ABSTRACT

Disclosed are devices and liners for containing item(s) or fluid(s) at a temperature below ambient temperature comprising: (a) a container or compartment having an interior space and (b) thermal insulation comprising a polymeric material having closed cells therein wherein said cells are formed from and/or contain a blowing agent, said container comprising a liner comprising (i) a first layer comprising ABS and having a surface facing toward said interior space; and (ii) at least a second layer having a surface facing away from said interior space and toward said thermal insulating foam, wherein said second layer of said liner is at least one of (1) a layer formed from an amorphous or semi-crystalline polyamide resin having sufficient composition and thickness to substantially inhibit the migration of said blowing agent toward said interior space; (2) a layer formed from a polymeric material capable of absorbing a substantial portion of said blowing agent molecules emitted from said insulation; and (3) a layer containing a material capable of reacting with a substantial portion of said blowing agent emitted from said insulation.
ABS LINERS AND COOLING CABINETS CONTAINING SAME

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Application No. 62/091,306 filed Dec. 12, 2014, which application is incorporated by reference herein.

FIELD OF THE INVENTION

[0002] The present invention relates to devices, such as cold boxes, refrigerators, freezers and the like which comprise an insulated cooling cabinet having improved liners.

BACKGROUND OF THE INVENTION

[0003] Devices such as refrigerators, cold boxes, freezers and the like include a cooling cabinet that usually contains an outer cabinet (usually metal), an inner plastic liner and an insulating foam core, typically polyurethane foam, in the space between the metal cabinet and the liner. The foam insulation contains cells that are filled with the blowing agent that was used to form the polyurethane foam. In the past, completely halogenated methane, such as fluorotrichloromethane (CFC-11), was most commonly used as the blowing agent. More recently, more environmentally acceptable substitutes, such as HCFCs, including 2-fluoro-2,4-dichloroethane (HCFC-141b) and 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123), and HFCs, including HFC-245fa, have been used. More recently, the use of 1,1,1-trifluoro,3-chloropropene (HFCO-1233zd) has also been proposed for use as a blowing agent in such applications.

[0004] In general, it is not uncommon for some portion of the blowing agent used to form polyurethane foams to escape over time from the cells that contain them. As a result, the design of such devices must take into account the interrelationship that the blowing agent will have with the liner of the refrigerator, freezer and the like. For this reason, many of the blowing agents which have been used to form polyurethane foams (such as Freon (CFC-11) and Freon substitutes, such as 2-fluoro-2,4-dichloroethane and 2,2-dichloro-1,1,1-trifluoroethane, (HCFC-141b and HCFC-123, respectively), have been studied for their impact onliners and have been found to potentially cause environmental stress cracking (ESC) such as liner blistering, catastrophic cracks, tiny cracks (crazing), and loss of impact properties (embrittlement), as well as stress whitening and/or dissolution. Applicants have come to appreciate that more recently used blowing agents, such as HCFC-141b, HCFC-123 and HFCO-1233zd, appear to have also exhibited a relatively high level of aggressiveness toward many liner materials.

[0005] The liner can be formed from a large variety of materials. (See for example, U.S. Pat. No. 6,589,646, which is incorporated herein by reference). One of the most important and commonly used materials to form the liner is acrylonitrile-butadiene-styrene (ABS) resin. One particular example of such ABS resins is disclosed in U.S. Pat. No. 5,524,589, which is incorporated herein by reference. Other materials of construction include glass-filled polystyrene (GPPS), impact-modified polystyrene (HIPS), styrene 6, copolymers, such as styrene-butadiene block copolymers, ASA, SAN, polyolefins, such as polyethylene or polypropylene, acrylates and methacrylates, such as PMMA, polycarbonates (PCs), polyvinyl chloride (PVC), polyethylene terephthalate (PET) and mixtures of these.

[0006] Applicants have come to recognize a need to provide solutions for the problem of environmental stress cracking (ESC) that can occur in such applications, especially when the liner is comprised of ABS.

SUMMARY

[0007] In preferred aspects the present invention provides devices, such as cold boxes, refrigerators, freezers and the like, and improved liners well adapted for use in such devices and other devices that utilize liners, especially liners made from thermoplastic resins and even more preferably liners made from relatively glassy polymers, such as thermoplastic ABS resin. Applicants have come to appreciate that ESC is a particular problem with glassy polymers, like ABS, when exposure to certain organic materials can result in cracking or crazing upon very modest applied stress (often an order of magnitude lower than the actual tensile or flexural strength of the polymer).

[0008] According to preferred embodiments, the present invention provides an improved liner comprising: (a) a first layer formed, and preferably thermoformed, from ABS polymer or resin; and a second layer or coating bound to the first layer, directly and/or indirectly, to provide said first layer with protection against exposure to blowing agent compounds that have or may have a deleterious effect on the properties of the first layer.

[0009] According to preferred embodiments, the second, protective layer or coating comprises a layer or coating formed from an amorphous or semi-crystalline polyamide resin or polymer having sufficient composition and/or thickness to substantially inhibit the migration of blowing agent there through, and even more preferably to inhibit the migration of blowing agent comprising HFCO-1233zd, and even more preferably trans 1233zd (1233zd(E)). In preferred aspects of such embodiments the second layer or coating is formed from a resin that forms a semi-crystalline polymer, and even more particularly from Nylon 6.

[0010] According to preferred embodiments, the second, protective layer or coating comprises a layer or coating formed from a material, and preferably a polymeric material, that is capable of absorbing a substantial portion of blowing agent molecules, and particularly HFCO-1233zd, preferably trans 1233zd. In preferred aspects of this embodiment, the second, protective layer is from a thermoplastic polyolefin, and even more preferably from polyethylene or polypropylene.

[0011] According to preferred embodiments, the second, protective layer or coating comprises a layer or coating formed from a material, and preferably a polymeric material, that includes components capable of reacting with the blowing agent molecules, and preferably blowing agent comprising HFCO-1233zd, and to thereby protect the first layer from exposure to such blowing agent molecules.

[0012] It will be appreciated that it is possible and may be desirably in certain applications to use a combination of any of the three embodiments described above to protect the first layer from exposure to a portion of blowing agent molecules, and particularly HFCO-1233zd, preferably trans 1233zd.

[0013] According to preferred device aspects of the present invention, the device comprises: a cabinet or cabinet-like structure having an inner compartment, preferably for con-
taining food, beverages and the like in a relatively cold condition; insulating foam to prevent passage of heat into or out of the inner compartment; and a liner comprising at least two layers according to the present invention between said insulating foam and said inner compartment, wherein at least a first layer of the liner has a surface facing toward the open space of the inner compartment and at least a second layer of the liner has a surface facing toward said insulating foam. Applicants have found that unexpected but highly desirable advantages can be achieved according to the preferred embodiments of the present invention wherein the foam is a closed cell foam, and more preferably a closed cell polyurethane foam, in which the blowing agent comprises in substantial part, and more preferably at least about 50% by weight, and even more preferably at least 75% by weight, of 1-chloro-3,3,3-trifluoropropene (1233zd), and even more preferably trans 1233zd. Applicants have found that the integrity and desirable characteristics associated with ABS liners can be maintained in such devices when a protective layer according to the present invention is configured to inhibit exposure of the first layer to such HFCO-1233zd molecules that are degassed or otherwise emitted from the foam.

Thus, according to preferred embodiments liners of the present invention are used in the refrigerator which is insulated with a foam containing a highly thermally efficient halogenated olefin blowing agent, and in particular HFCO-1233zd, preferably trans 1233zd, while maintaining durability of the liner and avoidance of stress cracking or other deleterious effects.

Accordingly, an object of one embodiment of the inventions is the provision of an thermal insulating device for keeping foodstuffs cool, cold or frozen in which the foam is a closed-cell foam having a halogenated olefin contained in at least a portion of the cells, and more preferably 1-chloro-3,3,3-trifluoropropene (1233zd), and even more preferably trans 1233zd and a liner according to the present invention, and even more preferably a liner of the present invention having a thickness of not greater than about 6 mm.

It is an object of certain embodiments of the present invention to provide a refrigeration appliance liner to be fabricated from a thermofromable, plastic sheet material which retains a high level of toughness (impact properties) and strength (tensile properties), even at low temperatures (at 5°F or less).

In one aspect, the present invention relates to a device for containing item(s) or fluid(s) and maintaining for at least an extended period of time (e.g., at least 1 hour) a temperature inside said container either below or above ambient temperature. Preferably the devices of the present invention include (a) a device or compartment, preferably having an opening that is either open or closable by a door, hatch, sliding cover or the like, for holding an item(s) or fluid(s), and preferably food and/or beverage items, to be maintained in a cooled or heated condition, relative to the ambient temperature, said container having an inner liner in accordance with the present invention and which corresponds at least in part to the interior shape of the compartment or container, and (b) thermal insulation comprising a polymeric material having closed cells therein wherein said cells are formed from and/or contain blowing agent comprising, and preferably comprising in major proportion by weight, a haloalkene according to Formula IA:

\[ \begin{align*}
    &C=CC=CR' \\
    &R
\end{align*} \]

[0018] where each R is independently Cl, F, H, or CF₃,

[0019] R' is (CR₂)ₓY,

[0020] Y is CF₃,

[0021] and n is 0 or 1.

said thermal insulation being disposed with respect to said container or compartment so as to inhibit the flow of heat into and/or out of the compartment and being adjacent or proximate to said liner, particularly such that said liner will be exposed to said blowing agent which escapes from said thermal insulation.

[0022] In certain preferred embodiments, the device further includes a heat transfer system for adding and/or removing heat from the compartment or container by use of a heat transfer fluid. In certain of said preferred embodiments, the heat transfer fluid comprises a haloalkene Formula IB:

\[ \begin{align*}
    &C=CC=CR' \\
    &R
\end{align*} \]

[0023] where each R is independently Cl, F or H

[0024] R' is (CR₂)ₓY,

[0025] Y is CF₃,

[0026] and n is 0 or 1.

[0027] While not limited thereto, the container or compartment for holding an item(s) or fluid(s) of the present invention include refrigerators, freezers, vending machines, reach-in coolers, transport refrigeration units, and water heater heat pumps.

[0028] In certain embodiments, the haloalkene according to Formula IA is selected from the group consisting of 1,1,1,4,4,4-hexafluoro-2-butenone (1336), 1-chloro-3,3,3-trifluoropropene (1233zd) (preferably trans 1233zd), 1,3,3,3-tetrafluoroalkane (1234ze) (preferably trans 1234zd), and combinations thereof. In further aspects, 1,1,1,4,4,4-hexafluoro-2-butenone (1336) is provided as the cis isomer, 1-chloro-3,3,3-trifluoropropene (1233zd) is provided as the trans isomer; and/or 1,3,3,3-tetrafluoroalkane (1234ze) is provided as the trans isomer. Applicants have found, however, that highly advantageous but unexpected results can be achieved, particularly with respect to thermal insulating quality and the durability and longevity of the device, by selecting from among these compounds monochloro trifluorohydrocarbons for use as a component of the blowing agent, and preferably as a component which comprises at least about 50% by weight, and even more preferably at least about 75% by weight of the blowing agent. Even more preferably, the monochloro, trifluorohydrocarbons comprises, in preferred embodiments comprises at least about 75% by weight, and even more preferably in certain embodiments consists essentially of trans 1-chloro-3,3,3-trifluoropropene (transHFCO-1233zd)).
Additional embodiments and advantages to the invention will be readily apparent to one of skill in the art based on the disclosure provided herein.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 is a schematic representation of a refrigerator cabinet.

FIG. 2 is a schematic drawing of the plastic liner serving as plastic wall of the refrigerator shown in FIG. 1.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Applicants have come to appreciate that advantageous properties of a liner, and particularly and preferably an ABS liner, can be achieved according to the present invention by desirable finish, chemical resistance, and impact resistance via the first layer of the liner, and without losing or negatively impacting those properties, utilizing the second layer to ensure the liner ensure that the liner does not undergo excessive blistering, cracking ( crazing) and loss of impact properties (embrittlement), after exposure during use to the halogenated hydrocarbon blowing agents, and particularly HFCO-1233zd, resulting from the insulation. In preferred embodiments, the insulation is foamed in place insulation.

The ABS Resin

It is contemplated that those skilled in the art will be able, in view of the disclosure contained herein, to select the appropriate resin, and preferably ABS resin, for use with each particular application. It is generally preferred, that the ABS resin is a grade that provides deep draw capability in thermo-forming operations. Furthermore, general purpose ABS grades which are commercially available for extrusion are particularly suitable for use as the first layer of the present liner. It is preferred that the ABS resin layer have a high gloss.

Generally, the ABS resin layer of this invention comprise three building blocks, unsaturated nitrile monomer, diene rubber, and vinyl aromatic monomer, (for example, acrylonitrile, polybutadiene rubber, and styrene), which can vary widely with respect to the percentage used. The proportion of these components can be tailored to desired needs such as chemical resistance, heat stability, impact resistance, toughness, rigidity, and processing needs. The relative proportion of these components will vary with respect to the desired end use according to the needs of those skilled in the art. For example, butadiene provides impact resistance. In providing a refrigerator liner, a larger proportion of butadiene may be utilized to provide low temperature impact resistance. The styrene component may be high so as to enhance processing ease and reduce costs. ABS is not a random terpolymer of acrylonitrile, butadiene, and styrene but a mixture of styrene-acrylonitrile copolymer grafted with butadiene. The butadiene provides a rubber phase which exists as discrete particles. The ABS resin may be prepared according to any of the methods well known in the art including emulsion, bulk, mass or suspension processes or a combination of these processes. Preferably the ABS resin is made by emulsion polymerization in order to have a high gloss appearance.

Examples of suitable, commercially available ABS resins are those provided by Cheil under the trade designation Starex QU-191S resin and by Inmos under the trade designation Linstar ABS 620, particularly the general purpose grades, the extrusion grades, and blow molding grades.

The Amide Resin

The amide resins commonly used and known by those skilled in the art generically as “nylon” may be adapted for use according to the present invention in view of the teachings contained herein. In general, the amide resins can be formed from condensation reactions of diamine(s) and dicarboxylic acid(s), such as is the case with nylon 6,6, or by ring opening polymerization of caprolactam (nylon 6).

The Polyolefin Resin

A wide variety of different grades of polyethylene are available for use, and it is contemplated that those skilled in the art will be able to make appropriate selections for individual applications based on the teachings contained herein. In general, it is contemplated that polyolefin according to the present invention is selected from high-density polyethylene (HDPE), cross-linked polyethylene (XLPE), medium-density polyethylene (MDPE), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), very-low-density polyethylene (VLDPE), copolymers with any of the above, and any combinations of any two or more of these. In certain preferred embodiments the polyolefin is PE wax. Although all such materials are considered available for use, polyethylene waxes according to certain embodiments have average molecular weights in the range of about 1500 grams per mole (g/mol) to about 20,000 g/mol. High grade polyethylene waxes may be obtained by the controlled polymerization of ethylene to obtain desired properties such as molecular weight, melting point, viscosity and hardness.

Polymers with Blowing Agent Reactive Components

In preferred embodiments, the second layer comprises a polymeric film, layer or coating having embedded therein a component that reacts with one or more of the blowing agent compounds, and preferably HFCO-1233zd, and in this way inhibit, and preferably substantially inhibit the exposure of those blowing agent compounds to the first layer of the liner.

In preferred embodiments, the polymer is polyethylene or polyamide, and the blowing agent reactive component is an amine and in certain embodiments preferably a tertiary amine. Preferred tertiary amines are triethylendiamine, pentamethyldiethylenetriamine, bis-(2-dimethylaminooethyl)ether, and mixtures of two or more of these.

In certain aspects of the invention, it is possible to combine the various embodiments so that synergistic effect can be achieved. For example, in certain embodiment the polymer which is used in the second layer comprises a polyolefin and/or polyamide and the blowing agent reactive component is embedded in at least a portion of one or both thereof.

Formation of the Layers

It is contemplated that methods and techniques known to those skilled in the art may be used to form the multi-layer liner of the present invention. For example, the multilayers can be produced by co-extrusion, including in preferred embodiments bilayer co-extrusion. In certain embodiments an adhesive or other material may be used to join or bond the first and second layer of the liner. In alternative embodiments, one layer is coated onto the other layer; such a technique is preferred for embodiments in which the second layer is a polyolefin layer but may be used with the other embodiments as well.

It is contemplated that any two or more of the embodiments described herein may be combined to form a three layer liner, or that all three embodiments may combined
to form a four layer liner. In such embodiments a variety of techniques may be used to form the multi-layer liner, and all such techniques are considered to be within the scope of the present invention.

[0049] Applications

The liners of the present invention may be used in a variety of applications. In preferred embodiments, the liners are included in relatively small refrigeration systems such as domestic refrigerators and freezers, vending machines, reach-in coolers, transport refrigeration units and the like, can provide such systems with highly advantageous energy performance while at the same time providing such systems that have extraordinarily low environmental impact and are durable and long-lasting.

[0050] One aspect of the present invention provides systems, devices and methods for containing item(s) or fluid(s) at a temperature either below or above the ambient temperature, preferably for an extended period of time (such as at least several hours or days). Such systems, devices, and methods include (a) a container or compartment for holding an item(s) or fluid(s) to be maintained in a cooled or heated condition relative to the ambient; (b) thermal insulation disposed with respect to said container or compartment so as to inhibit the flow of heat into and/or out of the compartment, said insulation comprising a polymeric material having closed cells wherein said cells are formed from and/or contain a blowing agent. In preferred embodiments the blowing agent comprises a haloalkene according to Formula IA:

\[
\begin{align*}
\text{R} & \quad \text{R'} \\
\text{R} & \quad \text{R'} \\
\end{align*}
\]

(IA)

where each R is independently Cl, F, H, or CF₃, provided that the total number of carbon atoms is either 3 or 4.

[0051] R' is (CR₂)ₙ Y,

[0052] Y is CF₃,

[0053] and n is 0 or 1;

and (c) a heat transfer system for adding and/or removing heat from the compartment or container by use of a heat transfer fluid comprising a haloalkene Formula IB:

\[
\begin{align*}
\text{R} & \quad \text{R'} \\
\text{R} & \quad \text{R'} \\
\end{align*}
\]

(IB)

where each R is independently Cl, F or H

[0054] R' is (CR₂)ₙ Y,

[0055] Y is CF₃,

[0056] and n is 0 or 1.

As used herein the terms container and compartment are used in the broad sense and are not limited to containers that fully enclose or surround the items or fluid being contained. Thus, for example, containers that have relatively permanent openings, such as would be the case in reach-in coolers and refrigerators, are encompassed within the meaning of this term.

[0060] In certain preferred embodiments the compound of Formula IA comprises, and preferably comprises at least about 25% by weight, and more preferably comprises at least about 30% by weight, and even more preferably consists essentially of one or more compounds selected from 1,1,1,4,4-hexafluoro-2-butene (1363mzz), 1-chloro-3,3,3-trifluoropropene (123zd), and 1,3,3,3-tetrafluoropropene (1234ze). In certain highly preferred aspects of such embodiments, the 1-chloro-3,3,3-trifluoropropene (123zd) is trans-1-chloro-3,3,3-trifluoropropene (123zd(E)), the 1,3,3,3-tetrafluoropropene (1234ze) is trans1,3,3,3-tetrafluoropropene (1234ze(E)), and the 1,1,1,4,4-hexafluoro-2-butene (1363mzz) is cis1,1,1,4,4-hexafluoro-2-butene (1363mzz(Z)).

[0061] In certain preferred embodiments, including particularly and preferably the embodiments in which the compound of Formula IA comprises, and preferably comprises at least about 50% by weight, and more preferably comprises at least about 70% by weight, and even more preferably consists essentially of one or more compounds selected from 1,1,1,4,4-hexafluoro-2-butene (1363mzz), 1-chloro-3,3,3-trifluoropropene (123zd), and 1,3,3,3-tetrafluoropropene (1234ze), and the compound of Formula IB comprises, and preferably comprises at least about 50% by weight, and more preferably comprises at least about 70% by weight, and even more preferably consists essentially of one or more compounds selected from 1-chloro-3,3,3-trifluoropropene (123zd(E)) and the 1,3,3,3-tetrafluoropropene (1234ze(E)) (preferably trans-1234ze(E)). In certain such embodiments, the 1-chloro-3,3,3-trifluoropropene (123zd(E)) is trans-1-chloro-3,3,3-trifluoropropene (123zd(E)), the 1,3,3,3-tetrafluoropropene (1234ze(E)) is trans1,3,3,3-tetrafluoropropene (1234ze(E)), and the 1,1,1,4,4-hexafluoro-2-butene (1336) is cis1,1,1,4,4-hexafluoro-2-butene (1336(Z)).

[0062] In certain preferred embodiments, the compound of Formula IA comprises, and preferably comprises at least about 50% by weight, and more preferably comprises at least about 70% by weight, and even more preferably consists essentially of one or more compounds selected from 1,1,1,4,4-hexafluoro-2-butene (1363mzz), 1-chloro-3,3,3-trifluoropropene (123zd(E)) (preferably trans-1233zd(E)), and the compound of Formula IB comprises, and preferably comprises at least about 50% by weight, and more preferably comprises at least about 70% by weight, and even more preferably consists essentially of one or more compounds selected from 2,3,3,3-tetrafluoropropene (1234ye) and 1,3,3,3-tetrafluoropropene (1234ze(E)) (preferably trans-1234ze).
essentially of 1,1,1,4,4,4-hexafluoro-2-butene (1336mzz) (preferably cis-1336mzz) and the compound of Formula IB comprises, and preferably comprises at least about 50% by weight, and more preferably comprises at least about 70% by weight, and even more preferably consists essentially of 1,3,3,3-tetrafluoropropene (1234ze), and even more preferably trans-1234ze.

[0065] In certain preferred embodiments, the compound of Formula 1A comprises, and preferably comprises at least about 50% by weight, and more preferably comprises at least about 70% by weight, and even more preferably comprises essentially one or more compounds selected from 1,1,1,4,4,4-hexafluoro-2-butene (1336mzz) (preferably cis-1336mzz) and the compound of Formula IB comprises, and preferably comprises at least about 50% by weight, and more preferably comprises at least about 70% by weight, and even more preferably consists essentially of and 1-chloro-3,3,3-trifluoropropene (1233zd) (preferably trans-1233zd).

[0066] In certain preferred embodiments, the compound of Formula 1A comprises, and preferably comprises at least about 50% by weight, and more preferably comprises at least about 70% by weight, and even more preferably consists essentially of one or more compounds selected from 1-chloro-3,3,3-trifluoropropene (1233zd) (preferably trans-1233zd) and the compound of Formula IB comprises, and preferably comprises at least about 50% by weight, and more preferably comprises at least about 70% by weight, and even more preferably consists essentially of and 1,3,3,3-tetrafluoropropene (1234ze), and even more preferably trans-1234ze.

[0067] In certain preferred embodiments, the compound of Formula 1A comprises at least about 50% by weight, and more preferably comprises at least about 70% by weight, and even more preferably consists essentially of 1-chloro-3,3,3-trifluoropropene (1233zd) (preferably transHFCO-1233zd), and the compound of Formula IB comprises, and preferably comprises at least about 50% by weight, and more preferably comprises at least about 70% by weight, and even more preferably consists essentially of 2,3,3,3-tetrafluoropropene (1234yf).

[0068] For the purposes of illustration, reference is now made to FIGS. 1 and 2 showing a refrigerator appliance which includes a cabinet and is defined by an outer cabinet metal wall 1, an inner liner wall 2, and a body of foamed-in-place insulation 3 therebetweent. It will be understood by those skilled in the art that the particular shape and configuration shown in FIGS. 1 and 2 is for illustration only and that numerous and various shapes and configurations of the cabinet, and therefore the cabinet liner wall 2, may be used within the broad scope of the present invention. In general, the thickness of the liner wall 2 is relevant to certain preferred embodiments of the present invention, but otherwise the particular shape and configuration of the cabinet formed by the liner wall can be according to any design as required for the particular application. In general, the inner liner wall 2 is thermoformed into the desired configuration, one example of which is shown in FIG. 2. Preferably, inner liner wall 2 is a thermoformed product of liner sheet made from one or more of the materials described herein, or a combination of sheets which have been laminated or otherwise integrated to form the liner wall 2.

[0069] Applicants have found that in highly preferred embodiments, including and preferably those in which the blowing agent is transHFCO-1233zd, the liner of the present invention has a thickness of not greater than about 10 mm, more preferably not greater than about 5 mm, more preferably not greater than about 4 mm, and even more preferably in certain embodiments not greater than 3 mm, or the other preferred thicknesses described herein.

[0070] Applicants have come to appreciate that the present systems and devices, including household refrigerators and the like, have a number of attributes for refrigerants and blowing agents that can, if the right combination of materials can be identified, potentially produce excellent and unexpected advantage over previously used materials. These attributes include:

[0071] good environmental properties, with preferred materials exhibiting zero ozone depletion potential (ODP), and low global warming potential (GWP);

[0072] low order of toxicity;

[0073] high performance, specifically with respect to efficiency and capacity for refrigerant gases;

[0074] thermal performance for blowing agents;

[0075] non-flammable, or low flammability risk characteristics;

[0076] relatively low cost;

[0077] durability, including particularly resistance to liner degradation.

[0078] Illustrated in Table 1, certain preferred systems utilize transHFCO-1233zd (which is sometimes also referred to herein as “1233ZD”) as a blowing agent which exhibits physical properties similar to 245fa. It would be noted that the global warming potential (GWP) of 1233ZD is more than two orders of magnitude lower than that of currently utilized HFCs, and more than one order of magnitude lower than the present language in the EU F-Gas Regulation, and within the rationale of the EU WEEE Directive pertaining to household refrigerator/freezers, with a GWP less than 15.

**TABLE 1**

<table>
<thead>
<tr>
<th>Property</th>
<th>trans 1233zd</th>
<th>245fa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>&lt;130</td>
<td>134</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>19</td>
<td>15.3</td>
</tr>
<tr>
<td>LFL/ULFL (vol % air)</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>GWP (100 yr)</td>
<td>17</td>
<td>858*</td>
</tr>
</tbody>
</table>


[0079] Preferred forms of the present invention utilize the preferred blowing agents in the various polyurethane (PUR) applications, including appliance foams. PUR foam properties of lambda (k-factor), compressive strength, and dimensional stability derived from characterization of hand mix foams or foam panels prepared by means of a high pressure foam machine have evidenced efficacy of the present systems in comparison to systems using 245fa foams. Furthermore, applicants have come to appreciate that until a commercial refrigerator product has been manufactured under industrial conditions, and assessed for energy performance and ancillary performance in other aspects, for example, liner compatibility, adhesion to liner and metal cabinet and doors, freeze stability, and other quality aspects, the full value and performance of the system will not be fully understood.
The following non-limiting examples serve to illustrate the invention.

EXAMPLES

Comparative Example

1233zd(E) Blowing Agent and ABS Liner

A single layer, 0.5 inch by 0.5 inch sheet of ABS liner is formed in a thickness of 0.06 inches. The sheet is exposed to 1233zd(E) vapor inside a Fisherport tube at a temperature of 70°C. The absorption of 1233zd(E) into the ABS was determined by recording the weight change after a one day and a four day exposure period. The sheet was found to increase in weight by 0.2% after one day and by more than 0.3% after four days.

Example 1

1233zd(E) Blowing Agent ABS/Nylon Liner

A two layer liner is formed using the ABS sheet of the Comparative Example by coextruding the ABS liner and nylon-6 at a temperature of from about 240°C to 260°C. A compatibilizer, such as Tritan 1120 (Bayer), is used to increase the affinity between these two polymer layers. The thickness of the ABS layer in the coextruded sheet is about 0.06 inch and the thickness of the nylon-6 is from about 0.005 to about 0.01 inch. The side of the sheet containing the Nylon-6 layer is exposed to 1233zd(E) vapor inside a Fisherport tube at a temperature of 70°C. The absorption of 1233zd(E) into the liner was determined by recording the weight change after a one day and a two day exposure period. The sheet was found to increase in weight by less than 0.03% after both the one day and the four day period, which is only one tenth of the absorption in the ABS layer of the Comparative Example. It is thus seen that the liner of the present invention had an ABS portion that was substantially protected from exposure to 1233zd(E). Other physical and chemical properties of liner remain substantially unchanged.

Example 2

1233zd(E) Blowing Agent ABS/PE Liner

A two layer liner is formed using the ABS sheet of Comparative Example 1 by spaying a hot melt of PE onto the ABS sheet of Comparative Example liner using a spray gun supplied with hot air. (Alternatively a co-extrusion as in Example 1 is used). The thickness of solidified PE layer is about 0.005 to about 0.01 inch and the thickness of the ABS layer is about 0.06 inch. The side of the sheet containing the Nylon-6 layer is exposed to 1233zd(E) vapor inside a Fisherport tube at a temperature of 70°C. The absorption of 1233zd(E) into the liner was determined by recording the weight change after a one day and a two day exposure period. The sheet was found to increase in weight by less than 0.03% after both the one day and the four day period, which is only one tenth of the absorption in the ABS layer of the Comparative Example. It is thus seen that the liner of the present invention had an ABS portion that was substantially protected from exposure to 1233zd(E). Other physical and chemical properties of liner remain substantially unchanged.

Example 3

1233zd(E) Blowing Agent ABS/PE-Tertamine Liner

20 g of a polyethylene emulsion (AC-680 from Honeywell) was blended with 12 g Dabco 33LV (33% triethylenediamine from Air Products). The blend was then coated onto one side of the ABS sheet of Comparative Example 1 and then air dried. The coating thickness was from about 0.005 to about 0.01 inch. The entire sheet is exposed to 1233zd(E) vapor inside a Fisherport tube at a temperature of 70°C. The absorption of 1233zd(E) into the liner was determined by recording the weight change after a one day and a two day exposure period. The sheet was found to not increase in weight after both the one day and the two day period. It is thus seen that the liner of the present invention had an ABS portion that was substantially protected from exposure to 1233zd(E). Other physical and chemical properties of liner remain substantially unchanged.

Example 4

1233zd(E) Blowing Agent ABS/Rubber-Tertamine Liner

A layer comprising about 20 g of a polybutadiene rubber and about 12 g Dabco 33LV (33% triethylenediamine from Air Products) is formed and bonded to the ABS sheet of Comparative Example 1 in a thickness was from about 0.005 to about 0.01 inch. The rubber-coated side of the sheet is exposed to 1233zd(E) vapor inside a Fisherport tube at a temperature of 70°C. The absorption of 1233zd(E) into the liner was determined by recording the weight change after a one day and a two day exposure period. The sheet was found to not increase in weight after both the one day and the two day period. It is thus seen that the liner of the present invention had an ABS portion that was substantially protected from exposure to 1233zd(E). Other physical and chemical properties of liner remain substantially unchanged.

What is claimed is:

1. A device for containing item(s) or fluid(s) at a temperature below ambient temperature comprising: (a) a container or compartment having an interior space for holding food and/or beverage in a cooled condition and (b) thermal insulation comprising a polymeric material having closed cells wherein said cells are formed from and/or contain a blowing agent, said container comprising a liner comprising (i) a first layer thermofomed from ABS resin and having a surface facing toward said interior space; and (ii) at least a second layer having a surface facing away from said interior space and toward said thermal insulating foam, wherein said second layer of said liner is at least one of (1) a layer formed from an amorphous or semi-crystalline polyamide resin having sufficient composition and thickness to substantially inhibit the migration of said blowing agent toward said interior space; (2) a layer formed from a polymeric material capable of absorbing a substantial portion of said blowing agent molecules emitted from said insulation; and (3) a layer containing a material capable of reacting with a substantial portion of said blowing agent emitted from said insulation.

2. The device of claim 1 wherein said liner has an average thickness of not greater than about 5 mm.

3. The device of claim 1 wherein said liner has an average thickness of not greater than about 2 mm.
4. The device of claim 1 wherein said liner has an average thickness of not greater than about 1 mm.

5. A refrigerator comprising the device of claim 1.

6. A refrigerator comprising the device of claim 3.

7. A freezer comprising the device of claim 1.

8. A freezer comprising the device of claim 3.

9. A vending machine comprising the device of claim 1.

10. A vending machine comprising the device of claim 3.

11. A reach-in cooler comprising the device of claim 1.

12. A reach-in cooler comprising the device of claim 3.

13. A transport refrigeration unit comprising device of claim 1.


15. The device of claim 1 wherein said blowing agent comprises transHFCO-1233zd.

16. A device for containing item(s) or fluid(s) at a temperature below ambient temperature comprising: (a) a container or compartment having an interior space for holding food and/or beverage in a cooled condition and (b) thermal insulation comprising a polymeric material having closed cells containing a blowing agent comprising at least about 50% by weight of trans-1-chloro-3,3,3-trifluoropropene (1233zd(E)), said container comprising a liner comprising (i) a first layer comprising ABS polymer and having a surface facing toward said interior space; and (ii) at least a second layer having a surface facing away from said interior space and toward said thermal insulting foam, wherein said second layer is at least one of (1) a layer formed from an amorphous or semi-crystalline polyamide resin having sufficient composition and thickness to substantially inhibit the migration of said blowing agent toward said interior space; (2) a layer formed from a polymeric material capable of absorbing a substantial portion of said blowing agent molecules emitted from said insulation; and (3) a layer containing a material capable of reacting with a substantial portion of said blowing agent emitted from said insulation.

17. The device of claim 16 wherein said blowing agent comprises at least about 75% by weight of transHFCO-1233zd.

18. The device of claim 16 wherein said blowing agent consists essentially of transHFCO-1233zd.

19. The device of claim 17 wherein said first layer is a layer of thermoformed ABS.

20. The device of claim 19 wherein said second layer comprises polyamide.