヒートシール性、低吸着性、易カット性、水蒸気バリア性のすべてを満足するシーラントフィルム（シーラント層）を備える低吸着性包装袋を提供することにある。

課題を解決するための手段

[0008] 本発明者は、上記課題を解決するために鋭意研究を重ねた。その結果、ガラス転移点が50℃以上190℃以下である環状オレフィン系樹脂を含むシーラント層を用いた積層体を低吸着性包装袋とすることで、上記の課題を解決できることを見出し、本発明を完成するに至った。より具体的には本発明は以下のものを提供する。

[0009] (1) 分子量800以下の揮発性の低分子化合物を含有する内容物を収容するための包装袋であって、一又は複数の層からなる基材層と、ガラス転移点が50℃以上190℃以下の環状オレフィン系樹脂を含むシーラント層と、を備える積層体が、前記シーラント層側を内面としてヒートシールによって形成されている低吸着性包装袋。

[0010] (2) 前記ガラス転移点が60℃以上150℃以下である、(1)に記載の低吸着性包装袋。

[0011] (3) 前記ガラス転移点が60℃以上100℃以下である、(1)又は(2)に記載の低吸着性包装袋。

[0012] (4) 前記内容物が、食品、医薬品、化粧品より選択される一つ以上である、(1)から(3)のいずれかに記載の低吸着性包装袋。

[0013] (5) 前記環状オレフィン系樹脂は、エチレンとノルボルネンとの共重合体である、(1)から(4)のいずれかに記載の低吸着性包装袋。

[0014] (6) 前記基材層の少なくとも1層が、2軸延伸ポリエチレンテレフタレートフィルムである、(1)から(5)のいずれかに記載の低吸着性包装袋。

[0015] (7) 前記基材層の少なくとも1層が、金属箔、金属蒸着層、金属酸化物蒸着層である、(1)から(6)のいずれかに記載の低吸着性包装袋。

発明の効果

[0016] 本発明によれば、ヒートシール性、低吸着性、易カット性、水蒸気バリア性のすべてを満足するシーラントフィルム（シーラント層）を備える低吸着性包装袋を提供することができる。

発明を実施するための形態

[0017] 以下、本発明の実施形態について詳細に説明する。なお、本発明は以下の実施形態に限定されるものではなく、本発明の目的の範囲内において適宜変更をして実施することができる。

[0018] <低吸着性包装袋>

本発明の低吸着性包装袋は、分子量800以下の揮発性の低分子化合物を含有する内容物を収容するための包装袋であって、当該低吸着性包装袋は、基材層と、シーラント層とを備える積層体であり、当該シーラント層は、ガラス転移点が50℃以上190℃以下の環状オレフィン系樹脂を含む。

[0019] 基材層と、シーラント層とを備える積層体は、例えばポリエチレンテレフタレート層を基材層とし、ポリエチレンテレフタレート層とシーラント層とを積層体や、ポリエチレンテレフタレート層とシーラント層との間にアルミニウム等の金属層を備えた積層体等を例示することができる。

[0020] 本発明の低吸着性包装袋の内側に配置されるシーラント層は、分子量800以下好ましくは分子量500以下の揮発性の分子化合物に対する吸着性の低い層である。本発明の低吸着性包装袋に包装される内容物は分子量800以下の揮発性の低分子化合物を含有する内容物であれば特に限定されないが、例えば、揮発性低分子化合物を有する医薬品、食品、化粧品等用の包装袋として特に好適に使用することができる。揮発性低分子化合物は、例えばd

1-カンフル、1-メントール、サリチル酸メチル、ツロブテロール、ニコチン、塩酸ブロムヘキシシン等を挙げることができる。以下、本発明の低吸着性包装袋を構成する各層について説明する。

[0021] [シーラント層]

本発明におけるシーラント層とは、低吸着性包装袋の内側に配置される層である。本発明におけるシーラント層に含まれる環状オレフィン系樹脂は、50℃以上190℃以下の環状オレフィン系樹脂であって、環状オレフィンの単独重合体又は環状オレフィン成分を共重合成分として含有する共重合体であり、環状オレフィン成分を主鎖に含有するポリオレフィン系樹脂である。本発明におけるシーラント層は、分子量800以下の揮発性の低分子化合物に対する吸着性が低い。また、同時にヒートシール性、易カット性、水蒸気バリア性が高い。シーラント層は従来公知のインフレーション法やTダイ法により熔融押出し成形でき、シーラント層の厚さは5 μm以上100 μm以下が好ましく、10 μm以上50 μm以下がより好ましい。

[0022] シーラント層に含有される環状ポリオレフィン系樹脂は、50℃以上190℃以下の環状オレフィン系樹脂であって、環状オレフィン成分を含有する環状オレフィン系樹脂であれば特に限定されるものではない。例えば、環状オレフィンの付加重合体又はその水素添加物、環状オレフィンと α -オレフィンとの付加共重合体又はその水素添加物等を挙げることができる。環状オレフィン系樹脂は、1種単独で使用することも、2種以上を併用することもできる。ガラス転移点が50℃以上190℃以下の環状オレフィン系樹脂を含むシーラント層を備えた積層体であれば、ヒートシール性、低吸着性、易カット性、水蒸気バリア性のすべてを満足する低吸着性包装袋とすることができる。以下、本発明におけるシーラント層に含まれる環状オレフィン系樹脂について説明する。

[0023] (環状オレフィン系樹脂)

環状オレフィン系樹脂としては、環状オレフィンに由来する構造単位を主鎖に含む上記重合体又は上記共重合体において、さらに極性基を有する不飽

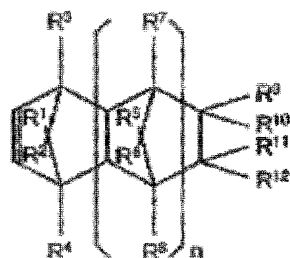
和化合物がグラフト及び／又は共重合したものも挙げられる。

[0024] 極性基としては、例えば、カルボキシル基、酸無水物基、エポキシ基、アミド基、エステル基、ヒドロキシル基等を挙げることができ、極性基を有する不飽和化合物としては、（メタ）アクリル酸、マレイン酸、無水マレイン酸、無水イタコン酸、グリシジル（メタ）アクリレート、（メタ）アクリル酸アルキル（炭素数 1 ～ 10）エステル、マレイン酸アルキル（炭素数 1 ～ 10）エステル、（メタ）アクリルアミド、（メタ）アクリル酸－2－ヒドロキシエチル等を挙げることができる。

[0025] また、本発明において環状オレフィン系樹脂として用いられる共重合体としては、市販の樹脂を用いることもできる。市販されている環状オレフィン系樹脂としては、例えば、TOPAS（登録商標）（TOPAS Advanced Polymers 社製）、アペル（登録商標）（三井化学社製）、ゼオネックス（登録商標）（日本ゼオン社製）、ゼオノア（登録商標）（日本ゼオン社製）、アートン（登録商標）（JSR 社製）等を挙げることができる。

[0026] 環状オレフィンと α -オレフィンとの付加共重合体として、特に好ましい例としては、〔1〕炭素数 2 ～ 20 の α -オレフィンに由来する構造単位と、〔2〕下記一般式（b）で示される環状オレフィンに由来する構造単位と、を含む共重合体を挙げることができる。

[化1]



(b)

（式中、 $R^1 \sim R^{12}$ は、それぞれ同一でも異なっていてもよく、水素原子、ハロゲン原子、及び、炭化水素基からなる群より選ばれるものであり、

R^9 と R^{10} 、 R^{11} と R^{12} は、一体化して2価の炭化水素基を形成してもよく、

R^9 又は R^{10} と、 R^{11} 又は R^{12} とは、互いに環を形成していてもよい。

また、 n は、0又は正の整数を示し、

n が2以上の場合には、 $R^5 \sim R^8$ は、それぞれの繰り返し単位のなかで、それぞれ同一でも異なってもよい。）

[0027] 〔〔1〕炭素数2～20の α -オレフィン〕

炭素数2～20の α -オレフィンは、特に限定されるものではない。例えば、特開2007-302722と同様のものを挙げることができる。また、これらの α -オレフィンは、1種単独でも2種以上を同時に使用してもよい。これらのなかでは、エチレンの単独使用が最も好ましい。

[0028] 〔〔2〕一般式(b)で示される環状オレフィン〕

一般式(b)で示される環状オレフィンについて説明する。一般式(b)における $R^1 \sim R^{12}$ は、それぞれ同一でも異なってもよく、水素原子、ハロゲン原子、及び、炭化水素基からなる群より選ばれるものである。一般式(b)で示される環状オレフィンの具体例としては、特開2007-302722と同様のものを挙げることができる。

[0029] これらの環状オレフィンは、1種単独でも、また2種以上を組み合わせて使用してもよい。これらのなかでは、ビシクロ[2.2.1]ヘプタ-2-エン（慣用名：ノルボルネン）を単独使用することが好ましい。

[0030] 〔〔1〕炭素数2～20の α -オレフィンと〔2〕一般式(b)で表される環状オレフィンとの重合方法及び得られた重合体の水素添加方法は、特に限定されるものではなく、公知の方法にしたがって行うことができる。

[0031] また、用いられる重合触媒についても特に限定されるものではなく、チーグラ-ナッタ系、メタセシス系、メタロセン系触媒等の従来周知の触媒を用いて周知の方法により環状オレフィン系樹脂を得ることができる。

[0032] また、得られた環状オレフィン系樹脂の水素添加方法も特に限定されず、従来公知の方法を適用可能である。

- [0033] なお、環状オレフィン系樹脂は、上記の〔1〕炭素数2～20の α -オレフィン成分と、〔2〕一般式（b）で示される環状オレフィン成分以外に、本発明の目的を損なわない範囲で、必要に応じて他の共重合可能な不飽和単量体成分を含有してもよい。任意に共重合されていてもよい不飽和単量体としては、特に限定されるものではないが、例えば、炭素-炭素二重結合を1分子内に2個以上含む炭化水素系単量体等を挙げることができる。炭素-炭素二重結合を1分子内に2個以上含む炭化水素系単量体の具体例としては、特開2007-302722と同様のものを挙げることができる。
- [0034] 環状オレフィン系樹脂のうち、エチレンとノルボルネンとの付加共重合体が、ヒートシール性、低吸着性、易カット性、水蒸気バリア性を特に有し、低吸着性包装袋として特に好適である。したがって、本発明における環状オレフィン系樹脂としては、エチレンとノルボルネンとの付加共重合体が特に好ましい。
- [0035] 環状オレフィン系樹脂のガラス転移点は、50℃以上190℃以下であり、60℃以上150℃以下が好ましく、60℃以上100℃以下がさらに好ましい。環状オレフィン系樹脂のガラス転移点が50℃未満であると、耐熱性の面で好ましくない。環状オレフィン系樹脂のガラス転移点が190℃超であると、ヒートシール性の面で好ましくない。
- [0036] 環状オレフィン系樹脂のガラス転移点（T_g）は、DSC法（JIS K 7121記載の方法）によって昇温速度10℃/分の条件で測定した値を採用する。
- [0037] 環状オレフィン系樹脂は、ISO 1133に準拠する方法で、260℃、荷重2.16kgの条件で測定されたMVRが1ml/10min以上100ml/10min以下であることが好ましい。環状オレフィン系樹脂のMVRが1ml/10min未満であると、流動性が損なわれてしまう場合がある。また、環状オレフィン系樹脂のMVRが100ml/10minより高くなると、環状オレフィン系樹脂自体の機械強度が低下し、低吸着性包装袋用途には不適となる場合がある。

[0038] 環状オレフィン系樹脂の含有量の下限値は特に限定されないが、シーラント層の全組成物中に好ましくは95質量%以上、より好ましくは98質量%以上である。環状オレフィン系樹脂の含有量の上限値は特に限定されないが、シーラント層の全組成物中に好ましくは100質量%以下である。

[0039] (その他の成分)

本発明におけるシーラント層には環状オレフィン系樹脂以外の成分を配合してもよい。このような他の成分としては、その他の種類の熱可塑性樹脂や、安定剤、強化剤、可塑剤、顔料等の添加剤が例示される。

[0040] [基材層]

本発明における基材層は、積層体に備えられる層であり、主に低吸着性包装袋の内側以外に配置される層である。本発明における基材層は、特に限定されるものではなく、例えば基材層の少なくとも1層が、ポリエチレンテレフタレート樹脂、ナイロン樹脂、ポリプロピレン樹脂、ポリエチレン樹脂等の樹脂フィルムにより構成される基材層を挙げることができる。耐久性及び汎用性の観点から、基材層の少なくとも1層が、2軸延伸ポリエチレンテレフタレートフィルムであることが好ましい。また、基材層は単層のみならず複数の層によって構成されていてもよい。

[0041] また、基材層の少なくとも1層にアルミニウム等の金属箔、金属蒸着層又は金属酸化物蒸着層を設けてもよい。基材層に金属箔、金属蒸着層又は金属酸化物蒸着層を設けることで、水蒸気バリア性を有する低吸着性包装袋とすることができる。

[0042] 基材層の厚さは特に限定されないが、例えば5 μm 以上50 μm 以下であることが好ましく、10 μm 以上40 μm 以下であることがより好ましい。

[0043] <低吸着性包装袋の製造方法>

本発明の低吸着性包装袋の製造方法は特に限定されない。例えば、押出しコーティング法、ホットラミネーション法、ドライラミネーション法等の公知ラミネート方法により積層体を形成する。そして、当該積層体のシートを2枚用意し、当該積層体のシートのシーラント層が向かい合うように重ね、

ヒートシールすることで製造することができる。

[0044] 本発明の低吸着性包装袋の製造方法の一例を示す。まず、基材層とシーラント層とを備える積層体を製造する。積層体は、上記のように、基材層として蒸着層等のその他の層を含んでもよい。その他の層は、本発明の効果を害さない範囲で従来公知のものを適用することができる。

[0045] 本発明における積層体の各層は、接着剤層を介して接着してもよい。接着剤層を形成する接着剤としては例えば１液、あるいは２液硬化型ウレタン系接着剤を用いることができる。

[0046] 次に、積層体を用いて低吸着性包装袋を製造する。延長シール部等のヒートシール装置を用いて積層体の外周をヒートシールすることで、容易に低吸着性包装袋を製造することができる。

実施例

[0047] 以下、実施例を示し、本発明を具体的に説明するが、本発明はこれらの実施例に限定されるものではない。

[0048] [揮発性の低分子化合物吸着試験１]

各樹脂シートについて揮発性の低分子化合物の吸着量を測定した。具体的には、本発明のシーラント層としてなる、表１に記載の各樹脂シート（５０mm×７０mm、厚さ５０μm）の両面に市販の湿布薬（揮発性物質として、d lーカンフル（分子量：１５２）、１ーメントール（分子量：１５６）、サリチル酸メチル（分子量：１５２）を含有）に貼付し、１６時間放置後、樹脂シートに吸収された揮発性物質（d lーカンフル、１ーメントール、サリチル酸メチル）の量をヘッドスペースＧＣ法により測定した。結果を表１に示す。

[0049] [表１]

樹脂シート	d lーカンフル	１ーメントール	サリチル酸メチル
ＣＯＣ	６ μ g	１ ９ μ g	７ ９ μ g
ＰＡＮ	５ μ g	３ ７ μ g	１ １ μ g
ＰＰ	２ ６ ６ μ g	１ １ ４ ２ μ g	５ ７ ０ １ μ g
ＨＤＰＥ	３ ７ ８ μ g	１ ９ ０ ３ μ g	３ ３ ３ ４ μ g
ＬＤＰＥ	７ ７ ７ μ g	２ ０ ４ ４ μ g	３ ９ ０ ７ μ g

(表中、PANはタマポリ社製ハイロトンBXを使用した。PAN以外は樹脂から成膜した。具体的には、COCは、エチレンとノルボルネンとの共重合体(TOPAS Advanced Polymers社製、商品名「TOPAS 8007F-04」、ガラス転移点78℃)から成膜した樹脂シートを意味し、PPは、ポリプロピレン(日本ポリプロ社製 ノバテックFX4E)から成膜した樹脂シートを意味し、HDPEは高密度ポリエチレン(日本ポリエチレン社製、商品名「ノバテックHD HJ580N」、融点134℃)から成膜した樹脂シートを意味し、LDPEは低密度ポリエチレン(日本ポリエチレン社製ノバテックLC522)から成膜した樹脂シートを意味する。)

[0050] 表1から、環状オレフィンであるCOC(エチレンとノルボルネンとの共重合体)の樹脂シートは、PP(ポリプロピレン)、HDPE(高密度ポリエチレン)及びLDPE(低密度ポリエチレン)の樹脂シートと比べ、d-リカンフル、1-メントール、サリチル酸メチルの吸収量が極めて少なく、PANの樹脂シートと同等の吸収量であることが分かる。本試験結果から、環状オレフィン系樹脂を含むシーラント層を備えた積層体を包装袋とした本発明の低吸着性包装袋は、揮発性の低分子化合物の吸収量が少なく、揮発性低分子化合物を有する内容物用の低吸着性包装袋として優れていることが分かる。

[0051] [揮発性の低分子化合物吸着試験2(気相吸着性)]

各樹脂シートについて揮発性の低分子化合物の吸着量を測定した。具体的には、デジケート内に揮発性物質(ツロブテロール 分子量:228、和光純薬(株) ツロブテロール(異性体混合物) 薬理研究用)及び表2に記載の各樹脂シート(50mm×50mm、厚さ30μm)を入れ密閉し、2週間放置後、樹脂シートに吸収された揮発性物質(ツロブテロール)の量をヘッドスペースGC法により測定した。結果を表2に示す。

[0052]

[表2]

樹脂シート	ツロブテロール
COC (TOPAS 8007F-04)	0.04 μ g
COC (TOPAS 6013F-04)	0.07 μ g
PAN	1.9 μ g
LLDPE	4.8 μ g

(表中、PANはタマポリ社製ハイロトンBXを使用した。PAN以外は樹脂から成膜した。具体的には、COC (TOPAS 8007F-04) は、エチレンとノルボルネンとの共重合体 (TOPAS Advanced Polymers社製、商品名「TOPAS 8007F-04」、ガラス転移点78℃) から成膜した樹脂シートを意味し、COC (TOPAS 6013F-04) は、エチレンとノルボルネンとの共重合体 (TOPAS Advanced Polymers社製、商品名「TOPAS 6013F-04」、ガラス転移点138℃) から成膜した樹脂シートを意味し、LLDPEは直鎖状低密度ポリエチレン (ダウケミカル社製 ELITE 5100G 密度0.92 g/cm³) から成膜した樹脂シートを意味する。)

[0053] 表2から、環状オレフィンであるCOC (エチレンとノルボルネンとの共重合体) の樹脂シートは、PAN (ポリアクリロニトリル) 及びLLDPE (直鎖状低密度ポリエチレン) の樹脂シートと比べ、ツロブテロールの吸収量が少ないことが分かる。本試験結果から、環状オレフィン系樹脂を含むシーラント層を備えた積層体を包装袋とした本発明の低吸着性包装袋は、揮発性の低分子化合物の吸収量が少なく、揮発性低分子化合物を有する内容物用の低吸着性包装袋として優れていることが分かる。

[0054] [積層体の易カット性試験]

表3に記載のインフレーションフィルム (厚み100 μ m) と、ポリエチレンテレフタレートとをドライラミネーションで一体化し積層体を製造し、積層体について易カット性試験を行った。具体的には手で積層体を容易にカットできるか以下の評価基準の下評価を行った。評価結果を表3に示す。

[0055] [評価基準]

○：容易にカットできる

△：カットが可能であるが、少々困難である

×：カットが不可能、又はカットが極めて困難である

[0056] [表3]

	シーラント層	易カット性
実施例	C O C	○
比較例 1	E V O H	△～×
比較例 2	P A N	○
比較例 3	P E T - G	△

(表中、P A Nはタマポリ社製ハイロトンB Xを使用した。P A N以外は樹脂から成膜した。具体的には、C O Cは、エチレンとノルボルネンとの共重合体(T O P A S A d v a n c e d P o l y m e r s社製、商品名「T O P A S 8 0 0 7 F - 0 4」、ガラス転移点7 8℃)から成膜した樹脂シートを意味し、E V O Hは、エチレン・ビニルアルコール共重合樹脂(クラレ製エバールF)から成膜した樹脂シートを意味し、P E T - Gは、ジメタノールーポリエチレンテレフタレート(E A S T M A N社製 E A S T A R G N O O 1)から成膜した樹脂シートを意味する。)

[0057] 表3より、シーラント層として、C O C(エチレンとノルボルネンとの共重合体)を用いた積層体は、他の樹脂シートをシーラント層として用いた積層体と比較して易カット性に優れた積層体であることが分かる。そのため、本発明の低吸着性包装袋は、易カット性に優れ、揮発性の低分子化合物を含有する内容物を収容するための包装袋として優れていることが分かる。

請求の範囲

- [請求項1] 分子量800以下の揮発性の低分子化合物を含有する内容物を収容するための包装袋であって、
- 一又は複数の層からなる基材層と、ガラス転移点が50℃以上190℃以下の環状オレフィン系樹脂を含むシーラント層と、を備える積層体が、前記シーラント層側を内面としてヒートシールによって形成されている低吸着性包装袋。
- [請求項2] 前記ガラス転移点が60℃以上150℃以下である、請求項1に記載の低吸着性包装袋。
- [請求項3] 前記ガラス転移点が60℃以上100℃以下である、請求項1又は2に記載の低吸着性包装袋。
- [請求項4] 前記内容物が、食品、医薬品、化粧品より選択される一つ以上である、請求項1から3のいずれかに記載の低吸着性包装袋。
- [請求項5] 前記環状オレフィン系樹脂は、エチレンとノルボルネンとの共重合体である、請求項1から4のいずれかに記載の低吸着性包装袋。
- [請求項6] 前記基材層の少なくとも1層が、2軸延伸ポリエチレンテレフタレートフィルムである、請求項1から5のいずれかに記載の低吸着性包装袋。
- [請求項7] 前記基材層の少なくとも1層が、金属箔、金属蒸着層、金属酸化物蒸着層である、請求項1から6のいずれかに記載の低吸着性包装袋。

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/063853

A. CLASSIFICATION OF SUBJECT MATTER

B65D65/40(2006.01)i, B32B27/32(2006.01)i

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)

B65D65/40, B32B27/32

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2016
 Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2012-236382 A (DIC Corp.), 06 December 2012 (06.12.2012), claims 1, 13, 15; paragraphs [0008], [0013], [0017], [0019], [0038] to [0039], [0047], [0068], [0073]; table 1 (Family: none)	1-7
A	JP 2012-111182 A (Dainippon Printing Co., Ltd.), 14 June 2012 (14.06.2012), entire text; all drawings (Family: none)	1-7
A	JP 2015-89619 A (DIC Corp.), 11 May 2015 (11.05.2015), entire text (Family: none)	1-7

☐ 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
26 July 2016 (26.07.16)Date of mailing of the international search report
09 August 2016 (09.08.16)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

A. 発明の属する分野の分類（国際特許分類（I P C））

Int.Cl. B65D65/40(2006.01)i, B32B27/32(2006.01)i

B. 調査を行った分野

調査を行った最小限資料（国際特許分類（I P C））

Int.Cl. B65D65/40, B32B27/32

最小限資料以外の資料で調査を行った分野に含まれるもの

日本国実用新案公報	1922-1996年
日本国公開実用新案公報	1971-2016年
日本国実用新案登録公報	1996-2016年
日本国登録実用新案公報	1994-2016年

国際調査で使用した電子データベース（データベースの名称、調査に使用した用語）

C. 関連すると認められる文献

引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求項の番号
X	JP 2012-236382 A (D I C株式会社) 2012.12.06, 【請求項1】、【請求項13】、【請求項15】、段落【0008】、段落【0013】、段落【0017】、段落【0019】、 段落【0038】-【0039】、段落【0047】、段落【0068】、段落【0073】、【表1】（ファミリーなし）	1-7
A	JP 2012-111182 A (大日本印刷株式会社) 2012.06.14, 全文, 全図（ファミリーなし）	1-7
A	JP 2015-89619 A (D I C株式会社) 2015.05.11, 全文（ファミリーなし）	1-7

C欄の続きにも文献が列挙されている。

パテントファミリーに関する別紙を参照。

* 引用文献のカテゴリー

「A」特に関連のある文献ではなく、一般的技术水準を示すもの
「E」国際出願日前の出願または特許であるが、国際出願日以後に公表されたもの
「L」優先権主張に疑義を提起する文献又は他の文献の発行日若しくは他の特別な理由を確立するために引用する文献（理由を付す）
「O」口頭による開示、使用、展示等に言及する文献
「P」国際出願日前で、かつ優先権の主張の基礎となる出願

の日の後に公表された文献

「T」国際出願日又は優先日後に公表された文献であって出願と矛盾するものではなく、発明の原理又は理論の理解のために引用するもの
「X」特に関連のある文献であって、当該文献のみで発明の新規性又は進歩性がないと考えられるもの
「Y」特に関連のある文献であって、当該文献と他の1以上の文献との、当業者にとって自明である組合せによって進歩性がないと考えられるもの
「&」同一パテントファミリー文献

国際調査を完了した日

26.07.2016

国際調査報告の発送日

09.08.2016

国際調査機関の名称及びあて先

日本国特許庁（I S A/J P）

郵便番号100-8915

東京都千代田区霞が関三丁目4番3号

特許庁審査官（権限のある職員）

佐野 健治

電話番号 03-3581-1101 内線 3361

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(71) Applicant: **BEMIS COMPANY, INC.** [US/US]; One Neenah Center 4th Floor, Neenah, WI 54956 (US).

(72) Inventors: **GLASER, Kevin, D.**; 65 Jacob Avenue, Oshkosh, WI 54902 (US). **ODUSANYA, Ayomide, O.**; 1750 N. Mccarthy Road # 6, Appleton, WI 54913 (US).

(74) Agent: **PARSONS, Christine, E.**; Bemis Company, Inc., Office Of Intellectual Property Counsel, PO Box 669, Neenah, WI 54957-0669 (US).

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AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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(54) Title: MULTILAYERED SHEET

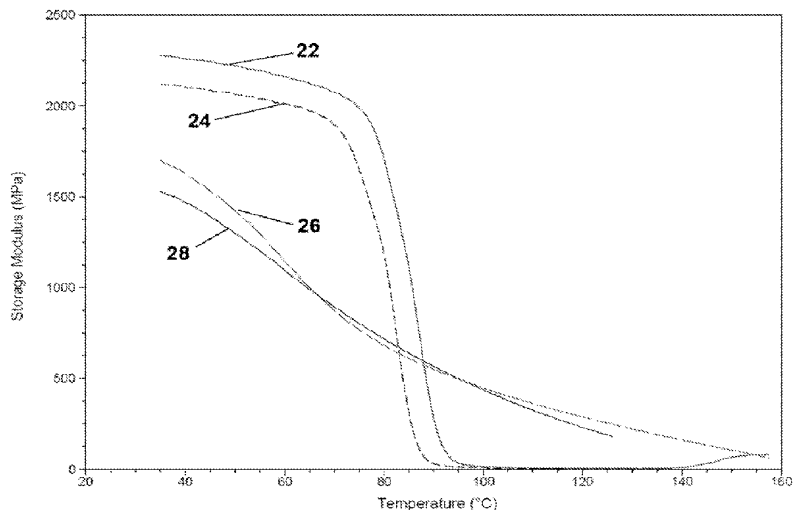


FIG. 2

(57) Abstract: A multilayered sheet is described. The sheet comprises a first layer comprising a polyolefin having a melting temperature, a storage modulus (G) greater than 100,000 psi (690 MPa) at ambient temperature, and a glass transition temperature less than ambient temperature; and a second layer comprising a polymer having a glass transition temperature greater than ambient temperature.

MULTILAYERED SHEET

BACKGROUND OF THE INVENTION

The present application describes a multilayered sheet, specifically a multilayered sheet that may be both thermoformable and thermally stable.

Packaging film and packaging sheet are used for many purposes. One of these many purposes includes thermoforming the film or sheet into packages, such as trays, plates or other containers, which may then be used to package products. Another of these many purposes includes packaging products subjected to thermal processing, including but not limited to retort, aseptic, hot-fill or microwave processing.

One packaging sheet that is currently used for thermoforming into packages is disclosed in U.S. Patent Application Publication Pub. No. US 2011/0104342 (published May, 5, 2011). This sheet comprises a first rigid component and a second rigid component and has a normalized combined tear initiation and propagation resistance in both machine direction and transverse direction of less than about 0.115 in*lb / mil (0.0511 Ncm / micron) energy to break and an elongation in both machine direction and transverse direction of less than about 0.800 % / mil (0.0315 % / micron) as measured in accordance with ASTM D1004. The first rigid component and the second rigid component are exemplified by identical blends of high impact polystyrene (HIPS) and general purpose polystyrene (GPPS). Thermoformed packages formed from this sheet having a first rigid component having an analogous composition as a second rigid component are expected to distort and deform when exposed to temperatures above 194 °F (about 90 °C) due to the presence of the polystyrene. One sheet that is currently used for thermoformed packages exposed to temperatures above 194 °F (about 90 °C) comprises a sheet having two exterior layers of polypropylene. However, a sheet with two exterior layers of polypropylene is expected to be difficult to thermoform. Additionally, the methods of manufacturing a sheet with two layers of polypropylene are expected to be limited due to

polypropylene's crystallinity and other properties. What is needed is a sheet that may be both thermoformable and thermally stable.

BRIEF SUMMARY OF THE INVENTION

This need is met by the multilayered sheet described in the present application. The sheet comprises a first layer comprising a polyolefin having a melting temperature, a storage modulus (G'_1) greater than about 100,000 psi (about 690 MPa) at ambient temperature, and a glass transition temperature less than ambient temperature. The sheet further comprises a second layer comprising a polymer having a glass transition temperature greater than ambient temperature. The first layer comprises different materials than the second layer. The melting temperature of the polyolefin of the first layer is greater than the glass transition temperature of the polymer of the second layer. Each of the polyolefin of the first layer and the polymer of the second layer has a storage modulus (G'_1 and G'_2 , respectively) at about 35 °C and a storage modulus (G') at a midpoint temperature that is the average of the glass transition temperature of the polymer of the second layer and the melting temperature of the polyolefin of the first layer. The ratio of G'_1 to G'_2 at about 35 °C is less than 1, and the ratio of G'_1 to G'_2 at the midpoint temperature is greater than one. The sheet has a thickness equal to or greater than 10 mil (254 micron). In some embodiments, the sheet has a thickness of from about 30 mil (about 762 micron) to about 50 mil (about 1270 micron). The first layer contributes at least about 30 % of the thickness of the sheet and the second layer contributes at least about 25 % but less than about 60 % of the thickness of the sheet. In some embodiments, the first layer contributes from about 30 % to about 65 % of the thickness of the sheet and the second layer contributes from about 25 % to about 55 % of the thickness of the sheet.

In some embodiments, the polyolefin of the first layer may comprise polypropylene, high density polyethylene or blends of such. As a non-limiting example, the polyolefin of the first layer may comprise from about 50 % (by weight) to about 70 % (by weight) polypropylene

homopolymer and from about 30 % (by weight) to about 50 % (by weight) high density polyethylene.

In some embodiments, the polymer of the second layer may comprise polyester, cyclic olefin copolymer, styrenic polymers or blends of such. More specifically, as non-limiting examples, the polymer of the second layer may comprise amorphous or semi-crystalline polyester (APET), glycol-modified polyethylene terephthalate (PETG), isophthalic acid (IPA)-modified co-polyester (PETI), polylactic acid (PLA), copolyesters, high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC) or blends of such.

In some embodiments, the sheet may include a first layer comprising from about 50 % (by weight) to about 70 % (by weight) polypropylene homopolymer and from about 30 % (by weight) to about 50 % (by weight) high density polyethylene and a second layer comprising amorphous or semi-crystalline polyester (APET).

In some embodiments, each of the first layer and the second layer of the sheet may be an exterior layer or an interior layer. In a further embodiment, the second layer may be an interior layer bonded to an exterior layer via an intermediate layer.

In some embodiments, the sheet may comprise an adhering layer positioned between the first layer and the second layer. As non-limiting examples, this adhering layer may comprise an adhesive, an extrudate, a coating, a tie material or a multilayer film. In a further embodiment, as a non-limiting example, the adhering layer may comprise a multilayer, blown film.

The sheet described in the present application may have various properties. As non-limiting examples, the sheet may have a normalized combined tear initiation and propagation resistance in both machine direction and transverse direction of greater than about 0.115 in*lb / mil (0.0511 Ncm / micron) energy to break and an elongation in both machine direction and transverse direction of greater than about 0.800 % / mil (0.0315 % / micron) as measured in accordance with ASTM D1004. The sheet may have between 0 and about 20 degrees of

transverse direction curl. The sheet may be thermoformable and, as such may be thermoformed into a package. Such package may exhibit a compression strength that is greater than about 125 % of a compression strength of an other package formed from an other sheet having an other first layer comprising the same polyolefin and having an analogous composition as an other second layer, wherein the other first layer contributes at least about 30 % of the thickness of the other sheet and the other second layer contributes at least about 25 % but less than about 60 % of the thickness of the other sheet. In some embodiments, this compression strength may be from about 150 % to about 300 % of the compression strength of the other package. The sheet may be thermally stable when exposed to temperatures from about 194 °F (about 90 °C) to about 284 °F (about 140 °C). As such, the sheet may form a package for retort, aseptic, hot-fill or microwave processing.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a first embodiment of a thermoplastic sheet according to the present application.

FIG. 2 is a graph depicting the storage modulus (G') temperature sweep of four materials.

FIG. 3 is a cross-sectional view of a second embodiment of a thermoplastic sheet according to the present application

FIG. 4 is a picture depicting two example cutting templates for use in the curl test method.

FIG. 5 is a picture depicting a curl tester placed on a prepared, cut sample to determine the degree of curl.

FIG. 6 is a graph depicting the oxygen transmission rates at various time intervals for identical trays formed from thermoplastic sheets according to the present application and formed from a comparative example.

DETAILED DESCRIPTION OF THE INVENTION

As used throughout this application, the term "sheet" refers to a plastic web having a thickness of equal to or greater than about 10 mil (about 254 micron). The term "film" refers to a plastic web having a thickness of less than about 10 mil (about 254 micron).

As used throughout this application, the term "about" refers to approximately, rounded up or down to, reasonably close to, in the vicinity of, or the like. The term "approximate" is synonymous with the term "about." Unless the context specifically requires otherwise, each quantified property (e.g., temperature, melting temperature, glass transition temperature, storage modulus, etc.) cited or referenced in this application is qualified by "about," whether or not "about" appears before the quantified property.

As used throughout this application, the term "thermoplastic" refers to a polymer or polymer mixture that softens when exposed to heat and then returns to its original condition when cooled to room temperature. In general, thermoplastic materials may include natural or synthetic polymers. Thermoplastic materials may further include any polymer that is cross-linked by either radiation or chemical reaction during manufacturing or post-manufacturing processes.

As used throughout this application, the term "polyolefin" (or "polyalkene") refers to any of a class of polymers produced from an alkene (or "olefin") with the general formula C_nH_{2n} .

As used throughout this application, the term "polymer" refers to a material which is the product of a polymerization or copolymerization reaction of natural, synthetic or combined natural and synthetic monomers and/or co-monomers and is inclusive of homopolymers, copolymers, terpolymers, quaterpolymers, etc. In general, the layers of the sheet described in the present application may comprise a single polymer, a mixture of a single polymer and non-polymeric material, a combination of two or more polymers blended together, a mixture of a blend of two or more polymers and non-polymeric material, or other such components. It will be

noted that many polymers may be synthesized by the mutual reaction of complementary monomers. It will also be noted that some polymers are obtained by the chemical modification of other polymers such that the structure of the macromolecules that constitute the resulting polymer can be thought of as having been formed by the homopolymerization of a hypothetical monomer.

As used throughout this application, the term "storage modulus" or "G'" refers to a measure of the elastic response of a material and may also be called also called the elastic modulus, the in-phase modulus, and the real modulus. This value is only ideally equivalent to Young's modulus. In reality (versus ideality), Young's modulus is calculated over a range of stresses and strains (as it is the slope of a line), while storage modulus is a point on the line. Furthermore, in reality, Young's modulus is determined via the stress-strain test and involves constantly stretching a material, while storage modulus is determined via the dynamic test and involves oscillating a material. As an example, if the material to be tested were a ball, the storage modulus (the elasticity) could be related to the amount of energy the ball gives back (how high it bounces). Therefore, as used throughout this application, storage modulus is different than Young's modulus.

As used throughout this application, the term "ambient temperature" generally refers to a surrounding environment or room temperature of about 68-77 °F (about 20-25 °C).

As used throughout this application, the term "rigid" refers to a plastic material having a storage modulus greater than about 100,000 psi (about 690 MPa) at ambient temperature.

As used throughout this application, the term "melting point" (or "melting temperature") refers to the temperature at which a solid and a liquid phase of a material may coexist in equilibrium. It is the temperature at which a solid melts to become a liquid and the material flows or begins to flow.

As used throughout this application, the term "glass transition temperature" or " T_g " refers to the temperature range over which a material transitions from a glassy state to a rubbery state (i.e., the temperature range over which a material "softens"). It is noted by the onset decrease in the storage modulus, accompanied by a peak in tan delta, during temperature scan heating. The glass transition temperature is, in actuality, a range. However, scientists have agreed to accept a single temperature as the indicator per certain standards, such as those associated with differential scanning calorimetry (DSC), thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA).

As used throughout this application, the term "midpoint temperature" refers to the temperature half-way between the glass transition temperature (T_g) of the polymer of the second layer and the melting temperature (T_m) of the polyolefin of the first layer. In other words, midpoint temperature is the average of the glass transition temperature (T_g) of the polymer of the second layer and the melting temperature (T_m) of the polyolefin of the first layer.

As used throughout this application, the term "polyester" refers to a homopolymer or copolymer having an ester linkage between monomer units. The ester linkage can be represented by the general formula: $[O-R-OC(O)-R'-C(O)]_n$, where R and R' are the same or different alkyl (or aryl) group and may be generally formed from the polymerization of dicarboxylic acid and diol monomers. The dicarboxylic acid (including the carboxylic acid moieties) may be linear or aliphatic (e.g., lactic acid, oxalic acid, maleic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, and the like) or may be aromatic or alkyl substituted aromatic (e.g., various isomers of phthalic acid, such as paraphthalic acid (or terephthalic acid), isophthalic acid and naphthalic acid). Specific examples of a useful diol include but are not limited to ethylene glycol, propylene glycol, trimethylene glycol, 1,4-butane diol, neopentyl glycol, cyclohexane diol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, and the like. Polyesters may include a homopolymer or copolymer of alkyl-

aromatic esters, including but not limited to polyethylene terephthalate (PET), amorphous polyethylene terephthalate (APET), glycol-modified polyethylene terephthalate (PETG), and polybutylene terephthalate (PBT); a copolymer of terephthalate and isophthalate including but not limited to polyethylene terephthalate/isophthalate copolymer, such as isophthalic acid (IPA) (modified polyethylene terephthalate (PETI)); a homopolymer or copolymer of aliphatic esters including but not limited to polylactic acid (PLA); polyhydroxyalkonates including but not limited to polyhydroxypropionate, poly(3-hydroxybutyrate) (PH3B), poly(3-hydroxyvalerate) (PH3V), poly(4-hydroxybutyrate) (PH4B), poly(4-hydroxyvalerate) (PH4V), poly(5-hydroxyvalerate) (PH5V), poly(6-hydroxydodecanoate) (PH6D); and blends of any of these materials.

As used throughout this application, the term "copolymer" refers to a polymer product obtained by the polymerization reaction or copolymerization of at least two monomer species. Copolymers may also be referred to as bipolymers. The term "copolymer" is also inclusive of the polymerization reaction of three, four or more monomer species having reaction products referred to terpolymers, quaterpolymers, etc.

As used throughout this application the term "cyclic olefin copolymer" or "COC" refers to a class of polymeric materials based on cyclic olefin monomers and ethane, with one or more different cyclic olefin units randomly or alternately attached to an ethylene polymer backbone. Ethylene/norbornene copolymers are a non-limiting example of cyclic olefin copolymers.

As used throughout this application, the term "polystyrene" or "PS" or "styrenic polymer" refers to a homopolymer or copolymer having at least one styrene monomer linkage (such as benzene (i.e., C_6H_6) having an ethylene substituent) within the repeating backbone of the polymer. The styrene linkage can be represented by the general formula: $[CH_2-CH_2(C_6H_5)]_n$.

As used throughout this application, the term "polypropylene" or "PP" refers to a plastomer, homopolymer or copolymer having at least one propylene monomer linkage within the repeating backbone of the polymer. The propylene linkage can be represented by the

general formula: $[\text{CH}_2\text{-CH}(\text{CH}_3)]_n$. Such propylene may be a polypropylene impact copolymer, a polypropylene random copolymer or a polypropylene homopolymer, may be syndiotactic or isotactic and/or may or may not be clarified.

As used throughout this application, the term "high density polyethylene" or "HDPE" refers to both (a) homopolymers of ethylene which have densities from about 0.960 g/cc to about 0.970 g/cc and (b) copolymers of ethylene with at least one alpha-olefin (e.g., 1-butene or 1-hexene) which have densities from about 0.940 g/cc to about 0.958 g/cc. HDPE includes polymers made with Ziegler or Phillips type catalysts and polymers made with single-site metallocene catalysts. HDPE also includes high molecular weight "polyethylenes." Non-limiting examples of high density polyethylene useful in various embodiments of the present application include those having a density of from about 0.950 g/cc to about 0.970 g/cc.

As used throughout this application, the terms "copolymer of ethylene with at least one alpha-olefin" or "ethylene alpha-olefin copolymer" refer to a modified or unmodified copolymer produced by the co-polymerization of ethylene and any one or more alpha-olefins. Suitable alpha-olefins include, for example, C_3 to C_{20} alpha-olefins such as propene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene and blends of such. The co-polymerization of ethylene and an alpha-olefin may be produced by heterogeneous catalysis, such as co-polymerization reactions with Ziegler-Natta catalysis systems, including, for example, metal halides activated by an organometallic catalyst (e.g., titanium chloride) and optionally containing magnesium chloride complexed to trialkyl aluminum. Additionally, the co-polymerization of ethylene and an alpha-olefin may also be produced by homogeneous catalysis, such as co-polymerization reactions with metallocene catalysis systems which include constrained geometry catalysts, (e.g., monocyclopentadienyl transition-metal complexes). In general, homogeneous catalyzed ethylene alpha-olefin copolymers may be characterized by one or more methods known in the

art, including but not limited to molecular weight distribution (M_w/M_n), composition distribution breadth index (CDBI), narrow melting point range and single melting point behavior.

As used throughout this application, the term "modified" refers to a chemical derivative, whether grafted onto a polymer, copolymerized with a polymer or blended with one or more polymers. The term also includes derivatives of such functionalities, such as acids, esters and metal salts derived from such.

As used throughout this application, the term "layer" refers to a discrete film or sheet component which may or may not be coextensive with the film or sheet but has a substantially uniform composition. In referring to a monolayer film or monolayer sheet, "film" and "layer" or "sheet" and "layer" are synonymous.

As used throughout this application, the term "exterior layer" refers to a layer comprising the outermost surface of a film, sheet or other article relative to the contents of the filled package (i.e., the layer of the film, sheet or other article farthest from the contents of the filled package). The term "interior layer" refers to a layer comprising the innermost surface of a film, sheet or other article relative to the contents of the filled package (i.e., the layer of the film, sheet or other article, closest to the contents of the filled package). Additionally, the exterior layer and the interior layer each have an inner surface and an outer surface. The term "inner surface" refers to a surface touching another layer, and the term "outer surface" refers to a surface not touching another layer.

As used throughout this application, the term "intermediate layer" refers to a layer that is positioned between two other layers. An intermediate layer has two inner surfaces.

As used throughout this application, the term "polyethylene" or "PE" refers (unless indicated otherwise) to ethylene homopolymers or copolymers. Such copolymers of ethylene include copolymers of ethylene with at least one alpha-olefin and copolymers of ethylene with

other units or groups such as vinyl acetate or otherwise. The term "polyethylene" or "PE" is used without regard to the presence or absence of substituent branch groups.

As used throughout this application, the term "tie material" refers to a polymeric material serving a primary purpose or function of adhering two surfaces to one another, presumably the planar surfaces of two sheet or film layers. A tie material may adhere one sheet or film layer surface to another sheet or film layer surface or may adhere one area of a sheet or film layer surface to another area of the same sheet or film layer surface

As used throughout this application, the term "multilayer" refers to a plurality of layers in a single structure generally in the form of a film or sheet which may be made from a polymeric material or a non-polymeric material bonded together by any conventional means known in the art (e.g., coextrusion, lamination, coating or blends of such).

As used throughout this application, the term "structural layer" or "bulk layer" refers to a layer that creates or provides structural support, substance or stability to the sheet or a layer that simply provides desired thickness for the sheet.

As used throughout this application, the term "blown film" refers to a film produced by the blown coextrusion process. In the blown coextrusion process, streams of melt-plastified polymers are forced through an annular die having a central mandrel to form a tubular extrudate. The tubular extrudate may be expanded to a desired wall thickness by a volume of fluid (e.g., air or other gas) entering the hollow interior of the extrudate via the mandrel, and then rapidly cooled or quenched by any of various methods known to those of skill in the art.

As used throughout this application, the term "sealant layer" refers to a layer of a film, sheet, etc. involved in the sealing of the film, sheet, etc. to itself and/or to another layer of the same or another film, sheet, etc.

As used throughout this application, the term "barrier" refers to any material which controls a permeable element of a film or a sheet and includes but is not limited to oxygen barrier, moisture barrier, chemical barrier, heat barrier and odor barrier.

As used throughout this application, the term "thermoformable" refers to a sheet capable of being formed or thermoformed into a desired shape by the application of a differential pressure between the sheet and a mold, by the application of heat, by the combination of the application of heat and a differential pressure between the sheet and a mold, or by any thermoforming technique known to those skilled in the art.

As used throughout this application, the term "package" refers to any article used to wholly or partially surround or contain an item. A package may take many, various forms. For example, the term "package" may include pouches that wholly surround or contain an item (or items) to be packaged. The term "package" may also include films, sheets, etc. that partially surround or contain an item (or items) to be packaged and, when used in conjunction with another film, sheet, etc. wholly surround or contain an item (or items). The term package may further include cups, trays, plates or other containers formed by thermoforming a sheet or film.

As used throughout this application, the term "thermally stable" refers to an article capable of maintaining dimensionality and shape and not distorting or deforming when exposed to temperatures from about 194 °F (about 90 °C) to about 284 °F (about 140 °C).

As used throughout this application, the term "retort" refers to a sterilization process in which a food item packaged in a flexible package is heated to about 220-250°F (about 104-121°C) or higher for several minutes under high pressure.

As used throughout this application, the term "aseptic" refers to a process in which a packaged product and its packaging component(s) are sterilized separately and then combined in a sterile or sterilized environment to form a shelf-stable package.

As used throughout this application, the term "hot-fill" refers to a process in which a packaged component (e.g., liquid such as juice or other beverage) is heated to about 194-203 °F (about 90-95 °C) and then packaged (e.g., dispensed into a package) and sealed at a slightly lower temperature (e.g., about 180-185 °F (about 82-85 °C)).

As used throughout this application, the term "microwave" refers to a process in which electromagnetic waves heat water in food to the boiling point of water (about 212 °F (about 100 °C).)

Referring now to the drawings, with some but not all embodiments shown, with elements depicted as illustrative and not necessarily to scale, and with the same (or similar) reference numbers denoting the same (or similar) features throughout the drawings, FIG. 1 is a cross-sectional view of a first embodiment of a thermoplastic sheet according to the present application. Sheet 10 depicted in FIG. 1 is a generalized embodiment and comprises first layer 12 and second layer 14.

First layer 12 comprises a polyolefin which has (a) some degree of crystallinity and, therefore, has a melting temperature, (b) a storage modulus (G'_1) greater than about 100,000 psi (about 690 MPa) at ambient temperature (i.e., about 68-77 °F (about 20-25 °C)), and (c) a glass transition temperature less than ambient temperature (i.e., about 68-77 °F (about 20-25 °C)).

As the polyolefin of first layer 12 has a storage modulus (G'_1) greater than about 100,000 psi (about 690 MPa) at ambient temperature (i.e., about 68-77 °F (about 20-25 °C)), the polyolefin is, by definition, a rigid material. In some embodiments, the polyolefin of first layer 12 may have a storage modulus from greater than about 100,000 psi (about 690 MPa) to about 500,000 psi (about 3,450 MPa) at ambient temperature.

In some embodiments, the polyolefin of first layer 12 may comprise polypropylene, high density polyethylene, or blends of such. As non-limiting examples, first layer 12 may comprise any one of the following:

- 100 % (by weight) polypropylene homopolymer;
- 100 % (by weight) high density polyethylene;
- from about 60 % (by weight) to about 90 % (by weight) polypropylene homopolymer and from about 10 % (by weight) to about 40 % (by weight) polypropylene random copolymer;
- from about 70 % (by weight) to about 80 % (by weight) polypropylene homopolymer and from about 20 % (by weight) to about 30 % (by weight) polypropylene random copolymer;
- from about 40 % (by weight) to about 80 % (by weight) polypropylene homopolymer and from about 20 % (by weight) to about 60 % (by weight) high density polyethylene; or
- from about 50 % (by weight) to about 70 % (by weight) polypropylene homopolymer and from about 30 % (by weight) to about 50 % (by weight) high density polyethylene.

Examples of polypropylene include but are not limited to polypropylene impact copolymer, polypropylene random copolymer and polypropylene homopolymer. Further non-limiting examples of polypropylene useful in various embodiments of the present application include syndiotactic or isotactic polypropylene. Polypropylene has a reported melting temperature of 119-186 °C. (See Howe, "Polypropylene, isotactic," *Polymer Data Handbook*, 1999, pp. 780-786 (Oxford University Press, Inc., New York, New York); and Myers, "Polypropylene, syndiotactic," *Polymer Data Handbook*, 1999, pp. 798-801 (Oxford University Press, Inc., New York, New York).) Polypropylene homopolymer has a reported storage modulus of 1,400 MPa (about 203,053 psi) at 20 °C (30 Hz). (See Howe, "Polypropylene,

isotactic," *Polymer Data Handbook*, 1999, pp. 780-786 (Oxford University Press, Inc., New York, New York).) Based on a review of literature, polypropylene has a reported glass transition temperature of -60-10 °C. Examples of polypropylene impact copolymer include but are not limited to Polypropylene 4170 and Polypropylene 4481WZ, both of which are available from Total Petrochemicals & Refining USA, Inc. (Houston, Texas). Examples of polypropylene random copolymer include but are not limited to Polypropylene RP650, which is available from Braskem (Philadelphia, Pennsylvania); and Polypropylene 6281KX, which is available from Total Petrochemicals & Refining USA, Inc. (Houston, Texas). Examples of polypropylene homopolymer include but are not limited to Inspire® 6021N and Polypropylene H110-02NZ, both of which are available from Braskem (Philadelphia, Pennsylvania); and Polypropylene Lumicene® M3382MZ, which is available from Total Petrochemicals & Refining USA, Inc. (Houston, Texas).

Examples of high density polyethylene include homopolymers and copolymers of ethylene. High density polyethylene is available in a wide range of molecular weights as determined by either melt index (MI) or HLMI (high-load melt index). (See Carter, "Polyethylene, High-Density," *The Wiley Encyclopedia of Packaging Technology*, Second Edition, 1997, pp. 745-748 (John Wiley & Sons, Inc., New York, New York).) Based on a review of literature, high density polyethylene useful in various embodiments of the present application has a reported melting temperature of 104-138 °C. Linear high density polyethylene has a reported storage modulus of 800 MPa (about 116,030 psi) at 25 °C, slow cooled. (See Mandelkern, et al., "Polyethylene, linear high-density," *Polymer Data Handbook*, 1999, pp. 493-507 (Oxford University Press, Inc., New York, New York).) High density polyethylene has a reported glass transition temperature of -111 °C. (See Norman, et al., "Detecting Weak Glass Transition (Tg) in Polymers by HyperDSC," ©2009-2011, (PerkinElmer, Inc. Waltham, Massachusetts).) Examples of high density polyethylene include but are not limited to Alathon®

M6020 which is available from Equistar Chemicals LP (Houston, Texas); Elite™ 5960G, which is available from The Dow Chemical Company (Midland, Michigan); Alathon® L5845, which is available from Lyondell Chemical Company (Houston, Texas); and Surpass® HPs167-AB (available from NOVA Chemicals Corporation (Calgary, Alberta, Canada)).

Second layer 14 of sheet 10 of FIG. 1 comprises a polymer having a glass transition temperature greater than ambient temperature (i.e., about 68-77 °F (about 20-25 °C)).

In some embodiments, the polymer of second layer 14 may comprise polyester, cyclic olefin copolymer, styrenic polymers, or blends of such. As non-limiting examples, second layer 14 may comprise 100 % (by weight) polyester or 100 % (by weight) styrenic polymer.

Examples of polyester include aromatic polyester and aliphatic polyester. Polyesters have a reported glass transition temperature of 69-115 °C. (See, Iroh, "Poly(ethylene terephthalate)," *Polymer Data Handbook*, 1999, pp. 558-560 (Oxford University Press, Inc., New York, New York.)) An example of aromatic polyesters includes but is not limited to polyethylene terephthalate (PET) which is processed (as a non-limiting example, via extrusion quench process) to be amorphous or semi-crystalline. Such processed PET includes but is not limited to amorphous polyethylene terephthalate (APET). Examples of APET (i.e., PET which may be processed to be amorphous or semi-crystalline) include but are not limited to Laser+® C 9921, which is available from DAK Americas LLC (Chadds Ford, Pennsylvania); Cleartuf® 8006C, which is available from M&G Polymers USA, LLC (Houston, Texas); and Preformance™ PET 1708, which is available from StarPet Inc, USA (Asheboro, North Carolina). Further examples of aromatic polyesters include but are not limited to glycol-modified polyethylene terephthalate (PETG) and isophthalic acid (IPA)-modified co-polyester (PETI). Examples of PETG include but are not limited to Skygreen® S2008, which is available from SK Chemicals America, Inc. (Irvine California); and Eastar™ Copolyester 6763, which is available from Eastman Chemical Company (Kingsport, Tennessee). An example of PETI includes but is not limited to Auriga

PET Type 8383, which is available from Auriga Polymers Inc. (Spartanburg, South Carolina). An example of aliphatic polyesters includes but is not limited to polylactic acid (PLA). An example of PLA includes but is not limited to Ingeo™ Biopolymer 4043D, which is available from NatureWorks LLC (Minnetonka, Minnesota) and has a reported density of 1.24 g/cc, a reported MFR (210 °C / 2.16 kg) of 6 g/10 min (in accordance with ASTM D1238), a reported peak melt temperature of 145-160 °C and a reported glass transition temperature of 55-60 °C (in accordance with ASTM D3418). Further examples of polyester include copolyesters. Such copolyesters include but are not limited to Tritan™ copolyesters, which are available from Eastman Chemical Company (Kingsport, Tennessee). An example of a Tritan™ copolyester includes but is not limited to Eastman Tritan™ Copolyester FX100, which is an amorphous copolyester having a reported density of 1.19 g/cc and a reported glass transition temperature of 110 °C (DSC). The polymer of second layer 14 may comprise amorphous or semi-crystalline polyester (APET), glycol-modified polyethylene terephthalate (PETG), isophthalic acid (IPA)-modified co-polyester (PETI), polylactic acid (PLA), copolyesters or blends of such.

Examples of cyclic olefin copolymers include but are not limited to ethylene/norbornene copolymers. An example of ethylene/norbornene copolymer includes but is not limited to TOPAS® 8007, which is available from Topas Advanced Polymers, Inc. (Florence, Kentucky) and has a reported density of 1.01 g/cc and a reported glass transition temperature of 78 °C (DSC).

Examples of styrenic polymers include but are not limited to high impact polystyrene (HIPS), general purpose polystyrene (GPPS) and styrene block copolymer (SBC). Styrenic polymers have a reported glass transition temperature of 100 °C. (See Pu, "Polystyrene," *Polymer Data Handbook*, 1999, pp. 829-836 (Oxford University Press, Inc., New York, New York).) Examples of HIPS include but are not limited to Polystyrene 825E and Polystyrene 945E, both of which are available from Total Petrochemicals & Refining USA, Inc.); Styrolution

PS 6210, which is available from Styrolution America LLD (Aurora, Illinois); and Styron® 487R, which is available from AmSty (The Woodlands, Texas). GPPS is often called crystal polystyrene or general purpose crystal polystyrene, as a reference to the clarity of the resin. An example of GPPS includes but is not limited to Polystyrene 524B, which is available from Total Petrochemicals & Refining USA, Inc. (Houston, Texas). Styrene block copolymers (SBC) include styrene butadiene copolymers. A non-limiting example of SBC is KR53 K-Resin® Styrene Butadiene Copolymer, which is available from Chevron Phillips Chemical Company (The Woodlands, Texas). The polymer of second layer 14 may comprise high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC) or blends of such.

First layer 12 and second layer 14 may also comprise processing aids and other additives. Processing aids and other additives include but are not limited to antiblock agents, slip agents, stabilizing agents, release agents, photo-initiators, primers and colorants.

Each of first layer 12 and second layer 14 may be an exterior layer or an interior layer of sheet 10. As a non-limiting example, sheet 10 may further comprise an exterior layer of glycol-modified polyethylene terephthalate or polyethylene adhered, attached or otherwise bonded via an intermediate layer of tie material or otherwise to first layer 12, second layer 14 or both first layer 12 and second layer 14. (Such alternative embodiments are not picture in FIG. 1.)

Sheet 10 has a thickness of equal to or greater than about 10 mil (about 254 micron). In some embodiments, sheet 10 has a thickness of greater than about 15 mil (about 381 micron) or greater than about 20 mil (about 508 micron). In further embodiments, sheet 10 has a thickness of from about 15 mil (about 381 micron) to about 55 mil (about 1397 micron) or from about 20 mil (about 508 micron) to about 50 mil (about 1270 micron) or from about 30 mil (about 762 micron) to about 50 mil (about 1270 micron).

First layer 12 contributes at least about 30 % of the thickness of sheet 10 and, as such, is a structural layer for sheet 10. At this contributed thickness, sheet 10 has thermoformability and thermal stability (as each is discussed below). In some embodiments, first layer 12 may contribute from about 30 % to about 65 % of the thickness of sheet 10.

Second layer 14 contributes at least about 25 % but less than about 60 % of the thickness of sheet 10 and, as such, is a structural layer for sheet 10. At this contributed thickness, sheet 10 has thermoformability and thermal stability. In some embodiments, second layer 14 may contribute from about 25 % to about 55 % of the thickness of sheet 10.

Based on the above, first layer 12 comprises different materials than second layer 14. In other words, the composition of first layer 12 is different than the composition of second layer 14. The composition of each layer is not analogous, not identical or not the same. Other various relationships between various properties of the polyolefin of first layer 12 and the polymer of second layer 14 further contribute to the utility of the sheet for thermal stability, thermoformability, and otherwise.

The melting temperature of the polyolefin of first layer 12 is greater than the glass transition temperature of the polymer of second layer 14. The temperature range between the glass transition temperature of the polymer of second layer 14 and the melting temperature of the polyolefin of second layer 14 is believed to provide a temperature range over which sheet 10 is sufficiently supple and deformable for stretching and shaping. Such temperature range may also be referred to as the thermoforming window.

The ratio of the storage modulus of the polyolefin of first layer 12 (G'_1) at about 35 °C to the storage modulus of the polymer of second layer 14 (G'_2) at about 35 °C is less than 1 (i.e., at about 35 °C, $G'_1 / G'_2 < 1$). As discussed in EXAMPLES – Set 1 below and as shown in FIG. 2, example polyolefins of first layer 12 (e.g., a polypropylene homopolymer (having a storage modulus temperature sweep depicted by line 26) and a medium molecular weight high density

polyethylene (having a storage modulus temperature sweep depicted by line 28)) have G'_1 at about 35 °C of 1702 MPa and 1528 MPa, respectively, whereas example polymers of second layer 14 (e.g., a polyethylene terephthalate copolymer (having a storage modulus temperature sweep depicted by line 22) and a glycol modified co-polyester (having a storage modulus temperature sweep depicted by line 24)) have G'_2 at about 35 °C of 2277 MPa and 2118 MPa, respectively. Each of the resulting four example combinations of G'_1 / G'_2 at about 35 °C is less than 1.

The ratio of the storage modulus of the polyolefin of first layer 12 (G'_1) at the midpoint temperature to the storage modulus of the polymer of second layer 14 (G'_2) at the midpoint temperature is greater than 1 (i.e., at midpoint temperature, $G'_1 / G'_2 > 1$). As defined above, the midpoint temperature is the average of the glass transition temperature of the polymer of second layer 14 and the melting temperature of the polyolefin of first layer 12. In other words, it is the temperature half-way between the glass transition temperature of the polymer of second layer 14 and the melting temperature of the polyolefin of first layer 12. As discussed in EXAMPLES – Set 1 below and as shown in FIG. 2, upon calculating the midpoint temperature and determining G'_1 and G'_2 at the midpoint temperature, each of the resulting four example combinations of G'_1 / G'_2 at the respective midpoint temperatures is greater than 1.

As such, at some temperature between about 35 °C and the midpoint temperature, the storage modulus temperature sweep of the polyolefin of first layer 12 crosses over the storage modulus temperature sweep of the polymer of second layer 14.

Returning now to the drawings, FIG. 3 is a cross-sectional view of a second embodiment of a thermoplastic sheet according to the present application. Sheet 30 depicted in FIG. 3 comprises first layer 32, second layer 34 and adhering layer 36 positioned between first layer 32 and second layer 34. First layer 32 is similar to first layer 12 described above and second layer 34 is similar to second layer 14 described above. Adhering layer 36 is any layer or multilayer

adhering, attaching or otherwise bonding first layer 32 to second layer 34. In some embodiments, adhering layer comprises an adhesive, an extrudate, a coating (including but not limited to a plasma coating), a tie material or a multilayer film. In some embodiments, adhering layer 36 is a multilayer, blown film. In such embodiments, the multilayer layer may comprise a sealant layer, a barrier layer, tie material or other components known to a person of ordinary skill in the art.

In the embodiments where adhering layer 36 of sheet 30 comprises a multilayer, blown film, sheet 30 may be produced as follows. The multilayer, blown film as adhering layer 36 is first produced on blown film equipment. A non-limiting example of such multilayer, blown film includes a first layer of a blend of ethylene vinyl acetate copolymer and linear low density polyethylene, a second layer of high density polyethylene, a third layer of tie material, a fourth layer of ethylene vinyl-alcohol copolymer, a fifth layer of tie material, a sixth layer of tie material and a seventh layer of polypropylene impact copolymer. Each of the exterior layers of the multilayer blown film (e.g., the first layer of the blend of ethylene vinyl acetate copolymer and linear low density polyethylene and the seventh layer of polypropylene impact copolymer) may be chosen to promote adherence to, for example, second layer 34 and first layer 32, respectively. In producing the multilayer, blown film, one extruder is used for each of the seven layers. (For the first layer comprising the blend of ethylene vinyl acetate copolymer and linear low density polyethylene, the resins for that layer may be pre-blended prior to being added to the extruder.) The layer components are then heated to form streams of melt-plastified polymers and extruded through a die. The coextruded plastified, extruded components then form a tubular extrudate (or bubble). The diameter of the tubular extrudate is expanded by air entering the extrudate at the die. The expanded tubular extrudate is then collapsed by a collapsing frame and flattened through nip rolls. The flattened extrudate is slit open to form two identical multilayer, blown films, each of which is conveyed to separate wind-up reels for

furthering process. To such multilayer, blown film (as adhering layer 36), first layer 32 is attached to a first surface of the film (e.g., the exterior layer of polypropylene impact copolymer). Second layer 34 is then attached to the opposing second surface of the film (e.g., the exterior layer of the blend of ethylene vinyl acetate copolymer and linear low density polyethylene). First layer 32 and second layer 34 may be attached by various methods known in the art. These methods include but are not limited to thermal lamination, adhesive lamination (including solvent and solvent-less lamination), extrusion lamination, extrusion coating and photolytic lamination. The parameters for such lamination or coating may be set by one skilled in the art without undue experimentation.

The various embodiments of the sheet (e.g., sheet 10, 30) described in the present application may exhibit various properties, as shown and further defined and described in the examples. For example, the sheet may have a normalized combined tear initiation and propagation resistance in both the machine direction and the transverse direction or greater than about 0.115 in*lb / mil (0.0511 Ncm / micron) energy to break and an elongation greater than about 0.800 % / mil (0.0315 % / micron) as measured in accordance with ASTM D1004. The sheet may also have between 0 and about 20 degrees of transverse direction (TD) curl. Curl less than or equal to about 20 degrees is generally acceptable, as this amount of TD curl causes minimal (if any) problems in further processing, including but not limited to subsequent thermoforming of the sheet. Curl greater than about 20 degrees is generally unacceptable, as this amount of TD curl causes problems in further processing.

As noted, the sheet described in the various embodiments of the present application may be thermoformable, in that it may be formed or thermoformed into a package, such as cups, trays, plates or other containers, with even material distribution. A description of "thermoformable" is provided above. Furthermore, thermoforming and other similar techniques are well known in the art for packaging. (See Throne, "Thermoforming," Encyclopedia of

Polymer Science and Technology, Third Edition, 2003, Volume 8, pp. 222-251 (John Wiley & Sons, Inc., Hoboken, New Jersey); see also Irwin, "Thermoforming," Modern Plastics Encyclopedia, 1984-1985, pp. 329-336 (McGraw-Hill, Inc., New York, New York); see also "Thermoforming," The Wiley Encyclopedia of Packaging Technology, Second Edition, 1997, pp. 914-921 (John Wiley & Sons, Inc., New York, New York).) Suitable thermoforming methods include standard, deep-draw or plug-assist vacuum forming. During standard vacuum forming, a thermoplastic web, such as the sheet described in the present application, is heated and a vacuum is applied beneath the web allowing atmospheric pressure to force the web into a preformed mold. When relatively deep molds are employed, the process is referred to as a "deep-draw" application. In a plug-assist vacuum forming method, after the thermoplastic web has been heated and sealed across a mold cavity, a plug shape similar to the mold shape impinges on the thermoplastic web and, upon the application of vacuum, the thermoplastic web conforms to the mold surface.

A thermoformed package formed from a sheet having a first layer comprising different materials (i.e., having a different composition) than a second layer (e.g., a package formed from sheet 10, 30 comprising first layer 12, 32 and second layer 14, 34) may exhibit a compression strength (or "top load compression") that is greater than about 125 % of a compression strength of an other package formed from an other sheet having an other first layer comprising the same polyolefin (e.g., polypropylene) and having an analogous composition as an other second layer, where the other first layer still contributes at least about 30 % of the thickness of the other sheet and the other second layer still contributes at least about 25 % but less than about 60 % of the thickness of the other sheet. In some embodiments, such compression strength may be greater than about 150 % or greater than about 200 % or greater than about 300 % or from about 150 % to about 300 % of the compression strength of the other package. Packages with higher compression strength may better withstand forces encountered in filling and transit.

In some embodiments, the thermoformed package comprising the sheet described in the present application may be thermoformed and filled on separate production lines. In other embodiments, such thermoformed package may be thermoformed and filled on the same production line, such as a form-fill-seal (FFS) machine.

The sheet described in the present application may be thermally stable. As described above, a thermally stable sheet maintains dimensionality and shape and does not distort or deform when exposed to temperatures from about 194 °F (about 90 °C) to about 284 °F (about 140 °C). As such, the sheet in the various embodiments of the present application may form a package for various heat processes, including but not limited to retort, aseptic, hot-fill or microwave processing.

EXAMPLES – Set 1

To further exemplify the various embodiments of the present application, storage modulus (G') of various materials was determined via dynamic mechanical analysis (DMA) using a Q800 Dynamic Mechanical Analyzer available from TA Instruments (New Castle, Delaware)). Multi-Frequency (Strain) mode was used to apply a sinusoidal stress (or strain) to a material and to measure the resultant sinusoidal strain (or stress).

The Dynamic Mechanical Analyzer was first equilibrated at 35.00°C. The temperature was held constant (isothermal) for 5.00 min. The temperature was then increased 3.00°C per minute up to 160.00°C to obtain a storage modulus (G') temperature sweep. FIG. 2 is a graph depicting the storage modulus (G') temperature sweep of four materials. Line 22 of FIG. 2 depicts the storage modulus (G') temperature sweep for Laser+® C 9921, a polyethylene terephthalate copolymer available from DAK Americas LLC (Chadds Ford, Pennsylvania), having a reported intrinsic viscosity of 0.80 ± 0.02 , a reported density of 1.32 g/cc, a reported melting point of 238-243 °C and a reported glass transition temperature of 78.0 °C. (For this example, Laser+® C9921 was processed via the extrusion quench process to be semi-

crystalline and, as such, was considered as APET.) Line 24 of FIG. 2 depicts the storage modulus (G') temperature sweep for Skygreen® S2008, a glycol modified co-polyester (i.e., a PETG) available from SK Chemicals America, Inc. (Irvine, California), having a reported specific gravity of 1.27 and a reported glass transition temperature of 80 °C. Line 26 of FIG. 2 depicts the storage modulus (G') temperature sweep for Polypropylene H110-02NZ, a polypropylene homopolymer available from Braskem (Philadelphia, Pennsylvania), having a reported density of 0.900 g/cc, a reported melt index (230 °C / 2.16 kg) of 2.0 g/10 min (in accordance with ASTM D1238) and a reported melting temperature of 161 °C. Line 28 of FIG. 2 depicts the storage modulus (G') temperature sweep for Alathon® L5845, a medium molecular weight high density polyethylene available from Lyondell Chemical Company (Houston, Texas), having a reported density of 0.958 g/cc, a reported melt index of 0.45 g/10 min (in accordance with ASTM D1238) and a reported melting point of 104-138 °C (average melting point of 121 °C).

Laser+® C 9921 and Skygreen® S2008 are examples of the polymer of the second layer of the sheet described in the present application. Polypropylene H110-02NZ and Alathon® L5845 are examples of the polyolefin of the first layer of the sheet described in the present application. As non-limiting examples (Examples 1-4), based on these materials, the sheet described in the present application may comprise a first layer and a second layer comprising the materials as in TABLE 1.

TABLE 1

	First Layer	Second Layer	Glass Transition Temperature (°C) (Second Layer)	Melting Point Temperature (°C) (First Layer)	Midpoint Temperature (°C)
Example 1	Polypropylene H110-02NZ	Laser+® C 9921	78.0	161	120
Example 2	Polypropylene H110-02NZ	Skygreen® S2008	80	161	121
Example 3	Alathon® L5845	Laser+® C 9921	78.0	121	100
Example 4	Alathon® L5845	Skygreen® S2008	80	121	101

(The "midpoint temperature" refers to the temperature half-way between the glass transition temperature of the polymer of the second layer and the melting temperature of the polyolefin of

the first layer.) TABLE 2 summarizes data obtained from FIG. 2, based on the sheets of Examples 1-4.

TABLE 2

	G' (MPa) at 35 °C	G' (MPa) at 100 °C	G' (MPa) at 101 °C	G' (MPa) at 120 °C	G' (MPa) at 121 °C
Laser+® C 9921	2277	14.06	na	4.797	na
Skygreen® S2008	2118	na	6.360	na	0
Polypropylene H110-02NZ	1702	na	na	288.6	281.9
Alathon® L5845	1528	436.4	424.4	na	na

(A data point is listed as "na" ("not applicable") if the G' at that temperature is not relevant for Examples 1-4. For example, Laser+® C 9921 as a second layer material when combined with either Polypropylene H110-02NZ or Alathon® L5845 as a first layer material has a midpoint temperature of 120 °C or 100 °C, respectively. Therefore, the G' at the other temperatures is not relevant for Examples 1-4.) Based on the above, at about 35 °C, the ratio of G'_1 (storage modulus of first layer material) / G'_2 (storage modulus of second layer material) is less than 1; and at the midpoint temperature, the ratio of G'_1 / G'_2 is greater than 1. These relationships are shown in TABLE 3.

TABLE 3

	First Layer	Second Layer	G'_1 / G'_2 at 35 °C	G'_1 / G'_2 at Midpoint Temperature
Example 1	Polypropylene H110-02NZ	Laser+® C 9921	0.7475	60.16
Example 2	Polypropylene H110-02NZ	Skygreen® S2008	0.8036	∞
Example 3	Alathon® L5845	Laser+® C 9921	0.6711	31.04
Example 4	Alathon® L5845	Skygreen® S2008	0.7214	

EXAMPLES – Set 2

To still further exemplify the various embodiments of the present application, several example and comparative example sheets were produced and evaluated for various properties. The materials included in the various example and comparative example sheets are as follows.

ADD is processing aids and other additives. The uses of processing aids and other additives varies depending on the equipment, materials, desired aesthetics, etc. Processing aids and other additives include but are not limited to antiblock agents, slip agents, stabilizing agents, release agents, photo-initiators, primers and colorants. Such aids are known to a person of ordinary skill in the art, and their use may be determined without undue experimentation

EVA1 is an ethylene vinyl acetate copolymer having a vinyl acetate content of about 26-28 % by weight (of total EVA composition). A non-limiting example of EVA1 is Escorene™ Ultra LD 768.MJ (available from ExxonMobil Chemical Company (Houston, Texas)), having a reported vinyl acetate content of 26.2 % by weight (of total EVA composition), a reported density of 0.914 g/cc and a reported melt index (190 °C / 2.16 kg) of 2.3 g/10 min (in accordance with ASTM D1238). A further non-limiting example of EVA1 is Ateva® 2861A (available from Celanese (Irving, Texas)), having a reported vinyl acetate content of 28 % by weight (of total EVA composition), a reported density of 0.949 g/cc and a reported melt index (190 °C / 2.16 kg) of 6.0 g/10 min (in accordance with ASTM D1238).

EVA2 is an ethylene vinyl acetate copolymer having a vinyl acetate content of about 18-18.5 % by weight (of total EVA composition). A non-limiting example of EVA2 is Escorene™ Ultra LD 721.IK (available from ExxonMobil Chemical Company (Houston, Texas)), having a reported vinyl acetate content of 18.5 % by weight (of total EVA composition), a reported density of 0.942 g/cc and a reported melt index (190 °C / 2.16 kg) of 2.5 g/10 min (in accordance with ASTM D1238). A further non-limiting example of EVA2 is DuPont™ Elvax®3170 (available from E.I. du Pont de Nemours and Company, Inc. (Wilmington, Delaware)), having a reported vinyl acetate content of 18 % by weight (of total EVA composition), a reported density of 0.94 g/cc and a reported flow rate (190 °C / 2.16 kg) of 2.5 g/10 min (in accordance with ASTM D1238).

EVOH1 is an ethylene vinyl-alcohol copolymer. A non-limiting example of EVOH1 is EVAL™ L171B (available from Kuraray America Inc. (Houston, Texas)), having a reported ethylene content of 27 mole percent, a reported density of 1.20 g/cc and a reported melting temperature of 191 °C.

GPPS1 is a general purpose crystal polystyrene. A non-limiting example of GPPS1 is Polystyrene 524B (available from Total Petrochemicals & Refining USA, Inc. (Houston, Texas)), having a reported density of 1.04 g/cc and a reported melt flow (200 °C / 5 kg) of 9.0 g/10 min (in accordance with ASTM D1238).

HDPE1 is a high-moisture-barrier high density polyethylene. A non-limiting example of HDPE1 is Surpass® HPs167-AB (available from NOVA Chemicals Corporation (Calgary, Alberta, Canada)), having a reported density of 0.966 g/cc and a reported melt flow (190 °C / 2.16 kg) of 1.2 g/10 min (in accordance with ASTM D1238).

HDPE2 is a medium molecular weight high density polyethylene. A non-limiting example of HDPE2 is Alathon® L5845 (available from Lyondell Chemical Company (Houston, Texas)), having a reported density of 0.958 g/cc, a reported melt index of 0.45 g/10 min (in accordance with ASTM D1238) and a reported melting point of 104-138 °C. Further non-limiting examples of HDPE2 are Elite™ 5960G (available from The Dow Chemical Company (Midland, Michigan)), having a reported density of 0.962 g/cc, a reported melt index (190 °C / 2.16 kg) of 0.85 g/10 min (in accordance with ASTM D1238) and a reported melting temperature of 134 °C and Alathon® M6020 (available from Equistar Chemicals, LP (Houston, Texas)), having a reported density of 0.960 g/cc, a reported melt index of 2.0 g/10 min (in accordance with ASTM D1238), and a reported melting point of 104-138 °C.

HIPS1 is a high impact polystyrene. A non-limiting example of HIPS1 is Polystyrene 825E (available from Total Petrochemicals & Refining USA, Inc. (Houston, Texas)), having a reported density of 1.04 g/cc and a reported melt flow (200 °C / 5 kg) of 3.0 g/10 min (in

accordance with ASTM D1238). Further non-limiting examples of HIPS1 are Polystyrene 945E (available from Total Petrochemicals & Refining USA, Inc. (Houston, Texas)), having a reported density of 1.04 g/cc and a reported melt flow (200 °C / 5 kg) of 3.5 g/10 min (in accordance with ASTM D1238), Styrolution PS 6210 (available from Styrolution America LLC (Aurora, Illinois)), having a reported density of 1.04 g/cc and a reported melt flow rate (200 °C / 5 kg) of 2.9 g/10 min (in accordance with ASTM D1238) and Styron® 487R (available from AmSty (The Woodlands, Texas)), having a reported specific gravity of 1.04 and a reported melt flow index (200 °C / 5 kg) of 2.8 g/10 min (in accordance with ASTM D1238).

LLDPE1 is a liner low density polyethylene. A non-limiting example of LLDPE1 is LLDPE LL 1001.32 (available from ExxonMobil Chemical Company (Houston, Texas)), having a reported density of 0.918 g/cc and a reported melt index (190 °C / 2.16 kg) of 1.0 g/10 min (in accordance with ASTM D1238). A further non-limiting example of LLDPE 1 is LLDPE LL 1002.YB (available from ExxonMobil Chemical Company (Houston, Texas)), having a reported density of 0.918 g/cc and a reported melt index (190 °C / 2.16 kg) of 2.0 g/10 min (in accordance with ASTM D1238).

LLDPE2 is an anhydride-modified, linear low density polyethylene. A non-limiting example of LLDPE2 is Bynel® 4164 (available from E.I. du Pont de Nemours and Company, Inc. (Wilmington, Delaware)), having a reported density of 0.93 g/cc and a reported melt flow rate (190 °C / 2.16 kg) of 1.2 g/10 min (in accordance with ASTM D1238).

LLDPE3 is an anhydride-modified, linear low density polyethylene tie resin concentrate. A non-limiting example of LLDPE3 is Bynel® 41E710 (available from E.I. du Pont de Nemours and Company, Inc. (Wilmington, Delaware)), having a reported density of 0.91 g/cc and a reported melt flow rate (190 °C / 2.16 kg) of 2.7 g/10 min (in accordance with ASTM D1238).

PET1 is a polyethylene terephthalate copolymer. A non-limiting example of PET1 is Laser+® C 9921 (available from DAK Americas LLC (Chadds Ford, Pennsylvania)), having a

reported intrinsic viscosity of 0.80 ± 0.02 , a reported density of 1.32 g/cc, a reported melting point of 238-243 °C and a reported glass transition temperature of 78.0 °C. Further non-limiting examples of PET1 are Cleartuf® 8006C (available from M&G Polymers USA, LLC (Houston, Texas)), having a reported intrinsic viscosity of 0.80 ± 0.02 dl/g and a reported melting point of from 248-253 °C and Prefromance™ PET 1708 (available from StarPet Inc, USA (Asheboro, North Carolina)), having a reported intrinsic viscosity of 0.80 ± 0.02 dl/g.

PETG1 is a glycol modified co-polyester. A non-limiting example of PETG1 is Skygreen® S2008 (available from SK Chemicals America, Inc. (Irvine, California)), having a reported specific gravity of 1.27 and a reported glass transition temperature of 80 °C (DSC). A further non-limiting example of PETG1 is Eastar™ Copolyester 6763 (available from Eastman Chemical Company (Kingsport, Tennessee)), having a reported density of 1.27 g/cc and a reported glass transition temperature of 80-81 °C.

PETI1 is an isophthalic acid (IPA) modified co-polyester. A non-limiting example of PETI1 is Auriga PET Type 8393 (available from Auriga Polymers Inc. (Spartanburg, South Carolina), having a reported IPA content of about 33 weight percent, a reported density of 1.32 g/cc and a reported glass transition temperature of 70.05 °C (DSC).

PP1 is a polypropylene impact copolymer. A non-limiting example of PP1 is Polypropylene 4170 (available from Total Petrochemicals & Refining USA, Inc. (Houston, Texas)), having a reported density of 0.905 g/cc and a reported melt flow (230 °C) of 0.75 g/10 min (in accordance with ASTM D1238). A further non-limiting example of PP1 is Polypropylene 4481WZ (available from Total Petrochemicals & Refining USA, Inc. (Houston, Texas)), having a reported density of 0.905 g/cc, a reported melt flow (230 °C) of 4.0 g/10 min (in accordance with ASTM D1238), a reported melting point of 160-165 °C and a reported glass transition temperature of -60 °C.

PP2 is a polypropylene homopolymer. A non-limiting example of PP2 is Inspire® 6021N (available from Braskem (Philadelphia, Pennsylvania)), having a reported nominal melt flow rate (230 °C / 2.16 kg) of 2 g/10 min (in accordance with ASTM D1238) and a reported melting point of 160-170 °C. Further non-limiting examples of PP2 are Polypropylene Lumicene® M3382MZ (available from Total Petrochemicals & Refining USA, Inc. (Houston, Texas)), having a reported density of 0.905 g/cc, a reported melt flow of 3.5 g/10 min (in accordance with ASTM D1238, Condition "L"), a reported melting point of 153 °C and a reported glass transition temperature of -5 °C and Polypropylene H110-02NZ (available from Braskem (Philadelphia, Pennsylvania)), having a reported density of 0.900 g/cc, a reported melt index (230 °C / 2.16 kg) of 2.0 g/10 min (in accordance with ASTM D1238) and a reported melting temperature of 161 °C.

PP3 is a polypropylene random copolymer. A non-limiting example of PP3 is Polypropylene RP650 (available from Braskem (Philadelphia, Pennsylvania)), having a reported nominal melt flow rate (230 °C / 2.16 kg) of 2 g/10 min (in accordance with ASTM D1238) and a reported melting point of 140-170 °C. A further non-limiting example of PP3 is Polypropylene 6281KZ (available from Total Petrochemicals & Refining USA, Inc. (Houston, Texas)), having a reported density of 0.900 g/cc, a reported melt flow of 1.7 g/10min (in accordance with ASTM D1238, Condition "L") and a reported melting point of 147 °C.

SBC1 is a styrene-butadiene copolymer. A non-limiting example of SBC1 is KR53 K-Resin® Styrene Butadiene Copolymer (available from Chevron Phillips Chemical Company LP (The Woodlands, Texas), having a reported specific gravity of 1.02 g/cc and a reported melt flow rate (200 °C / 5.0 kg) of 10.0 g/10 min (in accordance with ASTM D1238).

TIE1 is a modified polyolefin with functional groups for bonding. A non-limiting example of TIE1 is Admer™ QF500A (available from Mitsui Chemicals America, Inc. (Rye Brook, New York)), having a reported density of 0.900 g/cc and a reported melt flow rate (230 °C) of 3.0 g/10 min (in accordance with ASTM D1238).

ULDPE1 is an ultra low (or very low) density polyethylene. A non-limiting example of ULDPE1 is Attane™ NG 4701G (available from The Dow Chemical Company (Midland, Michigan)), having a reported density of 0.912 g/cc and a reported melt index (190 °C / 2.16 kg) of 0.80 g/10 min (in accordance with ASTM D1238). A further non-limiting example of ULDPE1 is Surpass® FPs016A (available from NOVA Chemicals Corporation (Calgary, Alberta, Canada)), reported density of 0.916 g/cc and a reported index (190 °C / 2.16 kg) of 0.65 g/10 min (in accordance with ASTM D1238).

Table 4 lists the structure and composition for Examples 5-12. Table 5 lists the structure and composition for Comparative Examples 1-4.

TABLE 4

Example 5			Example 6		
mil (micron)	% thickness (total structure)	layer composition (% by weight)	mil (micron)	% thickness (total structure)	layer composition (% by weight)
24 mil (610 micron)	59.6 %	100 % PET1	11 mil (279 micron)	28.8 %	100 % PET 1
4.25 mil (108 micron)	10.6 %	60 % EVA1 + 35 % LLDPE1 + 5 % ADD	4.25 mil (108 micron)	11.1 %	60 % EVA1 + 35 % LLDPE 1 + 5 % ADD
		100 % HDPE1			100 % HDPE1
		100 % LLDPE2			100 % LLDPE2
		100 % EVOH1			100 % EVOH1
		100 % LLDPE2			100 % LLDPE2
		90 % ULDPPE1 + 10% LLDPE3			90 % ULDPPE1 + 10% LLDPE3
12 mil (305 micron)	29.8 %	56 % PP2 + 38 % HDPE2 + 6 % ADD	23 mil (584 micron)	60.1 %	70% PP2 + 30 % PP3
Example 7			Example 8		
mil (micron)	% thickness (total structure)	layer composition (% by weight)	mil (micron)	% thickness (total structure)	layer composition (% by weight)
14 mil (356 micron)	36.6 %	100 % PET 1	17 mil (432 micron)	44.45%	100 % PET 1
4.25 mil (108 micron)	11.1 %	60 % EVA1 + 35 % LLDPE 1 + 5 % ADD	4.25 mil (108 micron)	11.1 %	60 % EVA1 + 35 % LLDPE 1 + 5 % ADD
		100 % HDPE1			100 % HDPE1
		100 % LLDPE2			100 % LLDPE2
		100 % EVOH1			100 % EVOH1
		100 % LLDPE2			100 % LLDPE2
		90 % ULDPPE1 + 10% LLDPE3			90 % ULDPPE1 + 10% LLDPE3
20 mil (508 micron)	52.3 %	70% PP2 + 30 % PP3	17 mil (432 micron)	44.45 %	70% PP2 + 30 % PP3
Example 9			Example 10		
mil (micron)	% thickness (total structure)	layer composition (% by weight)	mil (micron)	% thickness (total structure)	layer composition (% by weight)
20 mil (508 micron)	52.3 %	100 % PET 1	25 mil (635 micron)	50.0 %	100% PETG1
4.25 mil (108 micron)	11.1 %	60 % EVA1 + 35 % LLDPE 1 + 5 % ADD	5.0 mil (127 micron)	10.0 %	60 % EVA1 + 35 % LLDPE 1 + 5 % ADD
		100 % HDPE1			100 % HDPE1
		100 % LLDPE2			100 % LLDPE2
		100 % EVOH1			100 % EVOH1
		100 % LLDPE2			100 % LLDPE2
		90 % ULDPPE1 + 10% LLDPE3			90 % ULDPPE1 + 10% LLDPE3
14 mil (356 micron)	36.6 %	70% PP2 + 30 % PP3	20 mil (508 micron)	40.0 %	80% PP2 + 20 % PP3
Example 11			Example 12		
mil (micron)	% thickness (total structure)	layer composition (% by weight)	mil (micron)	% thickness (total structure)	layer composition (% by weight)
25 mil (635 micron)	50.0 %	100% PET1	20 mil (508 micron)	50.31 %	100 % HIPS1
5.0 mil (127 micron)	10.0 %	60 % EVA1 + 35 % LLDPE 1 + 5 % ADD	4.75 mil (121 micron)	11.95 %	93 % SBC1 + 6 % HIPS1 + 1 % ADD
		100 % HDPE1			100 % LLDPE2
		100 % LLDPE2			100 % HDPE1
		100 % EVOH1			100 % LLDPE2
		100 % LLDPE2			100 % EVOH1
		90 % ULDPPE1 + 10% LLDPE3			100 % LLDPE2
20 mil (508 micron)	40.0 %	80% PP2 + 20 % PP3	15 mil (381 micron)	37.74 %	90 % ULDPPE1 + 10 % LLDPE3
					100 % PP1
					56 % PP2 + 38 % HDPE2 + 6 % ADD

TABLE 5

Comparative Example 1			Comparative Example 2		
mil (micron)	% thickness (total structure)	layer composition (% by weight)	mil (micron)	% thickness (total structure)	layer composition (% by weight)
22.5 mil (572 micron)	45.0 %	78 % PP2 + 20 % PP3 + 2 % ADD	19 mil (483 micron)	46.9 %	56 % PP2 + 38 % HDPE2 + 6 % ADD
5.0 mil (127 micron)	10.0 %	100 % PP1	2.5 mil (64 micron)	6.2 %	100 % TIE1
		90 % ULDPE1 + 10 % LLDPE3			100 % EVOH1
		100 % LLDPE2			100 % TIE1
		100 % EVOH1	19 mil (483 micron)	46.9 %	56 % PP2 + 38 % HDPE2 + 6 % ADD
		100 % LLDPE2			
		100 % HDPE1			
		100 % EVA2			
		100 % HDPE1			
		100 % LLDPE2			
		100 % EVOH1			
		100 % LLDPE2			
		90 % ULDPE1 + 10 % LLDPE3			
		100 % PP1			
22.5 mil (572 micron)	45.0 %	78 % PP2 + 20 % PP3 + 2 % ADD			
Comparative Example 3			Comparative Example 4		
mil (micron)	% thickness (total structure)	layer composition (% by weight)	mil (micron)	% thickness (total structure)	layer composition (% by weight)
23 mil (584 micron)	60.1 %	100 % PET 1	26 mil (660 micron)	68.0 %	100 % PET 1
4.25 mil (108 micron)	11.1 %	60 % EVA1 + 35 % LLDPE 1 + 5 % ADD	4.25 mil (108 micron)	11.1 %	60 % EVA1 + 35 % LLDPE 1 + 5 % ADD
		100 % HDPE1			100 % HDPE1
		100 % LLDPE2			100 % LLDPE2
		100 % EVOH1			100 % EVOH1
		100 % LLDPE2			100 % LLDPE2
		90 % UDLPE + 10% LLDPE3			90 % UDLPE + 10% LLDPE3
		100 % PP1			100 % PP1
11 mil (279 micron)	28.8 %	70% PP2 + 30 % PP3	8 mil (203 micron)	20.9 %	70% PP2 + 30 % PP3

(Note: The thickness listed were target thicknesses. In practice, for this present application, due to manufacturing variation, the total thickness of a sheet may have varied ± 5 %. For example, the structure of Example 5 (listed as having a total thickness of 40.25 mil (about 1023 micron)) may have had a total thickness of from about 38.2 mil (about 970 micron) to about 42.3 mil (about 1074 micron). The structure of Comparative Example 2 (listed as having a total thickness of 40.5 mil (about 1030 micron) may had had a total thickness of from about 38.5 mil (about 978 micron) to about 42.5 mil (about 1080 micron). Additionally, 29.8 % (the thickness of the polypropylene homopolymer / high density polyethylene blend layer of Example 5) is an

example of about 30 %; however, 28.8 % (the thickness of the polypropylene homopolymer / polypropylene random copolymer blend layer of Comparative Example 3) is not an example of about 30 %. Also, 60.1 % (the thickness of the polyethylene terephthalate copolymer of Comparative Example 3 is an example of about 60 % or greater and is not an example of less than about 60 %. Example 5 is a non-limiting example of a sheet where the polyolefin of the first layer comprises from about 50 % (by weight) to about 70 % (by weight) polypropylene homopolymer and from about 30 % (by weight) to about 50 % (by weight) high density polyethylene and the polymer of the second layer comprises amorphous or semi-crystalline polyester (APET).)

The Examples and Comparative Examples were tested for various properties including combined tear initiation and propagation resistance, curl, top load compression, material distribution in thermoforming and retort recovery.

Combined Tear Initiation and Propagation Resistance is a measure of the torque required to both initiate and propagate (or continue) a tear in a plastic film or sheet. To determine this force, both energy to break and elongation are determined in both the machine direction and the transverse (or cross) direction of the sheet. Energy to break is expressed in in*lb (or "inch pounds" or "pounds inch") or Ncm (where 1 in*lb = 11.2985 Ncm) and elongation is expressed as a percentage. Both are measured in accordance with ASTM D1004, "Standard Test Method for Tear Resistance (Graves Tear) of Plastic Film and Sheeting." For this application, both measurements were normalized as per one mil (or one micron (where 1 mil = 25.4 micron)) of sheet thickness. As shown in TABLE 6, Example 5 had a normalized combined tear initiation and propagation resistance in both the machine direction and the transverse direction of greater than about 0.115 in*lb / mil (0.0511 Ncm / micron) energy to break and an elongation in both the machine direction and the transverse direction of greater than about 0.800 % / mil (0.0315 % / micron), as measured in accordance with ASTM D1004. The

normalized combined tear initiation and propagation resistance in both the machine direction and the transverse direction was from about 0.95 in*lb / mil (0.423 Ncm / micron) to about 1.10 in*lb / mil (0.489 Ncm / micron) energy to break and elongation in both the machine direction and the transverse direction was from about 1.30 % / mil (0.051 % / micron) to about 1.55 % / mil (0.061 % / micron), as measured in accordance with ASTM D1004.

TABLE 6

	Machine Direction		Transverse Direction	
	Energy to Break in*lb / mil (Ncm / micron)	Elongation % / mil (% / micron)	Energy to Break in*lb / mil (Ncm / micron)	Elongation % / mil (% / micron)
Example 5	0.96 (0.427) <i>(average of 8 samples)</i>	1.33 (0.0523) <i>(average of 8 samples)</i>	1.07 (0.476) <i>(average of 7 samples)</i>	1.52 (0.0598) <i>(average of 7 samples)</i>

Curl is a measure of the amount of curl in a film or sheet sample. It is expressed in degrees and is measured in accordance with the following test method: A sample is placed, sealant side up (if applicable) on a clean, flat cutting surface. A cutting template may then be placed in the center of a lane or in the center of the sample, with one edge of the template parallel to the edge of sample. FIG. 4 is a picture depicting two example cutting templates for use in this curl test method. Template 42 is a slit template. Template 44 is a corner template. If Template 42 is used, an "X" is cut in the sample using the two slits in Template 42. If Template 44 is used, a corner in both the machine direction and the transverse direction is cut using side edges 44a and 44b of Template 44. If no template is available, two-inch cuts are made along the edge of the curl tester used. A non-limiting example of a curl tester is the AET Curl Tester, available from Taghleef Industries Inc. (Wilmington, Delaware) (formerly known as Applied Extrusion Technologies, Inc. (AET Films)). After making the cuts, the cutting template is removed from the sample. If a portion of the sample does not rise (i.e., curl) from the cutting surface, the sample is turned over, and the above sample placement and cutting are repeated.

The sample is then allowed to sit for one minute. The point having the largest amount of rise (or curl) is visually determined and the curl at this point is measured using the curl tester. The curl tester is placed on its edge in the direction to be tested with the 0 ° on the curl scale placed about 0.0625 inch (1.59 millimeters) from the tip of the removed (i.e., "cut out") point opposite the curled (or risen) point to be measured. FIG. 5 is a picture depicting a curl tester placed on a prepared, cut sample to determine the degree of curl. Curl tester 52 is placed on its edge 52a, such that "zero point" 54 (i.e., the 0 ° on the curl scale) is about 0.0625 inch (1.59 millimeters) the "cut-out" opposite measured point 56. The amount of curl is determined by where the point to be measured is pointing on the curl scale of the curl tester. In FIG. 5, the degree of curl for the sample used in the test method is approximately 20 degrees.

As shown in TABLE 7, the amount of curl in the transverse direction (TD) for Example 5 (with a first layer of a blend of polypropylene homopolymer and high density polyethylene and a second layer of polyethylene terephthalate copolymer) was determined to be about 0 degrees, while the amount of curl in the TD for Comparative Example 1 (with a first layer of a blend of polypropylene homopolymer and polypropylene random copolymer and a second layer of a blend of polypropylene homopolymer and polypropylene random copolymer) was determined to be about 55 degrees.

TABLE 7

	Transverse Direction (TD) Curl
Example 5	0 degrees
Comparative Example 1	55 degrees

Top load compression (also referred to as "compression strength") is a measure of the force required to produce deformation and failure of a container. It is expressed in lbf (or "pounds force") or newtons (where 1 lbf = 4.44822 newtons) and is measured by placing a sample (e.g., a container as described below) in an Instron® Tensile Tester configured for

compression testing, with a load cell of 2000 pounds (about 908 kilograms) and a crosshead speed of one inch (2.54 centimeters) per minute. To determine the compression strength of Example 5 and Comparative Example 2, four samples of each sheet were thermoformed into circular trays having identical dimensions (e.g., a diameter of about 4.5 inches (about 11.43 centimeters), a depth of about 1.75 inches (about 4.445 centimeters) and a capacity of about 7-10 ounces (about 207-296 milliliters)). Each tray was then placed in the Instron® Tensile Tester configured for compression testing, with a load cell of 2000 pounds (about 908 kilograms) and a crosshead speed of one inch (2.54 centimeters) per minute. To allow for comparison, the compression strength for each of the sample trays was normalized to 40 mil (about 1016 micron) thickness (i.e., as if each starting sheet has a thickness of 40 mil (about 1016 micron)). The normalized compression strengths were then averaged. TABLE 8 reports the top compression strength data for the trays of Example 5 and of Comparative Example 2.

TABLE 8

		Sample Thickness mil (micron)	Compression Strength lbf (newtons)	Compression Strength (normalized to 40 mil (1016 micron)) lbf (newtons)
Example 5	Sample 1	42.1 (1069)	142.1 (632.1)	135.0 (600.5)
	Sample 2	38.8 (986)	133.3 (592.9)	137.4 (611.2)
	Sample 3	38.8 (986)	142.0 (631.6)	146.4 (651.2)
	Sample 4	39.7 (1008)	139.4 (620.1)	140.5 (625.0)
	Average			139.8 (621.9)
Comparative Example 2	Sample 1	41.2 (1046)	34.0 (151.2)	33.0 (146.8)
	Sample 2	41.5 (1054)	40.9 (181.9)	39.4 (175.3)
	Sample 3	41.6 (1057)	42.8 (190.4)	41.2 (183.3)
	Sample 4	41.3 (1049)	41.2 (183.3)	39.9 (177.5)
	Average			38.4 (170.8)

As shown in TABLE 8, the trays formed from the sheet of Example 5 (with a first layer of a blend of polypropylene homopolymer and high density polyethylene and a second layer of polyethylene terephthalate copolymer) exhibited a significantly higher compression strength than the trays formed from the sheet of Comparative Example 2 (with a first layer of a blend of polypropylene homopolymer and high density polyethylene and an identical second layer of a blend of polypropylene homopolymer and high density polyethylene). Therefore, in general, a package formed from a sheet having a first layer comprising different materials (i.e., having a different composition) than a second layer may exhibit a compression strength (or "top load compression") that is greater than about 125 % of a compression strength of an other package formed from an other sheet having an other first layer comprising the same polyolefin (e.g., polypropylene) and having an analogous composition as an other second layer, where the other first layer still contributes at least about 30 % of the thickness of the other sheet and the other second layer still contributes at least about 25 % but less than about 60 % of the thickness of the other sheet. In some embodiments, such compression strength may be greater than about 150 % or greater than about 200 % or greater than about 300 % or from about 150 % to about 300 % of the compression strength of the other package.

Material distribution in thermoforming is a measure of the performance of a sheet during thermoforming (i.e., how the material distributes or disperses or spreads during thermoforming). It is measured by determining the thickness of various locations or areas of a thermoformed part. TABLE 9 lists the average normalized thickness of various locations at various heating times for identical cups formed from the sheet of Example 5 and the sheet of Comparative Example 2. Each thickness was normalized to a starting sheet thickness of 40 mil (about 1016 micron) (i.e., as if each of Example 5 and Comparative Example 2 has a thickness of 40 mil (about 1016 micron)). For each cup, S1 was an average of thickness of the cup side at two data points (e.g., on opposite sides of the cup) at about 10 millimeters below the cup flange; S2 was

an average of thickness of the cup side at two data points (e.g., on opposite sides of the cup) at about 10 millimeters below S1; S3 was an average of thickness of the cup side at two data points (e.g., on opposite sides of the cup) at about 10 millimeters below S2; S4 was an average of thickness at two data points (e.g., on opposite sides of the cup) at about 10 millimeters below S3; B1 was an average of thickness of the cup bottom at two data points at about 5 millimeters from opposite corner radii; and B2 was a thickness of the cup bottom at its approximate center. For the sheet of Example 5, two cups had a heating time of 19 seconds, two cups had a heating time of 20 seconds, four cups had a heating time of 25 seconds and two cups had a heating time of 29 seconds. For the sheet of Comparative Example 2, three cups had a heating time of 25 seconds and six cups had a heating time of 29 seconds. The identical heating temperature was used to form all cups; only the heating time varied.

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TABLE 9

Heating Time	Normalized Thickness of Thermoformed Part mil (micron)											
	S1		S2		S3		S4		B1		B2	
	Example 5	Comparative Example 2	Example 5	Comparative Example 2	Example 5	Comparative Example 2	Example 5	Comparative Example 2	Example 5	Comparative Example 2	Example 5	Comparative Example 2
19 seconds	17.9 (455)	did not form	11.7 (297)	did not form	10.8 (274)	did not form	13.1 (333)	did not form	19.6 (498)	did not form	29.5 (749)	did not form
20 seconds	16.6 (422)	did not form	12.7 (323)	did not form	11.4 (290)	did not form	15.1 (384)	did not form	21.1 (536)	did not form	30.6 (782)	did not form
25 seconds	16.9 (429)	9.6 (244)	13.4 (340)	6.1 (155)	15.6 (396)	7.3 (185)	16.1 (409)	8.1 (206)	25.8 (655)	21.9 (556)	35.8 (909)	31.9 (810)
29 seconds	18.1 (460)	12.2 (310)	15.7 (399)	8.7 (221)	16.6 (422)	9.3 (236)	16.6 (422)	11.5 (292)	27.8 (706)	20.8 (528)	39.1 (993)	33.9 (861)

As shown in TABLE 9, the sheet of Example 5 (with a first layer of a blend of polypropylene homopolymer and high density polyethylene and a second layer of polyethylene terephthalate copolymer) formed with less energy than the sheet of Comparative Example 2 (with a first layer of a blend of polypropylene homopolymer and high density polyethylene and a second layer of a blend of polypropylene homopolymer and high density polyethylene). In fact, the sheet of Comparative Example 2 did not form at either 19 seconds or 20 seconds heating time. Additionally, the cups formed from the sheet of Example 5 formed with even distribution and with more consistency (e.g., a "tighter range") than the sheet of Comparative Example 2. Further, the cups formed from the sheet of Example 5 had greater thickness than the cups formed from the sheet of Comparative Example 2 at all locations of the cup. Generally, a greater thickness correlates to a better thermoformed and stronger formed part.

Retort recovery is a measure of a material's oxygen barrier after exposure to high temperature, moisture and pressure, such as those in the retort sterilization process. It is measured by determining the oxygen transmission rate of a material at various time intervals after such exposure, in accordance with the following test method. Identical trays are formed from sheets (such as those as described in the present application). Each tray is filled with water and sealed with a foil lid. Each filled, sealed tray is placed in a retort chamber, which is heated from about 72 °F (about 22 °C) to about 250 °F (about 121 °C) and pressurized from about 14.4 psi (about 99 KPa) to about 30 psi (about 207 KPa) in 20 minutes. The chamber is then held at about 250 °F (about 121 °C) and about 30 psi (about 207 KPa) for 60 minutes. The chamber is then cooled to about 90 °F (about 32 °C) and depressurized to about 14.4 psi (about 99 KPa) in 40 minutes. Each tray surviving the retort process is removed from the chamber and prepared for oxygen transmission rate testing.

Oxygen Transmission Rate (OTR) is a measure of the rate of the transmission of oxygen gas through film, sheet, laminates, coextrusions, etc. It is generally expressed in cc/100 in²/day

and is measured in accordance with ASTM D3985, "Standard Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using a Coulometric Sensor." For the present application, OTR was measured for the whole package (e.g., filled and sealed trays that were first emptied). As such, OTR was expressed as "cc/pkg /day" (i.e., the amount of oxygen transmitted through the whole package per day).

Identical trays were formed from the sheets of Example 7, Example 8, Example 9, Comparative Example 2, Comparative Example 3 and Comparative Example 4. Trays formed from the sheets of Example 7, Example 8 and Example 9 and Comparative Example 2 survived the retort process described above. Each tray formed from the sheets of Example 7, Example 8 and Example 9 and Comparative Example 2 maintained dimensionality and shape and not distort or deform when exposed to the temperatures of the retort chamber (e.g., about 72-250 °F (about 22-121 °C)). Therefore, the sheet for such trays was thermally stable. However, trays formed from the sheet of Comparative Example 3 (with the first layer contributing 28.8 % of the thickness of the sheet and the second layer contributing 60.1 % of the thickness of the sheet) and trays formed from the sheet of Comparative Example 4 (with the first layer contributing 20.9 % of the thickness of the sheet and the second layer contributing 68.1 % of the thickness of the sheet) did not survive the retort process described above. Each tray formed from the sheets of Comparative Example 3 and Comparative Example 4 distorted and deformed and did not maintain dimensionality or shape. Therefore, the sheet for such trays was not thermally stable.

FIG. 6 is a graph depicting the oxygen transmission rates at various time intervals for identical trays formed from thermoplastic sheets according to the present application and a comparative example. Line 62 of FIG. 6 shows the oxygen transmission rate at various time intervals for trays formed from the sheet of Example 7. Line 64 of FIG. 6 shows the oxygen transmission rate at various time intervals for trays formed from the sheet of Example 8. Line 66 of FIG. 6 shows the oxygen transmission rate at various time intervals for trays formed from

the sheet of Example 9. Line 68 of FIG. 6 shows the oxygen transmission rate at various time intervals for trays formed from the sheet of Comparative Example 2. The time interval is the amount of time elapsed since the trays were removed from the retort chamber. As depicted in FIG. 6, trays formed from the sheets of Examples 7-9 (with a first layer of a blend of polypropylene homopolymer and polypropylene random copolymer and a second layer of a polyethylene terephthalate copolymer) exhibited comparable to or improved OTR at 40 hours compared to a tray formed from the sheet of Comparative Example 2 (with a first layer of a blend of polypropylene homopolymer and high density polyethylene and a second layer of a blend of polypropylene homopolymer and high density polyethylene). As such, Examples 7-9 exhibited excellent retort recovery.

Each and every document cited in this present application, including any cross referenced or related patent or application, is incorporated in this present application in its entirety by this reference, unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any embodiment disclosed or claimed in this present application or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such embodiment. Further, to the extent that any meaning or definition of a term in this present application conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this present application shall govern.

The above description, examples and embodiments disclosed are illustrative only and should not be interpreted as limiting. The present invention includes the description, examples and embodiments disclosed; but it is not limited to such description, examples or embodiments. Modifications and other embodiments will be apparent to a person of ordinary skill in the art, and all such modifications and other embodiments are intended and deemed to be within the scope of the present invention as defined by the claims. What is claimed is as follows:

1. A sheet comprising

a first layer comprising a polyolefin having a melting temperature, a storage modulus (G'_1) greater than about 100,000 psi (about 690 MPa) at ambient temperature, and a glass transition temperature less than ambient temperature; and

a second layer comprising a polymer having a glass transition temperature greater than ambient temperature;

wherein the first layer comprises different materials than the second layer;

wherein the melting temperature of the polyolefin of the first layer is greater than the glass transition temperature of the polymer of the second layer;

wherein the polyolefin of the first layer has a storage modulus (G'_1) at about 35 °C and a storage modulus (G'_1) at a midpoint temperature that is the average of the glass transition temperature of the polymer of the second layer and the melting temperature of the polyolefin of the first layer;

wherein the polymer of the second layer has a storage modulus (G'_2) at about 35 °C and a storage modulus (G'_2) at a midpoint temperature that is the average of the glass transition temperature of the polymer of the second layer and the melting temperature of the polyolefin of the first layer;

wherein the ratio of G'_1 to G'_2 at about 35 °C is less than 1, and the ratio of G'_1 to G'_2 at the midpoint temperature is greater than one;

wherein the sheet has a thickness equal to or greater than 10 mil (254 micron) and the first layer contributes at least about 30 % of the thickness of the sheet and the second layer contributes at least about 25 % but less than about 60 % of the thickness of the sheet.

2. The sheet of claim 1, wherein the polyolefin of the first layer comprises polypropylene, high density polyethylene or blends of such.

3. The sheet of claim 1, wherein the polyolefin of the first layer comprises from about 50 % (by weight) to about 70 % (by weight) polypropylene homopolymer and from about 30 % (by weight) to about 50 % (by weight) high density polyethylene.
4. The sheet of claim 1, wherein the polymer of the second layer comprises polyester, cyclic olefin copolymer, styrenic polymers or blends of such.
5. The sheet of claim 1, wherein the polymer of the second layer comprises amorphous or semi-crystalline polyester (APET), glycol-modified polyethylene terephthalate (PETG), isophthalic acid (IPA)-modified co-polyester (PETI), polylactic acid (PLA), copolyesters, high impact polystyrene (HIPS), general purpose polystyrene (GPPS), styrene block copolymer (SBC) or blends of such.
6. The sheet of claim 1, wherein the polyolefin of the first layer comprises from about 50 % (by weight) to about 70 % (by weight) polypropylene homopolymer and from about 30 % (by weight) to about 50 % (by weight) high density polyethylene and the polymer of the second layer comprises amorphous or semi-crystalline polyester (APET).
7. The sheet of claim 1, wherein the sheet has a thickness of from about 30 mil (about 762 micron) to about 50 mil (about 1270 micron).
8. The sheet of claim 1, wherein the first layer contributes from about 30 % to about 65 % of the thickness of the sheet and the second layer contributes from about 25 % to about 55 % of the thickness of the sheet.
9. The sheet of claim 1, wherein the first layer is an exterior layer or an interior layer and the second layer is an exterior layer or an interior layer.
10. The sheet of claim 1, wherein the second layer is an interior layer bonded to an exterior layer via an intermediate layer.
11. The sheet of claim 1, wherein the sheet further comprises an adhering layer positioned between the first layer and the second layer.

12. The sheet of claim 11, wherein the adhering layer comprises an adhesive, an extrudate, a coating, a tie material or a multilayer film.
13. The sheet of claim 11, wherein the adhering layer comprises a multilayer, blown film.
14. The sheet of claim 1, wherein the sheet has a normalized combined tear initiation and propagation resistance in both machine direction and transverse direction of greater than about 0.115 in*lb / mil (0.0511 Ncm / micron) energy to break and an elongation in both machine direction and transverse direction of greater than about 0.800 % / mil (0.0315 % / micron) as measured in accordance with ASTM D1004.
15. The sheet of claim 1, wherein the sheet has between 0 and about 20 degrees of transverse direction curl.
16. The sheet of claim 1, wherein the sheet is thermoformable.
17. The sheet of claim 1, wherein the sheet is thermoformed into a package.
18. The package of claim 17, wherein the package exhibits a compression strength that is greater than about 125 % of a compression strength of an other package formed from an other sheet having an other first layer comprising the same polyolefin and having an analogous composition as an other second layer, wherein the other first layer contributes at least about 30 % of the thickness of the other sheet and the other second layer contributes at least about 25 % but less than about 60 % of the thickness of the other sheet.
19. The package of claim 18, wherein the package exhibits a compression strength that is from about 150 % to about 300 % of the compression strength of the other package.
20. The sheet of claim 1, wherein the sheet is thermally stable when exposed to temperatures from about 194 °F (about 90 °C) to about 284 °F (about 140 °C).
21. The sheet of claim 20, wherein the sheet forms a package for retort, aseptic, hot-fill or microwave processing.

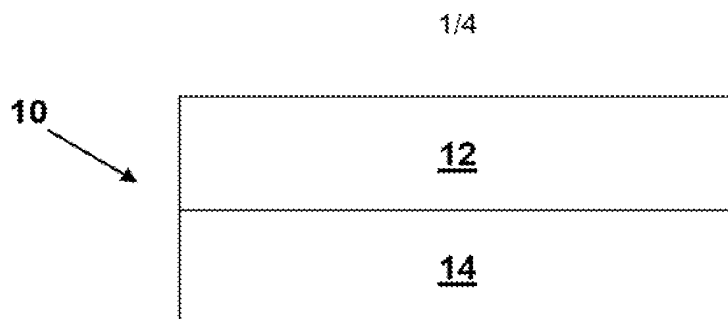


FIG. 1

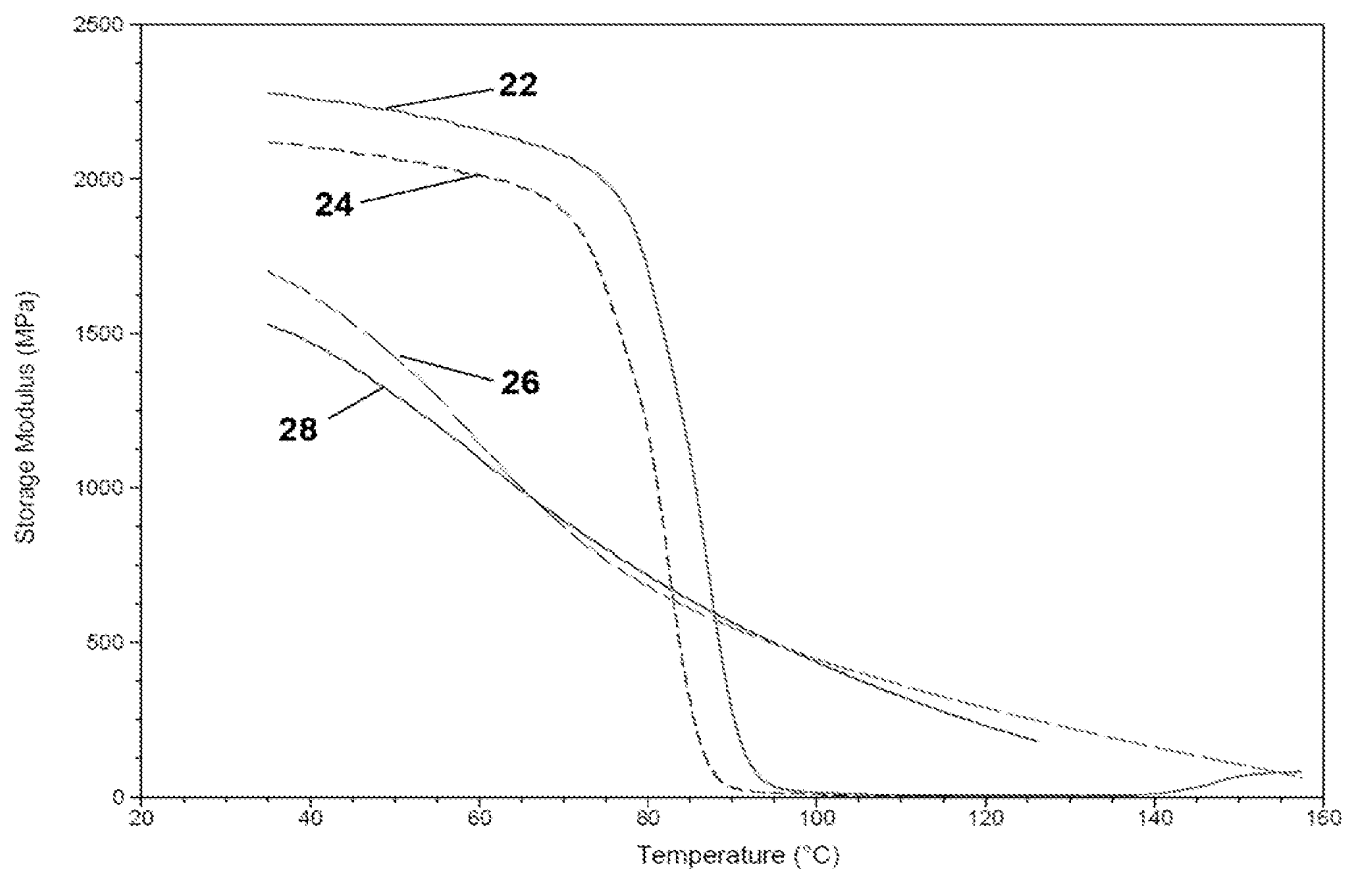


FIG. 2

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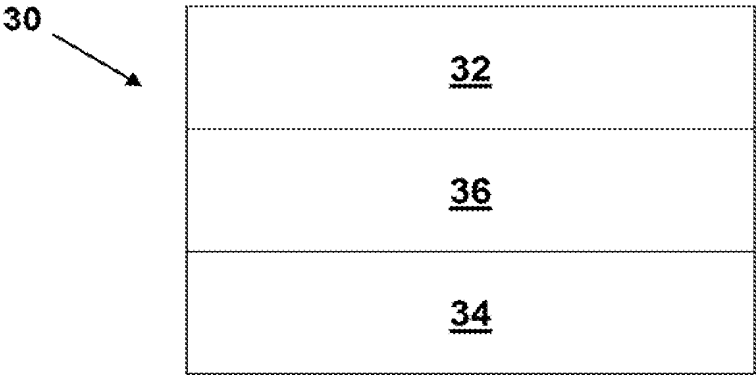


FIG. 3

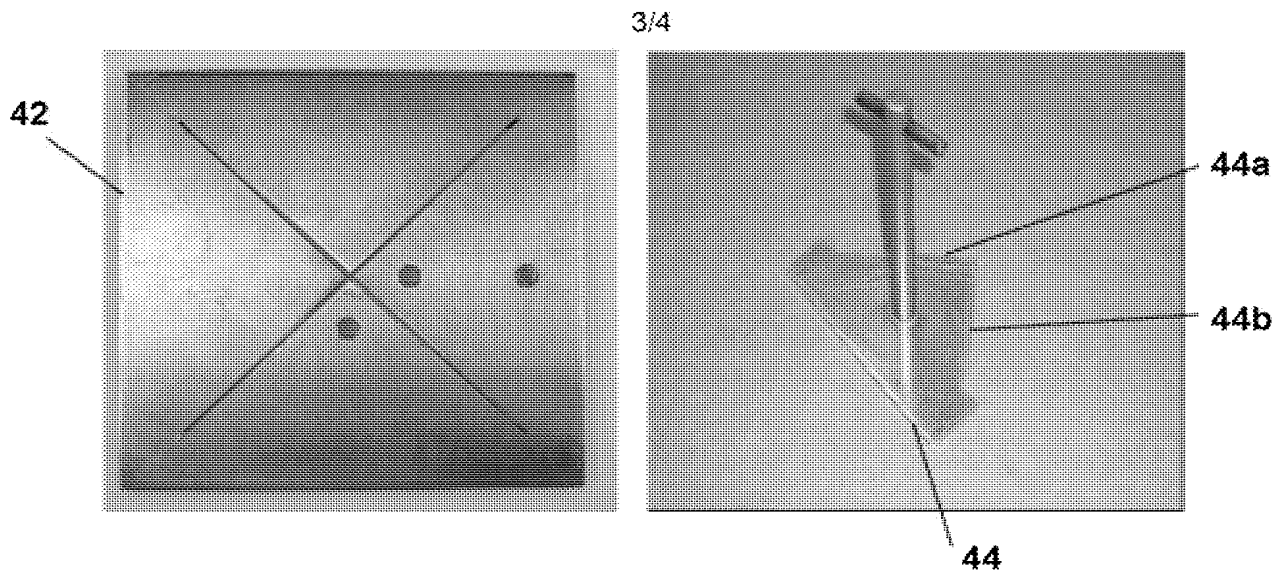


FIG. 4

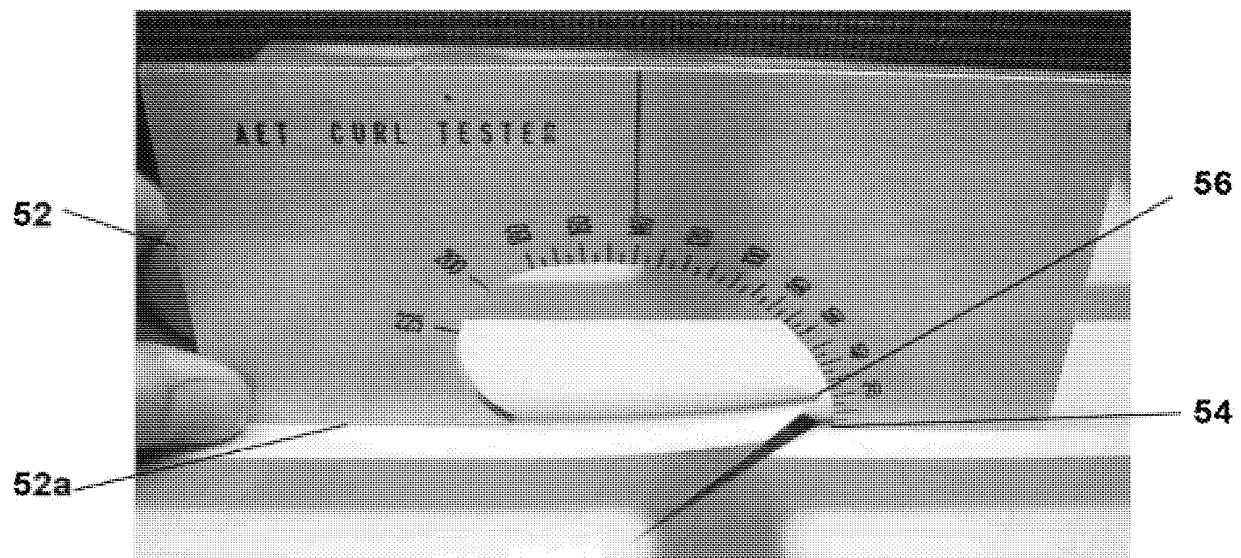


FIG. 5