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Walles

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[54] **HEAT INSULATING CONTAINER HAVING PLASTIC WALLS RETAINING VACUUM**

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[51] **Int. Cl.** **A47j 41/02**
[58] **Field of Search** .... 215/13 R, 12 A; 220/9 C, 220/9 D, 10; 117/47 A

[56] **References Cited**

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1,694,967	12/1928	Coolidge	215/13 R
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2,981,430	4/1961	Tsien	215/13 R
3,295,709	1/1967	Herrick	215/13 R X

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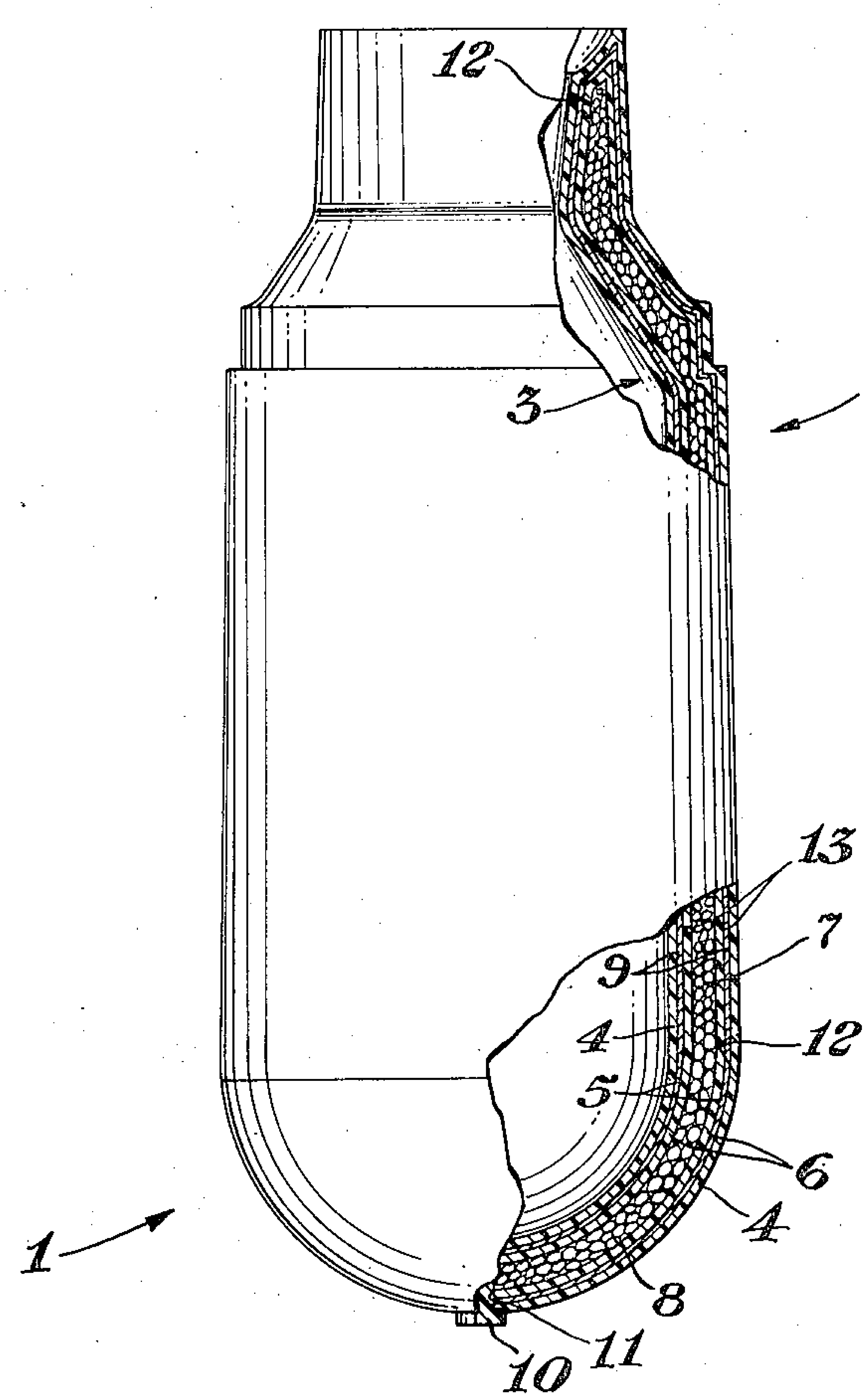
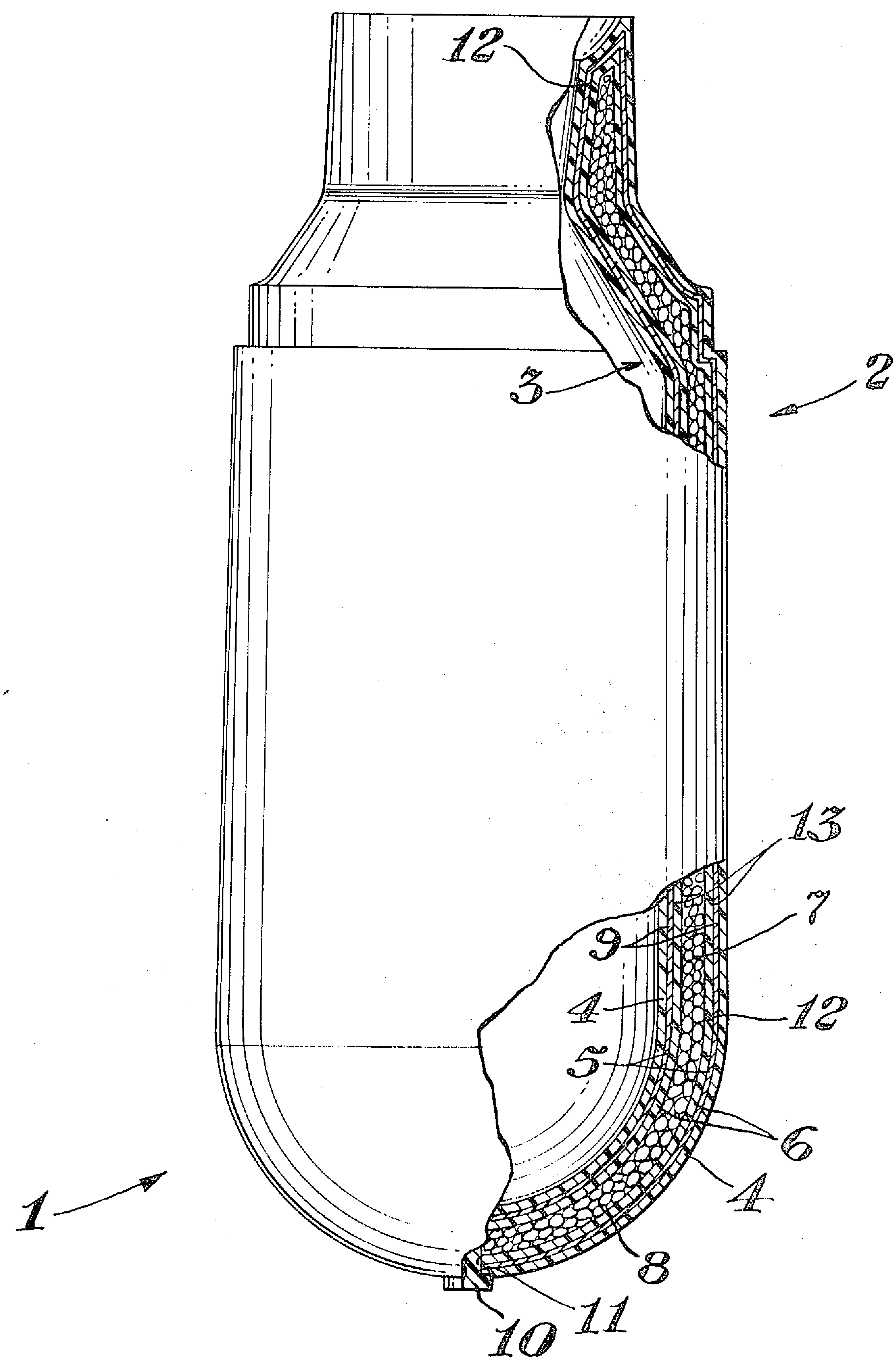
[57] **ABSTRACT**

A container having a double wall construction of a structural plastic material is provided with improved thermal insulative properties by (1) metallizing at least one surface of each wall of the container with metal such as silver to provide a light reflective surface and to produce a partial barrier to atmospheric gases, (2) coating the metallized surface with a barrier plastic such as saran, (3) evacuating the space enclosed by the walls of the container, and (4) adding to the evacuated space a gas-absorbing material.

10 Claims, 1 Drawing Figure

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HEAT INSULATING CONTAINER HAVING PLASTIC WALLS RETAINING VACUUM

BACKGROUND OF THE INVENTION

This invention relates to containers having vacuum retaining plastic walls and more particularly to containers having double wall construction of plastic materials with an evacuated space between the walls.

It is well known to form vacuum bottles and similar vacuum containers of glass by providing a double wall construction of the glass, coating the interior surfaces of the glass with a light reflective metal, then drawing a vacuum on the air space enclosed between the walls and sealing the double wall construction. While good thermal insulation is achieved with glass vacuum bottles, they are easily broken when subjected to almost any impact. The problem of breakage of the glass containers is overcome in the manufacture of stainless steel containers of double wall construction wherein the space between the walls is evacuated, filled with a gas-absorbing solid and sealed. However, such steel vacuum containers are substantially more expensive then the glass bottles.

In present commercial vacuum containers of glass and steel varieties, the temperature drop of water heated to 90°C and stored in the vacuum bottles at room temperature (≈ 25°C) is about 30°C per day. As is known by the vacuum bottle industry, this heat loss occurs as a result of (1) conduction through the evacuated space, (2) infrared radiation through the container, (3) conduction along the wall of the container around the stopper or other closure mechanism for the container and (4) conduction through the stopper or closure mechanism for the container. If a gas-absorbing solid particulate is included in the evacuated space, some heat loss results from conduction through the particulate. Heat loss as a result of (1) is insignificant at pressures below 10^{-4} mm Hg and becomes serious at pressures above 10^{-3} mm Hg. It is found that slightly higher pressures, e.g., 10^{-1} mm Hg, can be tolerated if a gas-absorbing solid such as activated charcoal is added to the evacuated space. Heat loss as a result of (2) is minimized by providing the container with a surface having an infrared wave reflectivity of 90 percent and higher and is negligible at reflectivity of 95 percent. Usually this is accomplished by applying a coating of a light reflective metal such as silver to the interior surfaces of the double wall construction of the containers. Heat loss as result of (2) can also be essentially eliminated by the inclusion of a one quarter inch layer of a powder, e.g., a gas-absorbing solid particulate, in the evacuated space. Heat losses resulting from (3) and (4) are minimized by decreasing the size of the opening through which the contents to be stored are added and by increasing the length or depth of the stopper or closure mechanism.

Attempts to manufacture double-walled vacuum insulated containers wherein one or both walls comprise a structural plastic polymer which has a higher impact strength than glass and is less expensive than steel have not been entirely successful. This lack of success is probably caused by the tendency of the plastic polymer to slowly release dissolved gases (so-called outgassing) and by the permeability of the plastic polymer to the gases of the stmosphere such as oxygen, nitrogen, carbon dioxide, argon and the like. In fact, these two characteristics of plastic polymers have caused vacuum container manufacturers to eliminate as much contact of plastic parts with the evacuated space between the double wall construction as possible. Recently, as shown in U.S. Pat. No. 3,295,709 and U.S. Pat. No. 3,225,954, the problem of plastic polymer permeability to atmospheric gases has been partially solved by metallizing the interior surfaces of double-walled plastic containers. Unfortunately, most metallization techniques do not provide the plastic walls of the container with sufficient impermeability to retain a vacuum for a period of a year or more. In addition, the metal surface is sometimes ruptured by impact caused by dropping the container in which case most, if not all, of the impermeability contributed by the metal layer is lost.

In view of the unsolved problems of conventional vacuum containers, it would be highly desirable to provide an economical plastic vacuum bottle having resistance to breakage and long-lasting thermal insulative properties comparable to those of glass or steel vacuum containers.

SUMMARY OF THE INVENTION

The present invention is a plastic container having a double-wall construction capable of retaining a vacuum for long periods of time. The plastic container exhibits considerable resistance to breakage and excellent thermal insulative properties lasting up to 5 years and longer.

More specifically, the plastic container comprises a boundary wall of a normally solid, plastic material enclosing an evacuated space, a layer of metal on at least one surface of said boundary wall, an overcoating of a barrier plastic adherent to the metal layer and a gas-absorbing material residing in the evacuated space. The plastic container is provided by metallizing at least one surface of the boundary wall and coating the metallized surface with the barrier plastic. The enclosed space is subsequently evacuated and sealed to provide the desired vacuum container. Advantageously, following evacuation and prior to sealing, the enclosed space is filled with a gas-absorbing material, e.g., a particulate solid.

Surprisingly, it is found that the plastic double wall containers of the present invention are superior in retaining the vacuum to similar containers in which the inner surface of the boundary wall has been metallized, but not coated with barrier plastic. Even more surprising is that the plastic containers of the invention maintain higher vacuum for longer periods of time than do containers in which the one surface of the boundary wall is metallized and the other surface is coated with barrier resin. Thus, in the practice of this invention, it is essential that the barrier plastic be applied to the metallized surface if the desired vacuum is to be maintained.

The plastic containers of the present invention are useful as containers for maintaining gaseous, liquid or solid materials in a hot or cold state for prolonged periods of time.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is an elevational view, partially in section, of a preferred plastic container of the invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

In the drawing, there is depicted a preferred plastic container **1** having a boundary wall **4** of a normally solid plastic material which encloses an evacuated space **7**. On inner surface **9** of wall **4**, there is deposited a light reflective metal layer **5**. On surface **13** of the metal layer **5**, there is deposited a layer **6** of a barrier polymer. The combined wall **4**, metal layer **5** and barrier polymer layer **6** comprise an interior portion **3** for holding contents and an exterior portion **2**. The interior portion **3** and exterior portion **2** are welded together at weld lines **12**. The exterior portion **2** has an opening **11** through which ingredients such as gas-absorbing solid particulate **8** can be inserted and gases occupying space **7** can be removed. Occupying at least a portion of space **7** is a gas-absorbing solid particulate **8** for capturing gases present in space **7** as a result of incomplete evacuation of space **7**, gases resulting from outgassing of the plastic material and barrier polymer and gases which permeate the combined boundary wall **4**, metal layer **5** and barrier polymer layer **6**. A plug **10** stoppers the enclosed space **7** after evacuation. The plug **10** may be of any material suitable for stoppering holes in plastics such that a vacuum of at least 10^{-1} mm Hg is maintained.

Plastic materials suitable for use in the boundary wall are those normally solid, organic polymers that are readily shaped or molded or otherwise fabricated into the desired container form and possess sufficient rigidity to retain said form under conditions to which they will be exposed. Preferably, the polymers are thermoplastic and are relatively inert to those materials which are to be contained. Because of their lower cost and superior structural properties, polymers used in structural applications, so-called engineering plastics, such as polystyrene, styrene/acrylonitrile copolymers, styrene/-butadiene copolymers, styrene/butadiene/acrylonitrile copolymers, rubber modified styrene polymers, and other polymers of monovinylidene aromatic carbocyclic monomers are generally preferred. Other polymers which may be suitably employed are acetal plastics such as polyformaldehyde resin, polyolefins such as polypropylene and polyethylene, polycarbonates, polyamides, such as nylon, rigid polyvinyl chloride, polyesters such as poly(ethylene terephthalate), acrylic resins such as poly(methyl methacrylate) and the other normally solid polymers which can be formed into the desired shape by conventional forming techniques, e.g., blow molding and injection molding. Of special interest, particularly for forming the portion of the boundary wall which will contain hot liquids, are the high temperature resistant plastics such as styrene/maleic anhydride copolymers, including their rubber modified variations, and other such polymers, including imide and lower N-alkyl imide forms. Such polymers of special interest are further described in U.S. Pat. No. 3,336,277 to Zimmerman et al., U.S. Pat. No. 3,401,153 to Zimmerman et al., U.S. Pat. No. 2,838,475 to Barrett and U.S. Pat. No. 2,971,939 to Baer. In addition to the foregoing polymers, the boundary wall may also contain one or more additaments such as fillers, stabilizers, surface modifiers, gas-absorbing materials, dyes and the like.

Because injection molding or similar procedures are preferred in fabricating the boundary wall, the plastic materials are preferably thermoplastic. However, thermosetting polymers can also be used. As a general rule, all synthetic polymers, whether thermoplastic or thermosetting, are incapable of retaining a high vacuum for an extended period. Accordingly, plastic materials usually employed in the boundary wall exhibit a degree of permeability to gases of the atmosphere such that a vacuum of 10^{-1} mm Hg can not be maintained in containers fabricated solely of such plastic materials.

The boundary wall has thickness in the range of about 40 to about 300 mils preferably from about 70 to about 100 mils. The wall should be generally thicker within said range when polymers somewhat lower in high temperature resistance are employed. Therefore it is understood that the wall thickness is suitable if it provides the container with sufficient strength to withstand deformation under normal conditions. The boundary wall is formed into desired shape by conventional polymer shaping techniques such as injection molding, blow molding and combinations thereof. It is understood that the boundary wall may be formed by molding the wall in two or more parts and then welding the parts together. In such instances welded portions of wall may comprise different polymers. For example, the interior portion of wall for containing the liquid or solid material may comprise high temperature resin such as styrene/maleic anhydride and the exterior portion of the wall may comprise a general purpose resin such as styrene/acrylonitrile copolymer.

The metal coating which imparts partial barrier characteristic to the boundary wall suitably comprises silver, lead, nickel, aluminum, copper, gold, titanium, tin, bismuth, antimony, chromium, manganese, iron, cobalt, metals of the platinum group and alloys of two or more of the aforementioned metals. Preferably the metal coating comprises silver, nickel or alloy thereof.

Metallization is preferably carried out by first rendering the wall surface of the plastic water wettable and subsequently plating metal on the surface with an electroless process such as the processes described by F. A. Lowenheim in Metal Coating of Plastics, Noyes Data Corporation (1970). See also Pinner, S. H., et al, Plastics: Surface and Finish, Daniel Davey & Co., Inc., 172–186 (1971) and U.S. Pat. No. 2,464,143. Preferably, the wall surface is rendered water-wettable by a gas phase sulfonation process as described in U.S. Pat. No. 3,625,751 to Walles. It is understood however, that other methods for rendering polymers water-wettable such as corona discharge, liquid phase sulfonation, etc., are also suitable. Other techniques for metallizing plastic surfaces such as electroplating can be suitably employed although such other techniques are not as desirable as the electroless plating techniques.

The quantity of metal deposited in forming the desired metal layer is that amount which forms an essentially continuous film over the desired surface of the boundary wall and thereby renders the wall partially impermeable. Preferably the quantity of metal deposited is in the range from about 2.0 to about 11,000 micrograms per square centimeter ($\mu g/cm^2$), especially from about 10 to about 500 $\mu g/cm^2$. Corresponding thicknesses of the metal layer are about 0.0001 to about 0.5 mil, preferably about 0.0004 to about 0.02 mil. The metal layer should be essentially continuous and extensive enough such that the evacuated space is essentially enclosed by the metal layer. Suitably, the metal layer is applied to at least about 95 percent of the total area of the boundary wall surface proximate to the evacuated space (hereinafter referred to as the inner surface), preferably to at least 99 percent. It is understood that the metal layer is composed of metal crystals with some open spaces therebetween. Alternatively or in addition, the metal layer may be applied to the outer surface of the boundary wall, i.e., surface distant from the evacuated space, although such practice is not as preferred as applying the metal layer to the inner surface of the boundary wall.

For the purposes of this invention, a barrier plastic is a normally solid, organic polymer that exhibits a permeance to gases of the atmosphere of less than about 6 cubic centimeters/100 square inches/mil of thickness/day (cc/100 square inches/mil/day), preferably less than about 0.9 cc/100 square inches/mil/day. The suitable barrier plastics can be formed into essentially continuous films which can be readily adhered to metal surfaces. Exemplary barrier plastics are vinylidene chloride/vinyl chloride copolymers, vinylidene chloride/acrylonitrile copolymers, and copolymers of such monomers as acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate and acrylamide. It is further understood that blends of such polymers are also suitable. Preferably the barrier plastics are the vinylidene chloride copolymers, especially those described in U.S. Pat. No. 3,617,368 to Gibbs et al.

The barrier plastics are preferably applied to the metal coatings in the form of latexes which form essentially continuous films upon drying at temperatures below the heat distortion point of the plastic material of the boundary wall. Heat distortion point of a polymer is the minimum temperature at which an article fabricated of the polymer distorts as a result of the tendency of the polymer to resume its prefabrication shape and/or as a result of minimal outside force. It is understood, however, that other forms of the barrier plastic such as solvent coatings, non-aqueous dispersions and powders are also suitably employed. Coating techniques such as dipping, spraying, powder coating, plasma jet and glow discharge and the like are suitable for applying the barrier plastic to the metal layer.

The quantity of the barrier plastic applied to the metal layer is in the range from about 6 to about 12,000 $\mu g/cm^2$, preferably from about 60 to about 5,000 $\mu g/cm^2$. Corresponding thicknesses of the coating of barrier plastic are in the range from about 0.001 to about 2.5 mils, preferably from about 0.01 to about 1 mil. The coating of barrier plastic should be extensive enough to essentially enclose the evacuated space. Advantageously, the barrier plastic coating is applied to at least about 95 percent of the total area of the metal layer, preferably at least about 99 percent.

A gas-absorbing material is added to the enclosed space prior to or after vacuumization of the space, preferably after evacuation. Usually, the gas-absorbing material is a finely divided solid or mixture of finely divided solids such as carbon black and activated charcoal powder, diatomaceous earth and other carbonaceous powders resulting from pyrolysis and/or steam activation of organic materials such as coconuts, corn husks, sugar; powdered metals and metal oxides and hydroxides, e.g., barium, lithium, sodium hydroxide, calcium oxide; metal silicates, calcium silicate, magnesium silicate, and finely divided, high surface area silicas. Generally porous powders of gas-absorbing solids having an average surface area of 100–2,000 square meters per gam are desirable. Most advantageously, the powder has an average particle size in the range from about 10^{-2} to about 10 microns. The amount of powder employed usually ranges from very small quantities such as about 0.3 gram up to large quantities which substantially fill the volume of the enclosed space. It is understood that the gas-absorbing solids capture atmospheric gases by both physical adsorption and chemical absorption mechanisms.

The space enclosed by the boundary wall is evacuated by any conventional vacuum pump such as one of a type used in evacuating conventional vacuum-insulated containers.

Following the addition of the gas-absorbing material to the enclosed space or evacuation of the enclosed space, whichever occurs later, the opening or openings through which the material is added and the vacuum is drawn are sealed such that a vacuum is retained (so-called hermetic seal). Conventional techniques for sealing vacuum containers fabricated of other materials can be adopted to seal the boundary wall. Preferably, however, a plug of a plastic material similar to or at least fusible with the plastic material of boundary wall is inserted into each opening and rotated until friction between the plug and the surfaces proximate to the opening fuses the plug to the boundary wall and thereby forms a hermetic seal. Alternatively, the plug may be sealed into the opening using an adhesive such as an epoxy resin.

The following examples are given for purposes of illustrating the invention and should not be construed as limiting its scope. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

1. Molding and Surface Treatment

Styrene/acrylonitrile copolymer (75/25) is molded by extrusion molding into an exterior portion of boundary wall as depicted in the drawing. The wall of the exterior portion has a thickness of 80 mils. Styrene/maleic anhydride copolymer having a heat distortion temperature of 285°F at a load of 264 psi is molded by extrusion molding into an interior portion of boundary portion as depicted in the drawing. The wall of the interior portion and exterior portion each have a thickness of 80 mils. The exterior and interior portions are welded together by heating with an ultrasonic means to form a boundary wall in the shape of container as depicted in the drawing. The inner surface of the boundary wall, i.e., that surface which borders or is proximate to the enclosed space, is surface sulfonated to a degree of 1 microgram of sulfur trioxide equivalents per square centimeter by passing dry air containing 2 percent sulfur trioxide gas into the enclosed space at 25°C for a period of a minute.

2. Metallization

A metallizing bath is prepared by mixing one part each of the following solutions:

0.60% $Ag(NH_3)_2NO_3$ in water

0.30% NaOH in water

0.15% glucose and 0.15 percent fructose in water.

Immediately after the bath is prepared, the boundary wall is dipped into the bath and metallization is completed within 1 minute.

3. Application of Barrier Plastic

The metallized boundary wall is overcoated with a barrier plastic by dipping it into a 50 percent solids latex of vinyl chloride/acrylonitrile/sulfoethyl methacrylate (90/8/2) terpolymer, said latex having an average particle size of about 0.22 micron. Thereafter, the boundary wall is removed from the latex and excess latex is allowed to run off the boundary wall. The boundary wall is then dried at 60°C for 15 minutes.

4. Evacuation and Addition of Gas-Absorbing Particulate

The space enclosed by the boundary wall is evacuated to a pressure of 10^{-2} mm Hg, and 80 g of activated charcoal having an average particle size of 0.2 micron is added to the enclosed space under vacuum. Prior to addition to the enclosed space, the charcoal is placed under a vacuum for a period of 48 hours at 10^{-7} mm Hg. The enclosed space is sealed hermetically by inserting a plug of styrene/acrylonitrile (75/25) copolymer into the opening into the enclosed space while maintaining the vacuum and spin welding the plug to the boundary wall to form the desired plastic container having double walls retaining the vacuum. Preferably, a portion of the plug surface is metallized and/or coated with barrier plastic to provide the boundary wall with a continuous barrier layer. The vacuum container is tested and is found to have heat insulative properties comparable to commercial glass and steel vacuum containers.

EXAMPLE 2

As evidence of the length of time that the vacuum containers of the present invention can maintain a vacuum, a vacuum bottle is prepared in accordance with Example 1 and is tested for air permeability. The bottle is a 1 quart vacuum bottle having a surface facing the evacuated enclosed space of 1,500 cm², an evacuated volume of 500 cm³ and a boundary wall thickness (excluding thickness of metal and barrier plastic) of 80 mils. The results are recorded in Table I and projected vacuum container life is calculated and is also recorded in Table I.

For purposes of comparison, various containers are prepared in a manner similar to Example 1 except that either metallization or coating with barrier plastic is omitted. The resulting containers and a control container which has not been treated or coated with any material are tested for air permeability and the results are recorded in Table I. In addition, the projected life for each of the containers is calculated and the results of these calculations are recorded in Table I.

TABLE I

Sample No.	Coating	Air Permeability(1) cc of air/day	Projected Container Life(2)
1	Metal and Barrier Plastic	0.056	1.2–4 years
2*	Metal	3.2	7.5–25 days
3*	Barrier Plastic	1.1	22.5–75 days
C*	None	9	3–9 days

*Not an example of the invention.

(1)Determined by using a mass spectrometer to measure permeated atmospheric gases.

(2)Assuming the gas-absorbing solid which fills the evacuated space can absorb a total of about 24–80 cc of air (activated charcoal used in Example 1 has such capacity), the projected life of the vacuum container is calculated from the equation:
Projected Life=Gas Absorbing Capacity of Solid/Air Permeability

EXAMPLE 3

As evidence of the synergistic effect of overcoating metal layer with the barrier plastic, several strips of polystyrene film (thickness = 5 mils) are surface sulfonated using the conditions described in Example 1 to provide a degree of sulfonation of 1.5 microgram of sulfur trioxide equivalents per cm² of film. Three strips of the surface sulfonated film are coated with varying thicknesses of the barrier plastic by applying a 50 percent solids latex of vinylidene chloride/acrylonitrile/-sulfoethyl methacrylate (90/8/2) terpolymer using various Meyer rods. The polystyrene strips coated with the different thicknesses of the barrier plastic, a strip of untreated polystyrene film and a strip of surface sulfonated polystyrene film are tested for oxygen permeance and the results in rate of oxygen transmission are recorded in Table II.

Two sulfonated strips of polystyrene film are metallized in accordance with the metallization procedure of Example 1. One metallized strip is overcoated with barrier plastic by the procedure of the foregoing paragraph. The resulting coated metallized strip and the uncoated metallized strip are tested for oxygen permeance and the results in rate of oxygen transmission are recorded in Table II.

TABLE II

Sample No.	Type	Coating Thickness μg/cm²(mil)(1)	Oxygen Transmission Rate, cc/100 sq in/day/atm Measured(2)	Calculated(3)
1	Silver Barrier Plastic	220 (0.01) 1200 (0.22)	0.013	0.24
2*	Silver	220 (0.01)	6.3	6.3
3*	Barrier Plastic	710 (0.13)	0.43	0.43
4*	Barrier Plastic	980 (0.18)	0.31	0.31
5*	Barrier Plastic	1420 (0.26)	0.20	0.21
6*	None, Surface Sulfonated	—	25.0	25.2
7*	None, Untreated	—	25.2	25.2

*Not an example of the invention.

(1)Coating thickness is measured in micrograms (μg)/square centimeter (cm²) from which thickness in mils is calculated using the equation: Thickness (mils)=393.7 mils/cm·[weight (μg)/Density (μg/cm³ × area (cm²)]. The densities for the layers of materials are as follows: silver=10.5 g/cm³ and barrier plastic=1 g/cm³.

(2)Determined by using a mass spectrometer to measure permeated oxygen at 25°C for 24 hours.

(3)Calculated using $1/Q=\Sigma(dn/Pn)$ wherein Q is the permeance of the total film structure to the named gas in cc/100 sq. in./day/atm, Pn is the permeability of a one mil layer in that film and dn is the thickness of the layer in mils. For example, in Sample No. 1, $1/Q=(5/125) + (0.01/0.083) + (0.22/0.056)=0.24$ where permeability of the layers is as follows: $P_{Boundary\ wall}=125$, $P_{Silver}=0.083$, and $P_{Barrier\ Plastic}=0.056$. Permeabilities of the various layers are measured by mass spectrometry.

As shown by Samples Nos. 3–5, the additivity rule of $1/Q = \Sigma(dn/Pn)$ is confirmed. Surprisingly, however, permeance for Sample No. 1 does not conform to the additivity rule since measured oxygen permeance of

0.013 cc/100 sq. in./day/atm is 1/18 of the calculated oxygen permeance of 0.24 cc/100 sq. in./day/atm.

What is claimed is:

1. A plastic container having double wall construction capable of retaining a vacuum for a substantial period of time, said container comprising a boundary wall of a normally solid, plastic material enclosing an evacuated space, a layer of metal on at least one surface of said boundary wall, an overcoating of a barrier plastic adherent to the metal layer and a gas-absorbing material residing in the evacuated space.

2. The plastic container of claim **1** wherein the metal layer is on the surface of the boundary wall which is most proximate to the evacuated space.

3. The plastic container of claim **1** wherein the barrier plastic exhibits a permeance to gases of the atmosphere of less than about 0.9 cc/100 sq. in./mil/day.

4. The plastic container of claim **3** wherein the barrier plastic is a vinylidene chloride copolymer.

5. The plastic container of claim **1** wherein the metal is silver.

6. The plastic container of claim **1** wherein the thickness of the boundary wall is in the range from about 40 to about 300 mils, the thickness of the metal layer is in the range from about 0.0001 to about 0.5 mil and the thickness of the overcoating is in the range from about 0.001 to about 2.5 mils.

7. The plastic container of claim **1** wherein the gas-absorbing material comprises activated charcoal in the form of a particulate solid.

8. The plastic container according to claim **1** wherein the plastic material of the boundary wall is a polymer of a monovinylidene aromatic carbocyclic monomer.

9. A method for making the plastic container of claim **1** comprising the steps of rendering a surface of the boundary wall water wettable, depositing a metal on the water wettable surface to form an essentially continuous layer thereof, applying the barrier plastic in the form of a latex to the resulting metal layer to form an essentially continuous layer of the barrier plastic adherent to the metal layer, evacuating the enclosed space, adding a gas-absorbing material to the enclosed space and hermetically sealing the evacuated space from the atmosphere.

10. The method of claim **9** wherein the metal is deposited on a surface of the boundary wall by an electroless plating process.

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