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MEANS FOR IMPROVING THERMAL INSULATION SPACE

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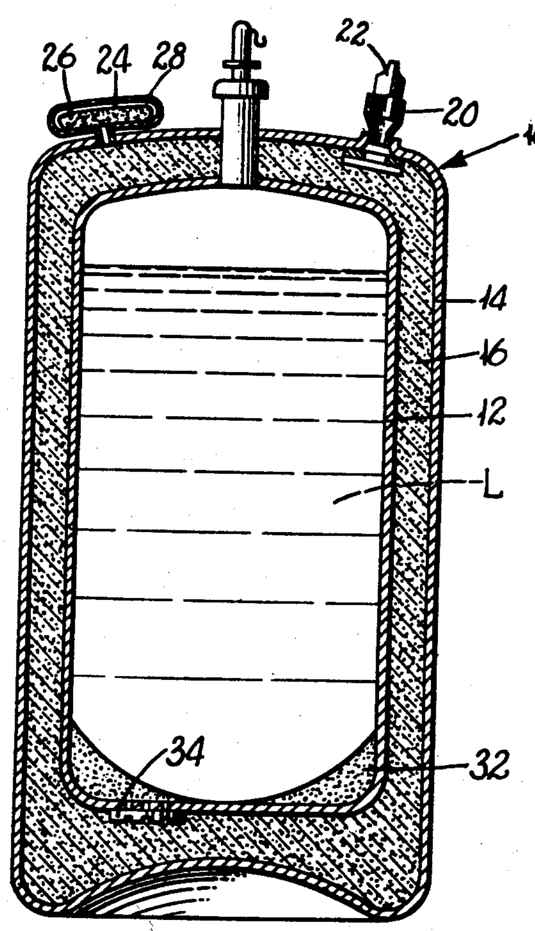

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MEANS FOR IMPROVING THERMAL INSULATION SPACE

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15 Claims. (Cl. 220—9)

This invention relates to a novel method and means for introducing getter material in its activated state into a vacuum insulated state. This application is a continuation of my copending application S.N. 792,250 filed January 27, 1959, now abandoned.

Heretofore, getter material has been widely used in the electron tube art to remove residual gases. The getter material is usually introduced into the electron tube in an inactive state and is activated after the tube is evacuated and sealed. This is accomplished by vaporizing or "flashing" the getter material by heating it electrically until it vaporizes rapidly and deposits as a film or spatter on a surface within the electron tube. In this form the getter is extremely active chemically and exhibits strong gettering action, resulting in an efficient removal of the residual traces of such gases as oxygen, nitrogen and carbon dioxide from the vacuum space.

Up to now the use of an active getter in a vacuum insulating space has been considered impractical. Getters are usually associated with very good vacuums on the order of 1 micron or lower absolute pressure. The degree of leak-tightness required to maintain such vacuums is a comparatively recent achievement in commercial vessels of welded or brazed construction. Moreover, a large amount of getter material is needed to remove residual gases not pumped out from the relatively huge vacuum spaces associated with thermal insulations. Even when insulation space fillers are used, substantial quantities of getter material must be used to remove adsorbed gases from the filler material. Furthermore, additional amounts of getter must be provided to remove gases that enter through leakage over the service life of the insulated container.

Up to now the use of large quantities of active getter material has not been known and special techniques are required for proper handling of these amounts. In addition, the flashing or vaporizing methods of introducing an activated getter into a vacuum tube space are not suited to thermal insulation spaces. In a straight vacuum system having polished metal surfaces a flashed getter will seriously impair the reflective qualities of the polished surfaces. Also, when an insulating filler material is used in the vacuum space, the flashed getter tends to deposit as a localized mass fused with the filler material in the immediate vicinity and in this form has limited surface areas and absorptive capacity. Furthermore in narrow insulation spaces the resultant mass will provide a path for a prohibitive amount of conductive heat-inleak. Moreover a temperature of at least 2000° C. is usually required to vaporize a metal getter such as barium. While the introduction of such heat is reasonable in electron tubes to vaporize milligram quantities of getter material, it is impractical when several gram quantities are involved because of the likelihood of damage to the insulation and metal walls.

It is therefore an important object of the present invention to provide an improved method of exposing a getter material in its activated state to an insulation space without requiring vaporization, flashing, or other physical or chemical treatment in situ of the getter material.

Another object of the invention is to provide in an insulation space a previously activated getter material

which is sealed from the insulating space and improved means for exposing such getter material to the insulating space and initiating its gettering action after the insulation space has been suitably evacuated, thereby to improve and maintain the vacuum.

Another object is to provide in the vacuum insulation space of a storage vessel containing solid insulating material, an improved method and apparatus for exposing a getter material in its activated state without perceptibly changing the insulating qualities of said solid insulating material, thereby removing residual traces of gases in said vacuum insulation space.

Another object of the invention is to provide in a vacuum insulating space, a novel combination of an adsorbent material and a getter material which cooperate to provide a high quality vacuum insulating condition which neither material could accomplish alone.

Other objects, features and advantages of the present invention will be apparent to those skilled in the art from the following detailed description of a preferred embodiment of the invention when considered in connection with the accompanying drawing in which:

The single FIGURE is a sectional view of a double walled container embodying the principles of the invention.

In accordance with the present invention, a novel sealed container of activated getter material is provided in the insulating space of a vacuum panel or double walled vessel. The sealed container is made at least in part of a breakable material, preferably glass and is constructed in such manner that at least the shatterable or rupturable portion extends into a suitable getter chamber in the outer wall of the vessel. After the insulating space has been evacuated and the evacuation connection sealed, the getter chamber is suitably distorted so as to fracture that portion of the sealed getter container therewithin. In this manner the getter material in the sealed container is exposed in its activated state to the insulating space after evacuation of the insulating space has occurred without requiring a vaporizing or flashing mechanism to initiate its gettering action.

The invention will be described in connection with the insulating space of a liquefied gas holding container, but it is to be understood that it is not intended to limit the invention thereto, but rather the invention is susceptible to use in other forms, e.g., vacuum insulating panels.

Illustrated in the single figure in the drawing is a liquefied gas holding vessel or double walled cylinder **10** embodying the principles of the present invention. The double walled liquid cylinder comprises an inner vessel or cold wall **12** of impervious metal which is not embrittled at low temperatures, such as stainless steel, for holding cold material such as liquefied gas L, such as oxygen, nitrogen, argon, helium or hydrogen. The inner vessel **12** is generally cylindrically shaped and is surrounded by a cylindrical gas-tight shell or jacket or warm wall **14** of suitable metallic material, completely encompassing the inner vessel **12** and providing an intervening evacuable insulating space **16** to provide substantial resistance to heat leakage therethrough.

The intervening space **16** may be a straight vacuum insulated space provided with polished metal surfaces or preferably provided with a low conductive thermal insulation, for example, a powder insulating material comprising a mixture of finely divided low conductive particles such as silica aerogel and finely divided radiant heat impervious bodies such as aluminum flakes such as disclosed in U.S. Patent No. 2,967,152 to L. C. Matsch et al., or a composite insulation such as disclosed in U.S. Patent No. 3,007,596 to L. C. Matsch. The latter may comprise alternate layers of a low conductive fibrous sheet material such as glass fiber and radiation-impervious barriers such as aluminum foil. Use of getter with the latter insulation is especially advantageous because the composite material tends to be more pressure sensitive than the powder material. Absorbents permit appreciable pressure rise when the cold container warms slightly, while a getter holds the gases permanently.

Exhaustion of the space between the container walls is accomplished by providing the shell **14** with a nipple **20** having a ductile metal evacuation tube **22**. The pressure within the insulating space **16** should be reduced to a value at least below 20 microns Hg and preferably below 10 microns. After exhaustion, the tube **22** is suitably crimped and soldered or welded to effectively seal the vacuous space **16**.

In accordance with the present invention a sealed capsule **24** made of glass or other frangible material, and containing a suitable amount of active getter material **26** in a vacuum or in an inert atmosphere preferably of argon, suitably disposed in a getter chamber or protuberance **28** which is in communication with the vacuous space **16**. At the desired time, preferably after the vacuous shell has been exhausted by a vacuum pump or other suitable apparatus and the evacuation tube **22** crimpingly sealed, the getter chamber **28** is suitably deformed as with a pair of plyers, thereby crushing the glass capsule **24** and exposing the active getter material **26** to the insulation space **16**. The capsule **24** preferably should be attached to the warm wall **14** of the storage vessel since the rate of gettering decreases with a reduction in temperature.

Any suitable getter having a compatible active form may be sealed in the capsule, the active powder form being preferred. The final selection may depend upon the temperatures at which the insulation will operate, because some getters become highly reactive only at temperatures well above ambient. Examples of elevated temperature getters are zirconium, titanium, thorium and uranium. These getters are particularly effective at temperatures above approximately 1,000° C.

Getters which operate satisfactorily at near ambient temperatures or below are barium, strontium, lithium and cesium, barium being the preferred getter. The invention will be described in terms of a barium getter, but it is to be understood that it is not intended to be limited thereby. Preferably, the barium getter is used in finely powdered pure form, although it may be supported on an extended-surface inactive carrier such as a zeolitic material, if so desired.

The theoretical capacity of barium getter for oxygen, nitrogen, and hydrogen are shown in Table I. The capacities are expressed in liters of gas at 0° C. and 1 micron Hg absolute pressure, and are calculated on the basis that the gases react with the metal getter to form barium oxide, barium nitride, and barium hydride, respectively.

TABLE I

Theoretical Capacity of 1 Mg. Barium Getter

Oxygen	liters	67.7
Nitrogen	do	45.1
Hydrogen	do	135.4

Barium will also getter other gases and vapors such as carbon dioxide, carbon monoxide, and water vapor.

How closely a given quantity of barium getter approaches the above theoretical capacities depends greatly on its physical form. An important requirement is a very large getter surface area exposed to the insulation space. Another requirement is a very thin section or thickness of getter metal beneath the getter surface. These features are needed in order to permit utilization of substantially all the barium metal introduced in the vacuum space, and to maintain a sufficiently high rate of gettering action throughout the life of the getter. If the metal is introduced in relatively large, fused particles, only the outer portion of the getter will react at a sufficiently high rate to be useful for maintaining a high vacuum.

A thin film of getter applied on a supporting base such

as an inert foil or powder is one form which provides a thin getter section. For example, a getter-coated or plated foil may be wound in a loose coil and sealed in the frangible capsule. Preferably, the getter coating is mossy in character so as to provide a large ratio of active metal surface area to volume. Alternatively, the getter may be vapor plated on an inert auxiliary powder such as finely divided silica.

The preferred form of the getter is a finely divided metal powder because the getter is readily prepared in this form and exhibits a large surface area with low cross-section. Such a powder exhibits very high gettering rates, and in tests it was found to permit effective utilization of up to 70% of the total getter introduced. Furthermore, the powdered getter is far more compact than supported types, since bulky supporting materials are eliminated.

A suitable powdered barium getter was prepared by vaporizing barium metal in an electrically heated section of a ceramic tube, and condensing the vapor while entrained in an inert gas stream in a cool section of the apparatus. The vaporizing barium was held in a molybdenum container to avoid contamination. A current of inert argon was used to entrain the barium vapor, and the solidified powder was then separated from the argon with a fabric filter, e.g. fiber glass cloth. The powder fell into a glass vial below the filter, and the vial was evacuated, sealed, and separated from the apparatus. The powder thus produced was found to have a density of .2 to .3 gm. per cubic centimeter, an average particle size of 150 to 250 Angstroms and a surface area of about 150 square meters per gram. By comparison, lamp black has a surface area of about 28 square meters per gram.

The quantity of getter required for a given vacuum insulation space will of course depend upon how tight the walls are made, and upon how well the insulation space and filler are degassed before exposing the getter. Using the normal care and precautions taken in fabricating high vacuum equipment, we have found that from 1–5 grams of powdered barium getter per 1,000 cu. in. of vacuum space gives good results. It will be recognized that theoretically there is not an upper limit to the amount of getter introduced. However, the quantity of getter should be minimized in the interests of economy, safety, and space.

As a feature of the invention, the barium getter material can be used in combination with an adsorbent material to achieve combined results which neither material could accomplish alone, thereby greatly extending the useful range of temperature and pressure conditions over which such materials can operate effectively. For example, we have found that the vacuum in a cylinder for storing liquid nitrogen is greatly improved by using both an absorbent and a getter. As seen from the following actually observed vacuums, the improvement of the combination of getter material and adsorbent material over the use of adsorbent alone is on the order of 100-fold with the container warm and 25-fold with the container cold.

TABLE II

	Pressure: Microns Hg Absolute		Pressure Sensitivity, $\frac{P_{warm}}{P_{cold}}$
	Container Warm, 70° F.	Container Cold, −300° F.	
Cylinder I: 5 A. Zeolite adsorbent only	6 (approx.)	0.1	60
Cylinder II: Barium Getter plus 5 A. Zeolite adsorbent	0.06	0.004	15
Improvement factor: Press. cyl. I, Press. cyl. II	100	25	

An important advantage for a combination of an adsorbent and a getter exhibited in the above Table II is that with the containers cold, the combination of getter material and adsorbent material produces a much lower absolute pressure. In cooling cylinder II from 70° F. to −300° F. the barium getter which was attached to the warm wall remained at 70° F. and was not affected. Therefore, the 15-fold improvement in vacuum from 0.06 to 0.004 microns was due to the adsorbent. Thus, it is apparent that a given quantity of adsorbent will reduce the pressure to a much lower value when a getter is present. This is attributed to mutual assistance between the adsorbent and the getter whereby the getter permanently removes the oxygen and nitrogen, thus reserving the capacity of the adsorbent for the removal of argon. Getter does not combine with argon and although argon constitutes only about 1% of air, this amount is very significant when very good vacuums are required.

The important effect of argon was demonstrated by a series of tests using powdered barium getter alone to remove traces of air from a vacuum space. A small sample of the active getter was exposed in a space of 3.7 liter capacity pre-evacuated to less than 1 micron Hg. Air was then admitted rapidly to the space until the pressure reached approximately 100 microns Hg, the space was sealed and an improved vacuum due to gettering was measured after about 30 minutes' time. Without re-evacuating the space, air was again admitted to a pressure of about 100 microns Hg, and the vacuum obtained by gettering was again measured. Four repetitions of this cycle produced final "gettered" vacuums of 1.1, 2.2, 3.2 and 4.5 microns Hg. This is a strong indication that the barium getter removes essentially all the constituents of air with the exception of the argon, for it is seen that in these tests an un-gettered gas accumulated in uniform steps, each step amounting to about 1% of the admitted air. The total amount of air involved in these tests was only 14.7 liters measured at room temperature and 100 microns of Hg. In actual container service, this amount of air may readily appear in a vacuum insulation space over an extended period of time, due either to minute leakage or to out-gassing from metals and insulating materials. Therefore, it is apparent that the use of a getter alone may eventually permit a significant amount of argon to accumulate, but by adding an adsorbent the argon is effectively controlled.

Another advantage in using a combination getter and adsorbent is that the ill effects due to temperature sensitivity of the adsorbent are greatly reduced. If a container of low temperature liquid is pressurized, its temperature rises, and an adsorbent in the insulation space will desorb due to warming. Without a getter, the insulation space pressure increases considerably which results in greater heat leak by gaseous conduction. This warms the liquid still more and causes further desorption in the insulation space. Thus, the rise in liquid temperature and the deterioration of the vacuum are self-promoting factors which accelerate a rising pressure in the storage compartment to the point that loss of valuable stored gas occurs through venting devices. To some extent, these ill effects can be reduced by increasing the amount of adsorbent installed in the vacuum space. However, the quantity needed to hold the absolute pressure below 0.1 micron of Hg during moderate increases in storage pressure would be excessive, and in a high quality insulation system may necessitate doubling the insulation space volume.

When the combination of a greater and an adsorbent is employed, any reactive gas released by the adsorbent when warm is quickly removed by the getter. Since the major portion of the gas appearing in the insulation space is reactive (e.g. oxygen and nitrogen), the increase in gaseous conductance is greatly reduced. Thus, when a getter is present, a relatively small amount of adsorbent holds the minor inert gas volume more securely so that pressurizing the stored liquid does not produce a serious effect on the vacuum. Furthermore, the temperature sensitivity of the adsorbent is turned to good advantage

for it permits the adsorbent to assist the getter by taking up minor traces of reactive gases when the vessel is in service and the adsorbent cold. Subsequently when the vessel is empty and the adsorbent relatively warm, it permits desorption of the reactive gases to the getter without undue pressure rise in the insulation space, thereby conserving the capacity of the adsorbent for the inert gases.

As shown in the drawing, an adsorbent container or blister **32** is preferably located against the cold wall **12** of cylinder **10**, and the getter chamber **28** is preferably associated with the warm wall **14**. In such locations, the gas removal rates and capacities will be maximum for both adsorbent and getter. The adsorbent may be silica gel or preferably, a zeolitic molecular sieve, either natural or synthetic, such as is disclosed in U.S. Patent No. 2,882,243 to R. M. Milton. Excellent performance is obtained with natural or synthetic zeolites having pores at least about 5 A. in size as disclosed in U.S. Patent No. 2,900,800 to P. E. Loveday. Preferred natural zeolites are faujazite, chabazite and erionite while preferred synthetic zeolites are sodium X and calcium A. A filter or screen **34** provided in the blister insures the retention of the adsorbent adjacent the cold wall, and prevents migration of insulating materials into the adsorbent blister.

It will be understood that modifications and variations may be effected without departing from the spirit and scope of the invention.

What is claimed is:

1. A thermal insulating structure comprising gas-tight walls enclosing an evacuable space; means for drawing a vacuum in such space; a capsule sealed from the atmosphere and an active metal powder getter material being active at ambient temperature and held in said capsule; gas communication means between said capsule and the gas-evacuated space so as to permit combination between the metal getter and reactive gases accumulating in such space.

2. A thermal insulating structure according to claim 1 including a compartment within said evacuable space, an adsorbent material being held in said compartment, and gas communication means between said compartment and the gas-evacuated space to permit removal of any non-reactive gases accumulating in such space by the adsorbent.

3. A thermal insulating structure according to claim 1 in which the evacuable space is at least partially filled with a solid low conductive insulating material.

4. A thermal insulating structure according to claim 1 in which the capsule is constructed of rupturable material, disposed within a chamber constructed of deformable material and sealed from the atmosphere, and arranged and constructed so as to maintain its seal after deformation and communicate with said gas communication means, said capsule being ruptured on said deformation so as to permit gas flow through said gas communication means.

5. A thermal insulating structure according to claim 1 in which said active metal powder getter material consists of at least one metal selected from the group consisting of barium, strontium, lithium and cesium.

6. A thermal insulating structure according to claim 1 in which said active metal powder getter material is barium.

7. A double-walled container comprising an inner product storing vessel and an outer gas-tight shell with an intervening evacuable insulation space therebetween; means for drawing a vacuum in such insulation space; a capsule sealed from the atmosphere and an active metal powder getter material being active at ambient temperature held in said capsule; gas communication means between said capsule and the gas-evacuated insulation space so as to permit combination between the metal getter and reactive gases accumulating in such space.

8. A double-walled container according to claim 7 including a compartment within said evacuable insulation space, an adsorbent material being held in said compart-

ment, and gas communication means between said compartment and the gas-evacuated insulation space to permit removal of any non-reactive gases accumulating in such space by the adsorbent.

9. A double-walled container according to claim 7 wherein the insulation space is at least partially filled with a solid, low-conductive insulating material.

10. A double-walled container according to claim 8 wherein the insulation space is at least partially filled with a solid, low-conductive insulating material.

11. A double-walled container according to claim 7 in which the capsule is constructed of rupturable material and disposed within a chamber constructed of deformable material and being sealed from the atmosphere, and arranged and constructed so as to maintain its seal after deformation and communicate with said gas communication means, said capsule being ruptured on said deformation so as to permit gas flow through said gas communication means.

12. A double-walled container according to claim 8 in which said active metal powder getter material consists of at least one metal selected from the group consisting of barium, strontium, lithium and cesium.

13. A double-walled container according to claim 8 in which said active metal powder getter material is barium.

14. A double-walled container according to claim 9 in which said active metal powder getter material is barium.

15. A double-walled container comprising an inner product storing vessel having a cold wall and an outer gas-tight shell having a warm wall with an intervening

evacuable insulation space therebetween; means for drawing a vacuum pressure in such space; an adsorbent containing blister adjoining said cold wall and in communication with said evacuable space for removal of non-reactive gases accumulating therein; a sealed, breakable active powder getter-containing capsule adjoining said warm wall, said getter being active at ambient temperature; gas communication means between said capsule and the evacuable insulation space; a sealed chamber constructed of deformable material enclosing said capsule and joining said gas communication means, the chamber being adapted to be sufficiently deformed while still maintaining its seal to break the capsule and thereby permit flow of accumulating reactive gases through said gas communication means for combination with the powder getter.

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