APPARATUS FOR THE MAINTENANCE OF LIQUEFIED PETROLEUM PRODUCTS AND METHOD OF MANUFACTURE THEREOF

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Fig. 1.

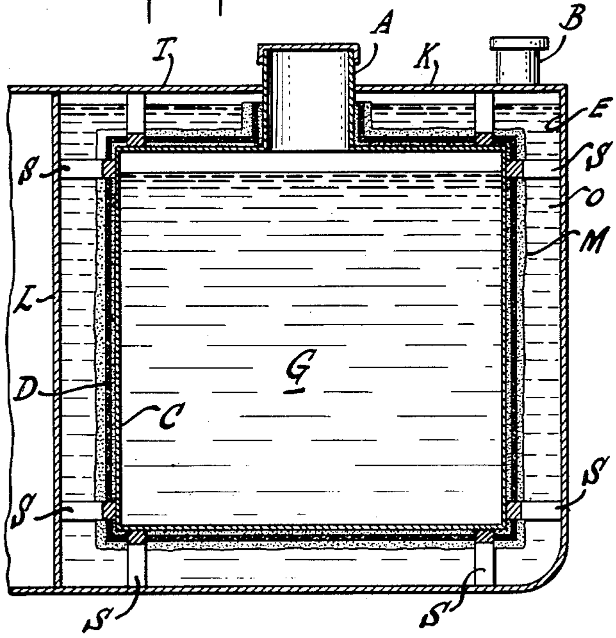


Fig. 2a.

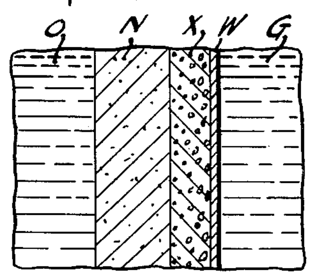


Fig. 2b.

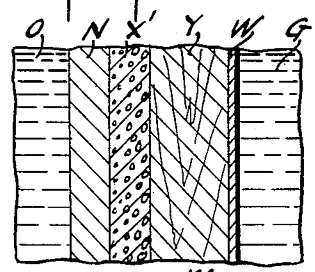


Fig. 3a.

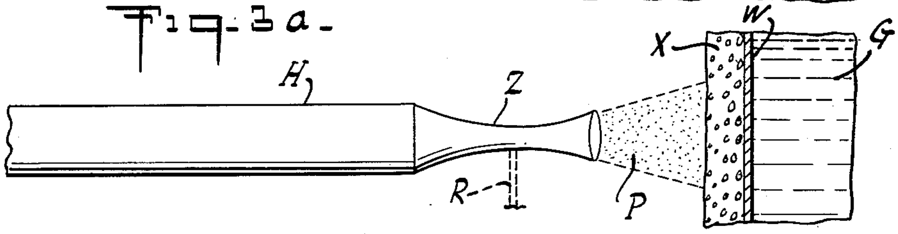


Fig. 3b.

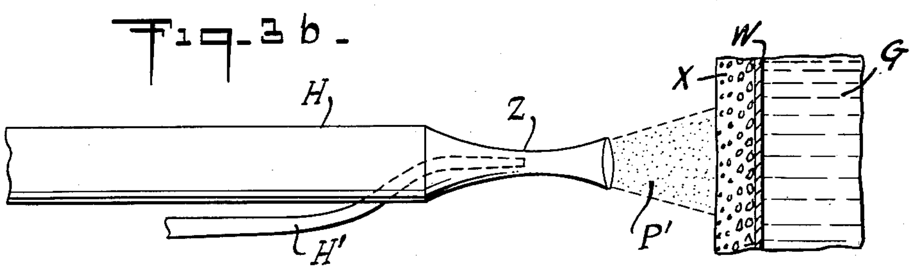
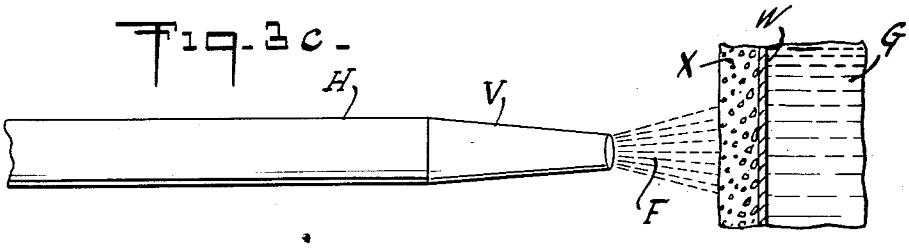


Fig. 3c.



United States Patent Office

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APPARATUS FOR THE MAINTENANCE OF LIQUEFIED PETROLEUM PRODUCTS AND METHOD OF MANUFACTURE THEREOF

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17 Claims. (Cl. 62—45)

This invention relates generally to low temperature insulation and specifically to a device for the maintenance of normally gaseous hydrocarbons in liquid condition, and the method of its manufacture. This device is adapted particularly for use with the invention disclosed in my copending application for patent, Serial No. 614,838, filed October 9, 1956.

In domestic petroleum production, utilization of large quantities of petroleum gases, including the butanes, propane, ethane and methane, is accomplished at nearby facilities, while the transportation of such gases from producing fields to relatively distance points is by transcontinental pipelines, to a great extent.

The shipment of liquefied petroleum gases for considerable distances is by containers which are built to withstand very high pressures. However, the cost of manufacture, due to the amount of material required, as well as the expense of transportation, of the heavy containers, restricts the shipment to closeby establishments. At the same time, the size of such containers is limited because of the maximum allowable metal wall thickness permitted without stress relief.

Other means for the transportation of liquefied petroleum gases at extremely low temperatures and at substantially atmospheric pressure have not proven successful in commercial operation and include the use of insulated tanks mounted on barges or in vessels, the tanks being considerably larger than the pressure containers and employing balsa wood for insulation. Because of the amount of such insulation required, both interior and exterior, the usable dimensions and hence the capacities of the tanks are reduced considerably. In addition, there is the danger of low temperature embrittlement of carbon steel tank walls which might occur should the insulation drop off and expose the walls to liquefied petroleum gas. In the absence of the use of high cost alloy steels for constructing the tanks, the shipment of liquefied petroleum gases is restricted by safety standards to the relatively heavier petroleum gases, such as the butanes and propane, which have the higher boiling points.

While it is known to transport and store liquefied gases, such as nitrogen and oxygen, in Dewar type containers consisting of spaced inner and outer receptacles, the problems involved in the construction of such type containers for the shipment of the large amounts of liquefied petroleum gas required to justify their economical transportation prevents the use of the same.

Accordingly, it is an object of the present invention to provide a new and improved apparatus in which liquefied petroleum gases may be shipped economically over long distances.

Another object of the invention is to provide a novel apparatus for storage and shipment of low temperature materials, the cost of which is negligible as compared with other means.

Still another object of the invention is to provide an economical device for the shipment of liquefied petroleum gases in which the dangers of construction failure are virtually eliminated.

And another object of the invention is to provide a novel method for producing an apparatus for the maintenance of normally gaseous hydrocarbons in liquid form.

These and other objects, advantages and feaures of the present invention will become apparent from the following description of the invention and by reference to the accompanying drawings wherein:

Fig. 1, disclosing a specific embodiment of the invention, is a partial diagrammatic view of a device for shipment of liquefied petroleum gases and is an elevation cross section taken through a cargo compartment of a tanker;

Figs. 2*a* and 2*b* are enlarged partial cross sections through the wall of a device such as in Fig. 1, showing the insulation of the liquefied petroleum gas container, and

Figs. 3*a*, 3*b* and 3*c* are diagrammatic views showing the manner of applying an initial layer of insulating material to the device.

In accordance with the illustrated embodiments of my invention, I employ a material having low thermal conductivity as an initial insulating layer around a container for a low temperature product which is surrounded by a petroleum product.

Referring to Fig. 1 of the drawing, disclosed as a partial diagrammatic view of a cross section through an ocean-going tanker, indicated as T, there is shown one of the separate cargo tanks K, formed by longitudinal and transverse bulkheads with the former indicated at L, and the outer shell E of the tanker. One or more of the cargo tanks contains a liquefied petroleum gas container, which may be either cylindrical, spherical, ellipsoidal or rectangular or some other geometrical figure defined by a surface of revolution and is indicated at C, immersed in and surrounded by the cargo of crude oil or a partially processed petroleum product such as fuel oil, O, carried in the separate cargo tanks K. These containers for the cargo of liquefied petroleum gas G are supported in spaced relationship to the walls defining the separate cargo tanks by appropriate composite spacer elements, as at S, formed of a steel member and a cap of wood or similar insulating material in contact with the container. The outlet for the container C is indicated generally at A and the access hatch for the petroleum product or oil cargo compartment is indicated at B, the cargo being discharged in the conventional manner through conduits leading to and from the pump room (all not shown).

The practice of the invention may include the build up from the cargo of an insulating deposit of a highly viscous material on the outer surface of the liquefied petroleum gas container C, this deposit including not only waxes contained in the cargo, but also other materials which cease to flow at low ambient temperatures and may include asphalt, grease and the like. In order to maintain this additional deposit in position adjacent the wall of the inner container, it is proposed to use foraminous support means, such as wire cloth, spaced from the inner container at a predetermined distance and may include a number of such support means as required by the cargoes carried in the inner container and the outer cargo tank. The deposit support means is shown at D, retaining the deposit of viscous material M in position.

In practice, the liquefied petroleum gas container is cooled at initial loading or after cleaning of the cargo tanks, by flash vaporization of the liquefied petroleum gas, compressing, condensing and recycling the evaporated gas in order to conserve the same, with the evaporation process reducing the temperature of the container C. In order to expedite the loading of liquefied petroleum gases which require very low temperatures in their containers, at times it is necessary to apply an initial insulating layer, e.g. a high melting point wax and/or asphaltic mix on the outer wall by mechanical means in order to provide immediate insulation from the cargo. This may be done either by spray application of a flowable mixture or by manual application of a paste mixture.

Figs. 2*a* and 2*b* disclose modifications of the insulating means by which the inner container C may be partially insulated prior to the utilization of the container for liquefied petroleum gases, the showing of the deposit support means being omitted for purposes of clarity. There is disclosed the wall W of the container C for liquefied petroleum gas G, upon which has been deposited a precalculated thickness of an initial insulating layer indicated as X. This initial insulating layer X on the wall W is made usually to expedite shipment, and once the voyage is under way, the automatic deposit of an additional insulating layer at N may continue as the cargo in contact with the initial layer X is cooled. This manner of initial insulation is most helpful where the pour point of the cargo O is so low that there must be a considerable flash evaporation at the start of the loading of the liquefied petroleum gas to deposit sufficient viscous material on the outer wall of container C to provide satisfactory insulation from the cargo.

Fig. 2*b* shows a modification of the embodiment of Fig. 2*a*, disclosing a wall W of a container for liquefied petroleum gas G, to which is attached externally a precalculated thickness of a layer of balsa wood Y, upon which is deposited a predetermined thickness of the initial insulating layer X'. As in the case of the structure in Fig. 2*a*, an additional deposit of viscous material N forms on the layer X' as the ambient temperature of the cargo O is lowered. This manner of insulation is to be used with liquefied petroleum gases having the lower boiling points and/or where the cargoes have lower pour points than those disclosed for use with the insulation construction of Fig. 2*a*. Alternatively, a layer of balsa wood or other insulating material may be attached to the inner wall surface for use with the modifications disclosed in Figs. 2*a* and 2*b*.

As the container C is cooled, a deposit begins to build up on the insulating layer on the outer wall in contact with the cargo. The thickness of this additional insulating deposit on the container C will build up automatically and adjust to the temperature of the liquefied petroleum gas container, with the deposit renewing itself automatically, should it be removed by violent movement of the cargo around the tank during the voyage of the tanker.

In some instances, it may be necessary to increase the wax content of the cargo so that a suitable thick insulating layer is deposited, and to aid in the depositing, some circulation of the cargo is helpful.

Figs. 3*a*, 3*b* and 3*c* illustrate different ways in which the initial insulating layer of low temperature insulation may be applied. In these ways, the insulating properties of wax and/or asphaltic material are improved so that the invention may be applied also to single wall installations such as storage tanks, refinery vessels, and the like.

It is well known that waxy and asphaltic hydrocarbon materials and bitumen have very low thermal conductivities. It is also well known that excellent insulating materials depend on small air cells to maintain low thermal conductivity. Several ways in which a cellular structure can be created in waxy or asphaltic hydrocarbon materials, thus making it equal, if not superior, to other known materials, in low temperature insulating properties, are illustrated in these figures.

Fig. 3*a* illustrates the manner in which waxy and/or asphaltic hydrocarbon material, heated above its melting point, is sprayed under pressure onto the wall to be insulated. The hose, H, ends in a convergent-divergent nozzle at Z, so that the foaming properties of waxy and asphaltic hydrocarbons entrap air as the molten material is sprayed onto the wall W to form the initial insulating layer indicated as X. If desired, an air inlet, shown dotted at R, can be provided at the vena contracta of nozzle Z to aspirate additional air. The thixotropic properties of the asphaltic materials will result in a low viscosity at high rates of shear throughout the nozzle and a high viscosity in the low shear conditions on the vessel wall. The importance of this property is to permit a fairly heavy layer of wax or asphaltic mixture to be sprayed onto the wall and hardened before start of running off the wall. The separation of the air bubbles from the fluid mixture will be reduced also. The cooling of the spray P in the air after leaving the nozzle Z will assist in preventing running and separation of the air bubbles.

As a variation of the method disclosed in Fig. 3*a*, the waxy or asphaltic hydrocarbon mixture used for the insulation could be mixed with a liquid refrigerant under pressure either in solution or emulsion form. When this material is sprayed, the refrigerant will vaporize and form vapor cells and the waxy or asphaltic material will be cooled immediately, so that a very thick layer of insulation can be applied in one operation with the vapor cells or spaces frozen in position. A number of gases at atmospheric conditions that can be liquefied under pressure include petroleum gases, sulfur dioxide, ammonia, and the non-toxic, incombustible, normal gaseous halogenated hydrocarbons known generally as Freons. Since the latter are the only ones in the group which are both non-toxic and incombustible, they may be used in restricted areas. It is to be noted that the thermal conductivity of Freon is about .0048 B.t.u./hr./ft./° F. compared to that of air of .014 B.t.u./hr./ft./° F.

Thus, insulation made with Freon vapor cells, produces an insulation considerably superior to any known which depend on still air thermal conductivity. Other refrigerants which have superior thermal conductivity values, as compared with air, produce comparable insulations.

In Fig. 3*b*, there is disclosed a means for the further improvement of the atomization of the waxy and/or asphaltic hydrocarbon mixture, which may or may not contain a refrigerant. Air or refrigerant is injected by the pipe H' into the restricted part or throat of the nozzle, and in addition to the venturi effect of the nozzle, the pressurized air or refrigerant, which is provided the spray P', results in the creation of additional cells or spaces to permit a thicker layer of high air or refrigerant content insulation with a single application. Known non-toxic refrigerants that could be used for atomization purposes, such as liquid carbon dioxide or liquid nitrogen, have too high a vapor pressure for mixing with a hot wax or asphalt. The disclosure of Fig. 3*b* shows how such cheap refrigerants can be used by injecting the refrigerant separately into the nozzle throat for atomization.

Fig. 3*c* discloses the means by which a flowable mixture may be used for application in the form of a thick spray or flowable paste F, with the hose H ending in a straight nozzle V. The flowable mixture yields a solid insulation of a silica gel (or foam glass) type mixed with a waxy or asphaltic hydrocarbon material in a slurry form, with the cells of entrapped air available for insulation and for additional structural strength in the asphaltic material. A common gelling agent mixed with the liquid wax or asphaltic hydrocarbon material prior to spraying in order to support the film while the wax is solidifying is Napalm, a sodium aluminum soap of palmitic acid, which imparts extreme thixotropic properties to the wax in its liquid state. Other agents include alkali metal salts of a relatively high molecular weight fatty acid (more than 7 carbon atoms) e.g. palmitic or stearic acid. A mixture of 5–10% of Napalm in a molten wax, along with a similar volume of liquefied gas, such as Freon, under pressure would provide an ideal means for applying a foam wax insulation. As soon as this mixture is ejected from any of the nozzles of Figs. 3*a*, 3*b* or 3*c* under pressure, the liquefied gas would tend to vaporize. Under the low shear conditions existing after the gelled material leaves the nozzle, the gel would have a high enough viscosity to hold the gas bubbles in suspension and avoid coalescing until the wax had solidified. The use of a gelling material will permit spraying a layer of insulation several inchs thick in a single application. Further, since the solubility of gases is lower in solid wax than in liquid wax, there would be a secondary formation of bubbles as the wax hardens. Since thermal conductivity of Freon gas is approximately ⅓ that of air, it becomes possible to create an insulation approaching ⅓ the thermal conductivity of silica gel or ⅕ that of balsa wood.

In addition, should this mixture be used for insulation at extremely low temperatures, there would be a tendency for the Freon gas to condense and form a partial vacuum in the vapor spaces. If the majority of large vapor spaces collapse, the smaller diameter vapor spaces would have sufficient structural strength to sustain a partial vacuum, thus leading to a vastly superior insulation based on partially evacuated cells or spaces. Such a phenomenon of creating a partial vacuum might be utilized in construction of silica based insulations having higher structural strengths.

Thus, there has been disclosed a device and method of its construction wherein the cost of low temperature insulation is negligible as compared with other similar insulation. In almost all the remote producing areas where low priced liquefied petroleum gases would be available, there also would be available crude oil or processed petroleum products for transportation to the consumer markets, so that the disclosed apparatus would be attractive economically.

The initial insulating layer formed and retained on the liquefied petroleum gas container, while increasing the dead weight of the tanker, is not particularly objectionable, since the liquefied petroleum gas carrier would have such a low bulk density that some ballast would be required.

The natural corrosion inhibition and water impermeability properties of wax and/or asphaltic materials are advantageous in normal painting procedure, since a cheap permanent insulation coating would no longer require removal for inspection. Thus, the cargo space surrounding the liquefied petroleum gas containers C can be used for water ballast service as required on the return voyage. The fire hazard in the use of asphaltic materials at low temperatures is almost nil since the flash point of these materials is in the range of 400–500° F. or higher and increases with gradual air oxidation.

Should there be a structural fault in the liquefied petroleum gas container C which allows leakage of the cargo inwardly, with the external static pressure of the cargo surrounding the liquefied petroleum container exceeding that of the internal pressure in the container, the leaks would tend to be self-sealing by the formation of deposits of wax or the like.

Although the foregoing description has been directed to the use of my invention for the transport of liquefied petroleum gas in an ocean-going tanker, it can be adapted quite readily to permanent shore installations for storage purposes and can be used in railroad tank cars for transport purposes. Furthermore, the invention is not limited to usage with liquefied hydrocarbons but is applicable also to the storage, transport and usage of gases in a low temperature, liquefied state including hydrogen, oxygen, nitrogen, ammonia and other common gases.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. An apparatus for maintaining a normally gaseous hydrocarbon in liquefied form comprising the combination of inner and outer receptacles and means for supporting and maintaining the inner receptacle in spaced relationship with the outer receptacle, said outer receptacle being subjected to atmospheric pressure and containing a petroleum product having low heat transmission characteristics and a material with low thermal conductivity which is deposited therefrom as the ambient temperature thereof is decreased, said inner receptacle being adapted to receive a low temperature liquefied gas whereby the ambient temperature thereof and adjacent the outer wall of said inner receptacle is lowered to cause a deposit of said material from said petroleum product to form thereon concomitantly with the presence of said low temperature liquefied gas in said inner receptacle, said inner receptacle being provided with a deposit thereon of an outer insulating layer of cellular construction including waxy and asphaltic hydrocarbons.

2. In the apparatus as defined in claim 1, said cellular construction having spaces containing entrapped air, gaseous hydrocarbons and refrigerants including ammonia, carbon dioxide, nitrogen, sulfur dioxide, Freons and liquefied petroleum gases.

3. In an apparatus as defined in claim 2, said petroleum product surrounding and adjacent said layer of cellular construction deposited on the outer wall of said inner receptacle having tendencies to form a deposit of wax and other viscous material thereon as the ambient temperature surrounding said inner receptacle is lowered.

4. An apparatus as defined in claim 3, wherein said inner receptacle has foraminous support means spaced from the outer wall surface thereof for retaining material deposited thereon.

5. In an apparatus as defined in claim 3, said petroleum product being enriched as required with material desired to be deposited.

6. In a combination of spaced inner and outer receptacles wherein a liquefied petroleum gas is shipped in the inner receptacle and a petroleum product containing a material having a pour point above the temperature of said liquefied petroleum gas is maintained between said receptacles, insulating means for the outer wall surface of said inner receptacle comprising a deposit of an inner insulating layer of cellular carbonaceous material and an outer insulating layer of material deposited thereon from said petroleum product as the ambient temperature adjacent said inner insulating layer is lowered, the cells of said carbonaceous material comprising said inner insulating layer containing a suitable gaseous medium such as ammonia, carbon dioxide, nitrogen, sulfur dioxide, air, carbon tetrachloride, liquefied petroleum gases and Freon.

7. In the combination as defined in claim 6, said inner insulating layer being spaced from said outer wall surface of said inner receptacle by a predetermined thickness of an insulating material having low heat conducting properties such as balsa wood.

8. In the combination as defined in claim 6, said inner receptacle having a layer of insulating material attached to the inner wall surface thereof.

9. In the combination as defined in claim 6, said cellular carbonaceous material being taken from the class including waxy hydrocarbons, asphaltic hydrocarbons and bitumen.

10. In the combination as defined in claim 9, said carbonaceous material being admixed with a solid cellular material such as silica gel or glass foam and a gelling agent such as a salt of a high molecular weight fatty acid.

11. The method of manufacture of a device for the maintenance of a normally gaseous hydrocarbon in liquid state which comprises the provision of an inner container for the reception of the liquefied hydrocarbon, the provision of an outer container held in spaced relationship thereto for the reception of a petroleum product containing material subject to deposition as the am-

bient temperature thereof is lowered, and the provision of an initial insulating layer of cellular construction obtained by spraying carbonaceous material onto the outer wall surface of said inner container, said carbonaceous material being taken from the class comprising waxy hydrocarbons, asphaltic hydrocarbons and bitumen.

12. In the method as defined in claim 11, said spraying including the entrainment of air as said carbonaceous material passes through a convergent-divergent nozzle.

13. In the method as defined in claim 12, said spraying including the entrainment of a refrigerant at the throat of said nozzle.

14. In the method as defined in claim 11, said carbonaceous material including a salt of a high molecular weight fatty acid as a gelling agent.

15. In the method of forming an initial layer of insulation on the surface of a container for a low temperature product, the steps of mixing a carbonaceous material with a solid cellular material such as silica gel or foam glass and a salt of a high molecular weight fatty acid such as Napalm to obtain a thixotropic mixture and applying the same through a nozzle.

16. In the apparatus as defined in claim 1, said low temperature liquefied gas being chosen from the group including hydrogen, oxygen, nitrogen, ammonia and hydrocarbon containing gases.

17. In the method as defined in claim 13, said refrigerant being taken from the class comprising sulfur dioxide, carbon dioxide, nitrogen, ammonia, petroleum gases and Freon.

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