United States Patent [19]

Budd et al.

[11] **3,788,545**

[45] **Jan. 29, 1974**

[54] **GAS PERMEATION TUBE AND METHOD FOR THE FILLING THEREOF**

[75] Inventors: **Allan L. Budd**, San Diego; **Robert E. Foster**, Delmar, both of Calif.; **Jonathan S. Greenberg**, Arlington, Va.

[73] Assignee: **Monitor Labs Inc.**, San Diego, Calif.

[22] Filed: **Dec. 27, 1971**

[21] Appl. No.: **212,272**

[52] **U.S. Cl.** **239/34**, 239/56

[51] **Int. Cl.** **A24f 25/00**, A61l 9/04

[58] **Field of Search** 239/34, 56

[56] **References Cited**

UNITED STATES PATENTS

3,412,935	11/1968	O'Keeffe	239/34
3,623,659	11/1971	Maierson et al.	239/56
3,283,787	11/1966	Davis	239/34
3,679,133	7/1972	Sekiguchi et al.	239/34
3,111,091	11/1963	Hopkinson	239/34 X

Primary Examiner—Lloyd L. King

[57] **ABSTRACT**

A first permeation tube embodiment has a housing with exterior circular grooves at one end thereof. A gas permeable, Teflon membrane is fitted over the grooved end and an annular retaining ring is then press fitted over the grooved end to create a tortuous seal. An opposite end of the housing contains a needle valve inlet through which a precisely metered volume of gas is introduced by a gas transfer technique.

A second permeation tube embodiment includes a container from which liquified gas flows to envelop the exterior surface of a tubular membrane. Air flows through the membrane to dilute gas permeating inwardly through the membrane.

6 Claims, 8 Drawing Figures

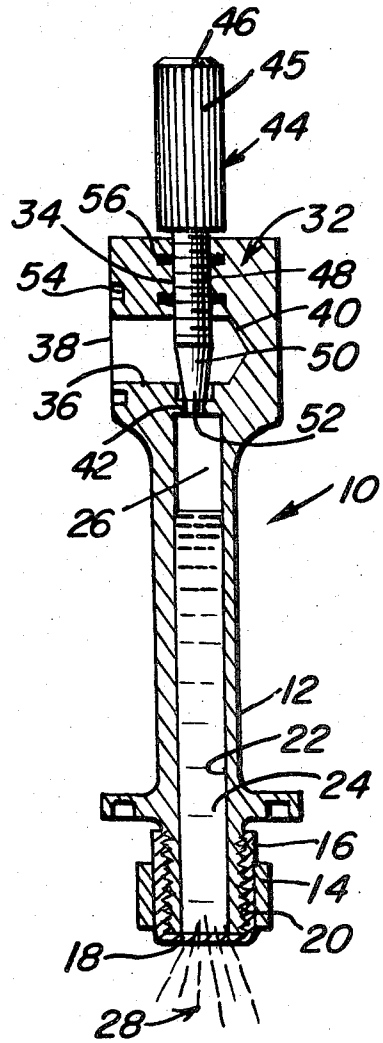


Fig. 1

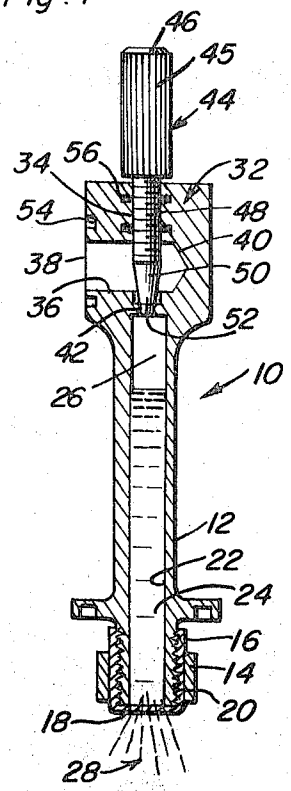


Fig. 3A

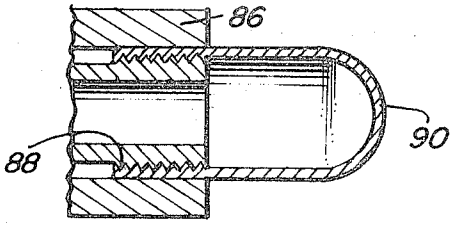


Fig. 3B

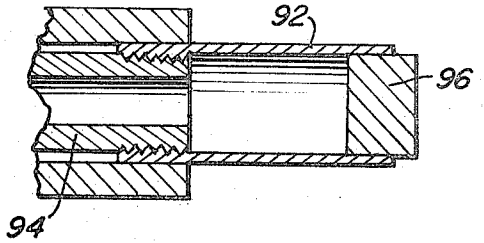


Fig. 2

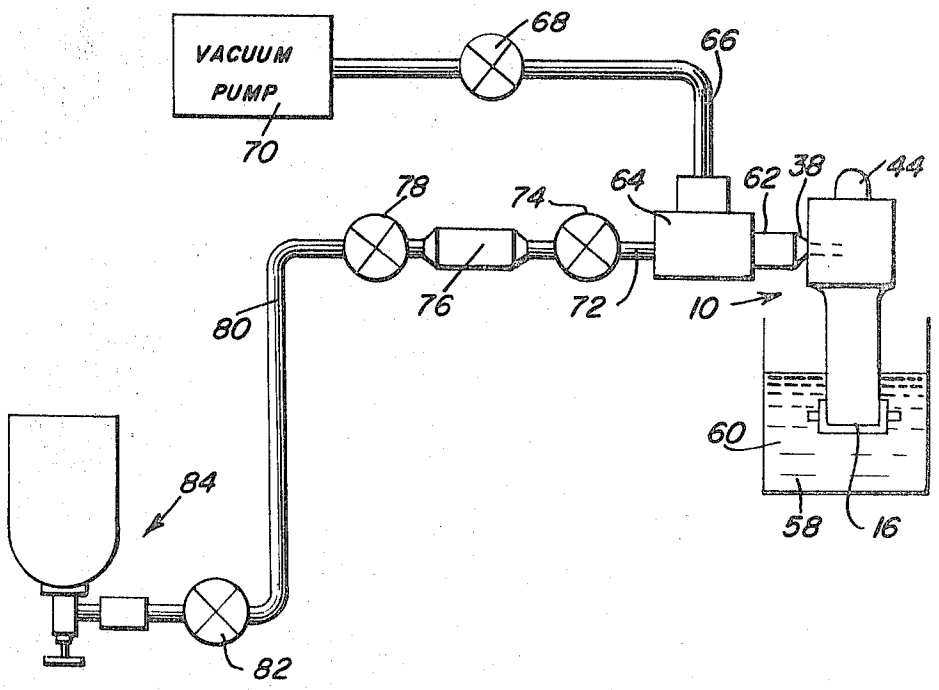


Fig. 4A

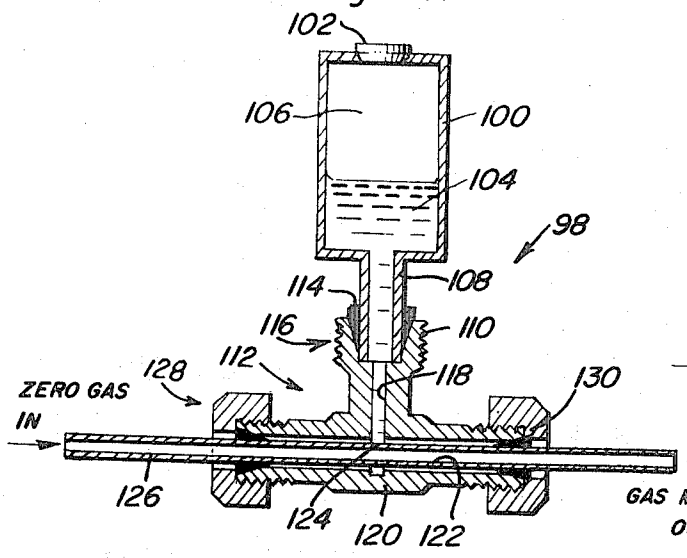


Fig. 4B

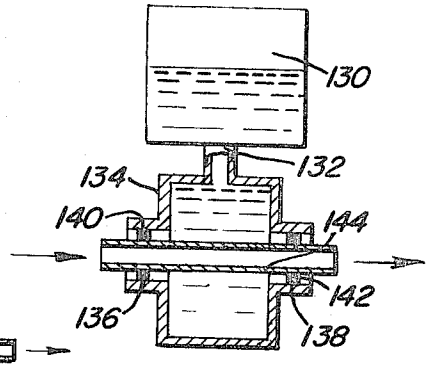


Fig. 4C

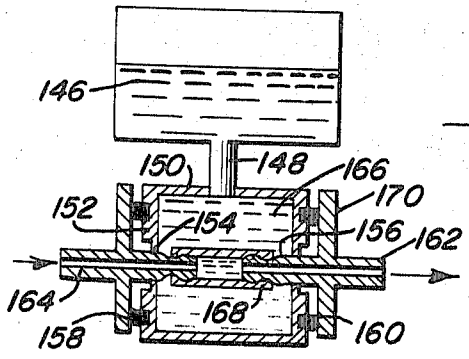
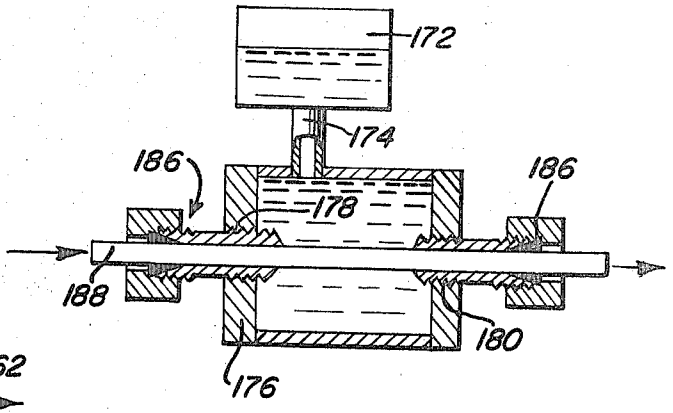


Fig. 4D



GAS PERMEATION TUBE AND METHOD FOR THE FILLING THEREOF

BACKGROUND OF THE INVENTION

The present invention relates to a gas dispensing device, and more particularly to a sealed vessel containing a gaseous substance in equilibrium with its liquid phase and having a permeation membrane through which gas can pass and be diluted by another gas.

BRIEF DESCRIPTION OF THE PRIOR ART

In the past, permeation tubes have been popularly used as standards for generating gas mixtures. These tubes are usually made by filling a vessel having at least a portion thereof made from FEP Teflon (Du Pont) tubing having known size and characteristics. Permeation of the gas through the Teflon generates a small concentration of this gas into a diluent gas which is generally air. In the area of pollution instrumentation, the permeation tube is employed to generate a small quantity of precisely measured pure pollutant gas where the pollutant gas is stored in the permeation tube.

Typical permeation tube designs are disclosed in U.S. Pat. No. 3,412,935 to O'Keeffe. Although conventional tubes, such as disclosed in this patent, work satisfactorily for certain applications, they suffer from several disadvantages.

Initially, it must be pointed out that for use in pollution instrumentation, permeation tubes must be designed to produce a permeate gas that when diluted with purified air (zero gas), an atmospheric pollutant is simulated. However, the prior art devices are constructed with a relatively large permeating surface so that a small concentration value cannot be obtained easily.

Further, prior art permeation tubes have suffered from inadequate seals. As a result, these tubes not only permeate the gas contained therein, but they also leak.

As to the conventional method of filling permeation tubes, a permeation tube is usually maintained at a low temperature to allow transfer of liquid gas from a large storage cylinder to the permeation tube. However, it has been found that very cold temperatures cause a Teflon membrane to crack due to brittleness.

Because of these and other problems of the prior art permeation tubes, it is highly desirable to improve existing permeation tubes so that smaller concentrations of permeate gas can be obtained. Also, an improved filling method is desirable which would allow the transfer of gas into a permeation tube kept at a temperature sufficiently high to prevent cracking of a Teflon membrane.

BRIEF DESCRIPTION OF THE INVENTION

The present invention is a marked improvement of presently existing permeation tubes. Further, there is disclosed a novel method for filling a permeation tube such as the one described herein.

The present permeation tube includes a permeating membrane that can be made controllably small so that a "pollutant gas" of small concentration is formed.

The invention includes a tortuous seal between the Teflon membrane and a vessel containing the permeand gas. This seal eliminates leakage of the permeand which would add an error factor to the permeation rate.

By employing a needle valve within the structure of the permeation tube, the presently disclosed permeation tube can be reliably filled at a high enough temperature to prevent the cracking of the permeation Teflon membrane.

The above-mentioned objects and advantages of the present invention will be more clearly understood when considered in conjunction with the accompanying drawings, in which:

FIG. 1 is a cross-sectional view illustrating the internal structure of one embodiment of the permeation tube disclosed in the present invention.

FIG. 2 is a diagrammatic illustration of a method for filling the permeation tube of FIG. 1.

FIG. 3*a* is a partial sectional view illustrating a modification of the end portion of the permeation tube shown in FIG. 1.

FIG. 3*b* is a partial sectional view illustrating a second modification of the permeation tube structure shown in FIG. 1.

FIG. 4*a* is a sectional view illustrating a second embodiment of the present invention.

FIG. 4*b* shows an additional modification of the structure shown in FIG. 4a.

FIGS. 4*c* and 4*d* show further modification of the permeation tube structure shown in FIG. 4*a*.

Referring to the figures and more particularly FIG. 1, reference numeral **10** generally indicates a first permeation tube embodiment. The permeation tube includes a hollowed housing **12** having a central cylindrical body terminating outwardly in an end portion **14** that has circular (non-helical) grooves formed therein. Because of the corrosive nature of the substance contained in the permeation tube **10**, it is preferable that the material from which the tube is manufactured be highly corrosion resistant, for example stainless steel.

A membrane **16** is slipped over the grooved end **14** of the housing **12**. By way of example, the membrane is indicated as being cup-shaped. The membrane must be permeable to the enclosed gaseous contents (permeand) of the tube. In a preferred embodiment of the invention, the membrane **16** is made from FEP Teflon (Du Pont). The outward closed end **18** of the membrane **16** forms a membrane closure for the axially formed bore chamber **22** that contains liquid gas **24**.

When assembling the permeation tube, the membrane **16** is slipped over the grooved end **14** and thereafter, a retainer ring **20** is force fitted over the membrane. This causes the Teflon material to cold flow into the grooves to effect a tortuous seal. This seal is far superior to the permeation tube seals of the prior art.

Above the liquid gas column **24** is the gaseous phase **26**. The liquid and gaseous phases are in equilibrium. Reference numeral **28** characterizes the permeation path of gas molecules.

The permeation tube has an enlarged, generally cylindrical head **32** containing a needle valve assembly. An axial bore portion **34** is formed in axially spaced relation to the aforementioned bore chamber **22**. Threads are formed along the interior surface of the bore **34** to accommodate a valve stem **44** therein.

Another bore **36** is formed in perpendicular, intersecting relation with the aforementioned threaded bore **34**. The bore **36** has an inlet port **38** which engages a

fill tube during filling of the permeation tube, as discussed hereinafter. The valve stem **44** allows filling of the tube when the stem is unscrewed, and after filling is completed, the valve stem is tightened to shut off the needle valve in the permeation tube head **32.** As will be observed, the inward end of the bore **36** terminates in a tapered end **40** which receives the mating end of a fill tube (not shown). A restricted, narrow passage **42** connects confronting ends of the bores **34** and **22.** This passage is adapted to receive the inward tapered end **50** of the valve stem **44.** As will be observed, the tapered end **50** of the valve stem is flat at **52,** and a cylindrical intermediate portion **48** connects the tapered end portion **50** and an enlarged cylindrical head section **45** that terminates outwardly in a slot **46,** adapted to receive a screwdriver.

An O-ring **54** surrounds the inlet opening **38** in bore **36.** This O-ring serves to seal the interface between the permeation tube and a separate fill tube during the filling of the permeation tube. An O-ring **56** is also provided at the outward end of bore **34** to seal the interface between the valve stem **44** and the bore **34.**

Equivalent means for clamping the membrane **16** to housing **12** includes the formation of threaded grooves at the transverse outer end of the housing instead of the grooves where illustrated. A retainer ring having mating threads would then clamp the membrane against the outer end of the housing.

FIG. **2** diagrammatically illustrates a method and apparatus for filling the permeation tube **10.** The tube **10** is positioned in a temperature bath vessel **58** containing crushed ice. The membrane **16** is thereby kept at freezing temperature which is not sufficiently low to cause cracking of the Teflon material. However, the freezing temperature is cold enough to maintain gas, in the permeation tube, in the liquified phase. As will be observed from the figure, the enlarged valve portion of the permeation tube **10** rises above the ice pack **60** and is exposed to allow connection of a filler tube **62** into the inlet port **38** of the permeation tube. The opposite end of the filler tube **62** is connected to a T-connector **64.** A second leg of the T-connector is fastened to tubing **66** having a shutoff valve **68** along its length. The outward end of the tubing **66** terminates in a vacuum pump **70.** The third leg of the T-connector **64** is connected to a coupling **72** that is in turn connected to a shutoff valve **74.** The opposite end of the valve **74** communicates with a chamber **76** that is bounded at its opposite end by a shutoff valve **78.** The volume of the chamber **76** is important. The volume is intentionally designed to be substantially equal to the volume of the liquid column in bore **22** of the permeation tube. Thus, chamber **76** serves as a metering device. As will be explained hereinafter, the metered volume of liquid gas filling chamber **76** is transferred to the permeation tube **10.**

Tubing **80** is connected between the shutoff valve **78** and another shutoff valve **82.** An inverted fill tank **84** containing liquified gas therein directly communicates with the valve **82.**

In operation of the system illustrated in FIG. **2,** valve **82** is closed and valves **78, 74, 68** and **44** are opened. Then, the vacuum pump **70** is operated to evacuate the entire system, including the permeation tube, of air and water vapor. Next, valve **74** is closed and valve **82** is opened thereby resulting in the flow of liquid gas from tank **84** into chamber **76** via tubing **80.** Valves **78** and **68** are closed. When the permeation tube valve **44** is opened, gas equilibrates in the system and most of the liquid contained in the chamber **76** is transferred to the permeation tube **10.** The transfer of liquid gas from chamber **76** to the permeation tube incorporates a change to the gaseous phase along the path between chamber **76** and the permeation tube **10.** However, due to the packing of the permeation tube **10** in the ice bath **60,** the gaseous phase is cooled and again changes to the liquid phase once inside the permeation tube. After the gas has been transferred out of chamber **76,** the valve **44** in the permeation tube **10** is closed. The ice bath **60** is removed and then the permeation tube **10** is disconnected from the filler tube **62.** Now, the permeation tube **10** is ready for use. When the filled permeation tube is removed from the filler tube **62,** the conduit path between valve **78** and the outlet end of filler tube **62** are filled with air. However, the portion of the system from valve **78** back to valve **82** does not contain air. Accordingly, when the next permeation tube is positioned in place against the outlet end of filler tube **62,** the permeation tube, and the conduit portion between valve **78** and the outlet end of filler tube **62** must be evacuated by the vacuum pump **70.** This requires that evacuation take place at the beginning of the next filling cycle. Thereafter, valves **68** and **74** are closed and valve **78** is opened and liquid gas flows to fill the chamber **76.** From this point in the procedure, the aforementioned filling steps are repeated.

As will be appreciated, the filling of the permeation tubes are conducted under relatively high pressure. Also, since the membrane **16** is maintained at a high enough temperature to prevent cracking, a high degree of quality control for the membrane can be realized.

Although the preceding discussion has been with respect to a cup shaped membrane **16,** this particular shape is noncritical and other designs are fully in keeping with the invention.

FIG. **3***a* illustrates the permeating end of a permeation tube similar to the previously discussed permeation tube **10.** However, the illustration depicts an elongated test tube shaped membrane **90** that is sealed between the retainer ring **86** and the grooved end **88.**

FIG. **3***b* illustrates a further variation wherein a hollow cylindrical permeating membrane **92** is fastened to the housing **94** of the permeation tube as in previous embodiments. However, a stainless steel or other noncorrosive plug **96** is inserted in the outward end of the permeation membrane **92.**

An alternate embodiment of the present invention is shown in FIG. **4***a* wherein a permeation tube assembly is generally denoted by **98.** The assembly includes an inverted container **100** having a fill plug **102** therein. It should be understood that any suitable means for filling the container **100** is permissible. Accordingly, the needle valve of permeation tube **10** can be used instead of the fill plug **102.** Inside the container **100** is a desired permeand in the gaseous phase **106** and the liquid phase **104,** that are in equilibrium with one another. The container includes an elongated neck portion **108** that has a centrally formed bore therein which communicates directly with the interior of the main container body. A leg **110** of a T-connector **112** has a bore **114** formed therein for receiving the neck portion **108** of the container **100.** A swagelock fitting **116** secures a seal between the container **100** and the leg **110** of the T-connector **112.** This leg of the T-connector includes

an axially formed passageway **118** communicating with the container **100.** The passageway **118** has a lower annular portion **120** that is positioned in central coaxial relationship to the other legs of the T-connector **112.** A central bore **122** is formed through these horizontally illustrated legs. A tubular permeation membrane **126** is positioned in the bore **122** and swagelock fittings **128** and **130** seal the exterior ports of the horizontal T-connector legs to the permeation membrane **126.**

Thus, in operation of the device, when liquid permeand **104** flows through the container neck **108** passageway **118,** annular passageway **124,** and bore **122,** the liquid gas envelops the membrane **126** and is contained between the swagelock seals **128** and **130.** Thereafter, the liquid permeand permeates radially inwardly to the inside of the permeation membrane **126.** As zero gas flows axially through the permeation membrane **126,** the zero gas mixes with the generated permeate to form a gas mixture that exists from the outlet end of a permeation member **126.**

FIG. 4*b* illustrates a further variation employing permeation of the liquid permeand in a radially inward direction. In this embodiment, a container **131** has a neck portion **132** that communicates with a cylindrical housing **134** having axially projecting annular flanges **136** and **138.** A tubular permeation membrane **144** passes through the flanges **136** and **138.** O-ring seals **140** and **142** seal the confronting surfaces of the flanges **136, 138** and the permeation membrane **144.** The gas flow is as indicated by arrows.

Still another embodiment is illustrated in FIG. 4*c* wherein the container **146** has its neck portion **148** extending into a cylindrical housing **150** that has transverse flattened ends **152.** Axial openings **154** and **156** are formed in the transverse ends **152.** O-rings **158** and **160** seal the confronting surfaces between the flattened housing ends **152** and the circular flanges **170** of conduit fittings **164** and **162.** A short length of tubular permemation membrane **166** is fitted to nipples **168** that extend axially inwardly and are an integral part of the fittings **162** and **164.**

A still further variation of the radially inward permeating device is illustrated in FIG. 4*d.* In this embodiment, a container **172** includes gaseous and liquified gas in equilibrium as in the preceding embodiments. A container neck **174** extends into a cylindrical housing **176.** Gas tight bulkhead fittings **178** and **180** extend axially through the transverse ends of the cylindrical housing **176.** A tubular permeation membrane **188** is axially positioned to pass through the bulkhead fittings **178** and **180** as well as the cylindrical housing **176.** Swagelock fittings **186** prevent the escape of gas through the interface between the permeation membrane **188** and the swagelock fittings **186.** As in the case of the last three discussed embodiments, air flows into the permeation membrane at the left end thereof and as it passes to the left outlet end of the membrane, the contained permeand permeates radially inwardly into the membrane **188.** After the gas enters the membrane, it is diluted by the zero gas flowing through the permeation membrane **188** and is delivered to the outlet end of the membrane.

With the exception of FIG. 3*b*, each of the illustrated and described embodiments exclude conventional end plugs for the permeation membrane. Elimination of these plugs is advantageous for several reasons. First, excluding end plugs eliminates the hazard of plug ejection at high temperature. Second, the seals of all embodiments of the present invention provide more positive gas sealing then end plugs.

In the instance of all embodiments presented herein, the permeation tubes eliminate short lifetime due to small fill volumes. The proposed devices can be recharged without adjustment of permeation membrane length. Also, use of a stainless steel housing and container provides more constant heat sinking for contained liquids than a permeation tube alone. As an extension of this advantage, the constructions herein provide rapid temperature change for better control due to the high thermoconductivity of the housing of permeation tube **10.** In the embodiments of FIGS. 4*a*–4*d*, a gas containing container adds to the high thermoconductivity characteristic.

Accordingly, from the aforementioned specification and accompanying claims it can be appreciated that the present invention offers distinct advantages over the prior art permeation tubes.

It should be understood that the invention is not limited to the exact details of construction shown and described herein for obvious modifications will occur to persons skilled in the art.

Wherefore, the following is claimed:

1. A permeation device comprising:
a casing for storing liquid gas therein;
an outer end of the casing having grooves therein;
a permeation membrane positioned over the grooved end of the casing; and
fastener means clamping the membrane against the grooved end of the casing for causing cold flow of membrane material in the grooves and creating a tortuous seal between the membrane and the grooved end of the casing.

2. The structure recited in claim **1** wherein the permeation membrane is cup-shaped and includes a cylindrical wall bounded on one transverse end by a circular integral closure.

3. The structure as set forth in claim **1** wherein the permeation membrane is characterized as test tube shaped with an open end and an oppositely disposed oblong closed end.

4. The structure as defined in claim **1** wherein the permeation membrane has a hollow tubular shape having opened ends, and further wherein a sealing plug is inserted in an outlet end of the membrane.

5. A permeation device comprising:
a container having liquified gas;
a permeation membrane positioned adjacent the container; and
conduit means having a diluent passing therethrough, the conduit means communicating between the container and the permeation membrane to channel flow of the liquified gas around the exterior of the membrane; whereby the gas permeates from the outside of the membrane to the inside where it is mixable with the diluent.

6. The structure of claim **1** wherein the membrane is composed of a polymeric plastic material.

* * * * *