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3,526,095

LIQUID GAS STORAGE SYSTEM

Filed July 24, 1969

2 Sheets-Sheet 1

FIG. 1

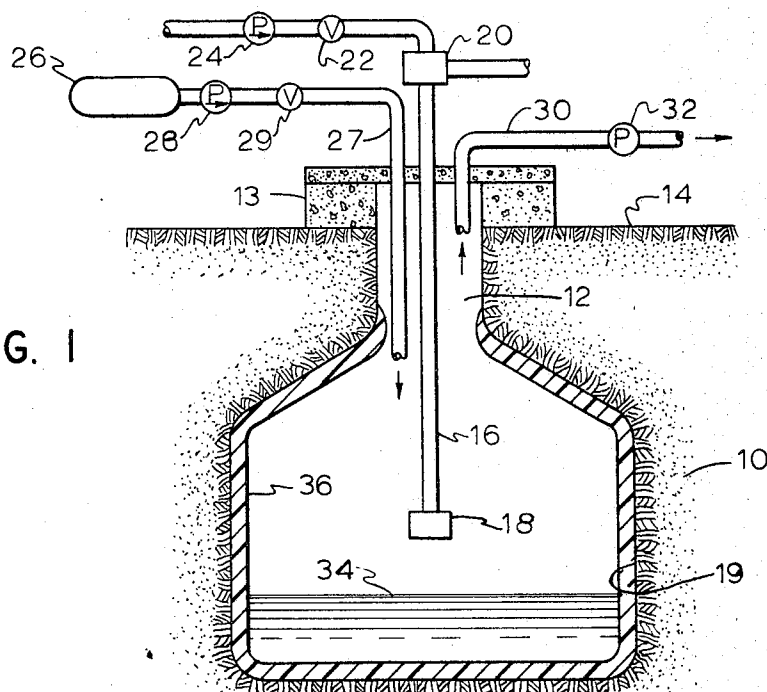
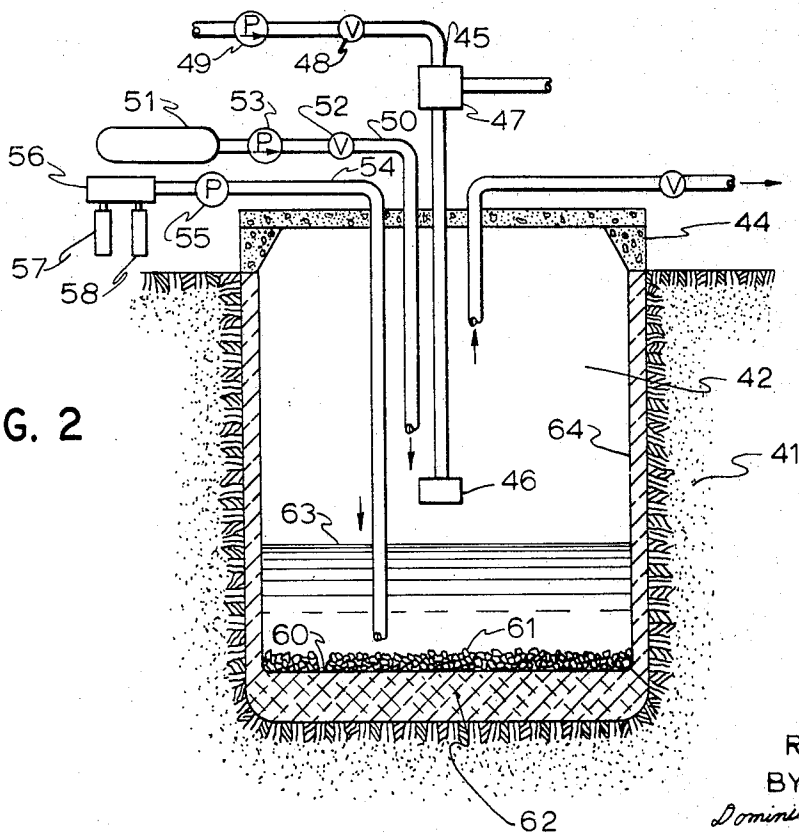


FIG. 2



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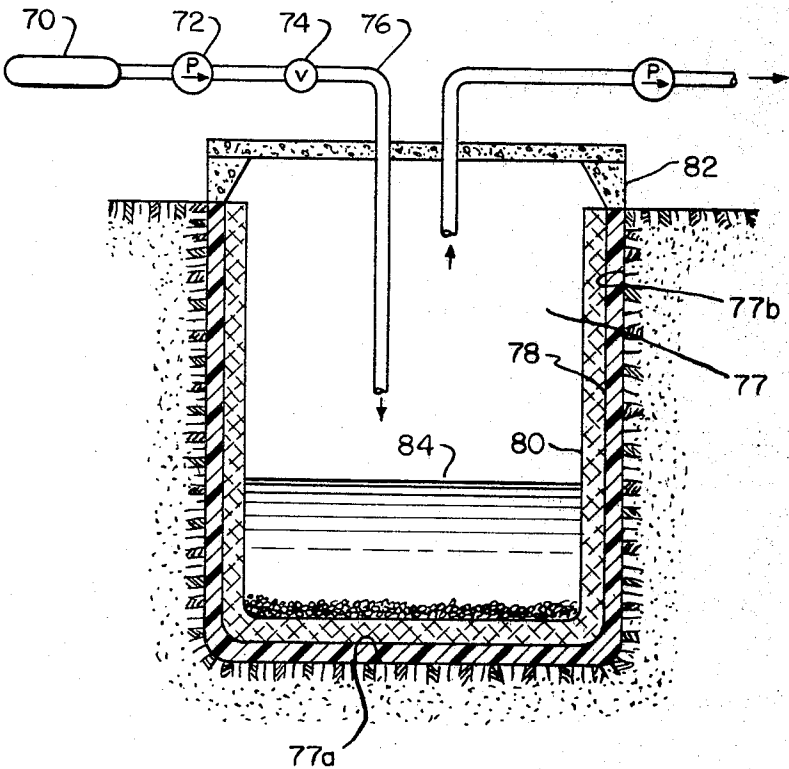
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2 Sheets-Sheet 2

FIG. 3



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LIQUID GAS STORAGE SYSTEM

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Continuation-in-part of application Ser. No. 739,520,
June 24, 1968. This application July 24, 1969, Ser.
No. 845,940

Int. Cl. B65g 5/00

U.S. Cl. 61—5

17 Claims

ABSTRACT OF THE DISCLOSURE

A system and method for storing liquefied gases in chambers. The walls of the chamber are coated with a petroleum fraction which is at least partly a liquid at room temperature, and which boils at temperatures below levels which would obtain petroleum oils. The petroleum fraction may be a mixture of such liquid hydrocarbons and heavier hydrocarbons applied to the walls of the chamber and solidified to a non-brittle, wax-like state after charging the chamber with a liquefied gas having temperatures which are sufficiently low to flexibly solidify said petroleum fraction.

This invention relates to a storage system for liquefied gases, and to a method for conditioning chambers to store liquefied gases in an improved manner.

This application is a continuation-in-part of U.S. patent application, Ser. No. 739,520, filed June 24, 1968 by the applicant named herein, and now abandoned.

Subterranean chambers of various formations have been employed for storing liquefied gases such as liquefied natural gas, liquefied petroleum paraffins, anhydrous ammonia and other liquefied gases. The art has been principally concerned with utilizing such underground storage chambers for liquefied natural gas and for petroleum gases.

The use of the term "chamber" is intended to refer to above ground and below ground storage systems, as well as in-ground systems. Such systems may include tanks installed above ground, and tanks partially or totally within the ground, that is, inground tanks. The use of the term "subterranean chambers" is intended to refer to various below ground storage systems, such as naturally present caverns or vaults in salt formations, and excavations or mines such as strip or pit type mines. Such mines may be formed in various ground formations which may be water bearing, or impermeable shale or limestone formations.

A subject of concern in this art is the heat transfer or heat leak due to fissures, cracks or other ruptures in the wall of the cavern or chamber. Heat leak is detrimental to retaining volumes of liquefied gases originally deposited in the chambers. Such boiloff losses can be serious.

The art has recognized that means should be provided to seal these ruptures to prevent or reduce the boiloff losses due to heat leak. Many attempts to seal such ruptures have involved complex or expensive procedures which, additionally, have not been characterized by the degree of success which is desired by practitioners. One particular approach which has presented some attraction utilizes the low temperature of a liquefied gas to freeze liquids into a solid form to seal the ruptures. Another approach involves freezing water which is naturally present in ground formations, or freezing water which is added to ground formations. This technique is not without problems because it is difficult to control the amounts of distribution of the water itself has some walls of the chamber, and frozen water itself has some objectionable features as a sealant.

It is accordingly one object of the invention to provide a system and method for effectively sealing above ground, inground and below ground chambers by relatively simple and economical means to provide improved storage.

Another important object is to provide a system and method whereby chambers are conditioned in an improved manner to provide improved storage means for liquefied gases, such as liquefied natural gas.

Yet another important object is to provide a system and method in which improved coatings, provided on the interior walls of a chamber, are particular liquid petroleum fractions which can be conveniently provided as liquids and which can be easily and advantageously converted to effective sealants by the low temperatures of liquefied gases.

A still another object is to provide a system and method whereby a heavier, viscous petroleum fraction of mixed hydrocarbons is used to provide improved coatings for upright walls in a storage chamber, with or without porous thermal layers.

Still another important object is to provide a system and method whereby particular petroleum fractions are advantageously used to coat and seal the interior walls of a chamber by forming coating layers which are hard but yet free from objectionable brittleness.

A still further object is to provide a system and method which includes porous thermal layers and solidified petroleum fractions in a chamber to thereby store liquefied gases with reduced boiloff losses from heat leak.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

Objects such as those recited are accomplished with the system and method of the present invention which, generally, contemplates coating the walls of a chamber with a petroleum fraction which includes at least partly a liquid at room temperature and atmospheric pressure, such liquid boiling at temperatures below levels which would obtain petroleum oils in fractional distillations. The applied petroleum fraction is solidified to a non-brittle, wax-like state after charging the chamber with a liquefied gas, which temperature is sufficiently low to harden said petroleum fraction.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings in which:

FIG. 1 is a highly diagrammatic sectional view illustrating an underground system for storing liquefied gases, and the method for providing such a system;

FIG. 2 is a highly diagrammatic sectional view similar to FIG. 1, but which illustrates an alternative embodiment of the storage system; and

FIG. 3 is a highly diagrammatic sectional view which illustrates an alternative embodiment in which a petroleum fraction is in the form of a viscous mixture for better adherence to upright walls of a chamber.

For purposes of illustration, the description will make particular reference to conditioning underground chambers, but such description could likewise apply to various above ground and inground installations.

The invention generally provides for sealing the interior walls of subterranean chambers, by introducing a petroleum fraction into the chamber to coat the walls therewith. The petroleum fractions may be an easily handled liquid hydrocarbons at room temperature which is thereafter solidified on the walls by low ambient temperatures within the chamber. The low temperatures are attained by the liquefied gases introduced into the chamber, which temperatures are preferably at least about -150° F. The particular petroleum fractions employed,

which are solidified to effectively seal the ruptures, are not characterized by features which would detract from the recommended use thereof. In particular, the solidified petroleum fraction has a characteristic resembling that of a wax and is, therefore, non-brittle. A very hard coating would be brittle and would be subject to substantial cracking which would understandably detract from the advantages obtained in the sealing step.

In one form, the petroleum fraction is of the type that is a liquid at room temperature and atmospheric pressure, but which is not an oil or a heavy or a viscous material. The heavier petroleum fractions alone do not operate in the preferred and advantageous manner. In general, the utilizable petroleum fractions boil between 70° F. and 600° F. A particularly useful petroleum fraction is gasoline which boils at atmospheric pressure between about 100° F. and 230° F.; and kerosene which boils between about 350° F. and about 600° F. The petroleum hydrocarbon fractions obtained in later distillation steps, such as coal oil and light lubricating oils, are characterized by a decrease in desirable properties in the solidified state. Such undesirable properties increase at an accelerated rate when the petroleum fraction becomes heavier, such as the higher viscosity oils or residue oils.

The heavier and higher viscosity oils or residue oils, however, are usefully applied in admixture with the foregoing liquid hydrocarbon petroleum fractions. Such a mixture is used to advantage particularly in application of the petroleum fraction to upright walls. The heavier hydrocarbon component imparts better retention of the mixture to upright walls, that is, walls positioned so that gravity tends to make materials deposited therein to fall. The lighter liquid hydrocarbons, such as gasoline, imparts desirable sealing properties to the mixture when the mixture is solidified by the liquid gas. In the preferred practice, the mixture is applied to the upright walls, and then the mixture is covered with a porous thermal or insulating layer, such as foamed urethane. The thermal layer contributes to retaining the mixture on the wall and to improving insulation of the chamber. After the liquid gas is introduced, such thermal layer tends to shrink, but the properties of the solidified mixture is sufficiently flexible to stay in the walls. Heavy hydrocarbons, as such, would become embrittled when solidified, and the resultant ruptures would seriously detract from the desired levels of sealing.

The petroleum fraction mixture preferably contains a solid hydrocarbon, by which is meant, a material which pour point is preferably greater than room temperature, or about 68° F. A hydrocarbon of such viscosity provides better retention following application to the upright walls. The liquid hydrocarbon has a boiling point range as previously described, namely, about 100° F.-600° F., with the majority of components containing no more than six carbons. The major portion of such components will generally be of the C₅-C₆ type. It is preferred that such liquid hydrocarbons remain a liquid at temperatures slightly below the temperature of the liquid gas introduced into the chamber. For example, gasoline is a liquid at -240° F. but solidified when LNG, which boils at -260° F., is introduced into the chamber.

The liquid hydrocarbon may be present in the mixture from about 10% to about 40% by weight. In general, a higher amount of a given liquid hydrocarbon is present if the chamber is made progressively more cold. The temperature of the chamber is determined, of course, by the boiling point of the liquid gas and the volume of liquid gas deposited in a chamber. The mixture is, therefore, a combination of the heavier petroleum fraction, preferably solid, and the foregoing liquid petroleum fractions. It will be understood that the practitioner may utilize various combinations of the heavier hydrocarbons and the liquid hydrocarbons to attain advantages of the

invention, although the foregoing types of combinations are better suited for application to the upright walls.

The liquefied gases which are introduced into the subterranean chambers have temperatures sufficiently low to solidify the described petroleum fractions. Liquefied natural gas or LNG boils at about -259° F., ethylene boils at about -155° F. and propylene boils at about -54° F. It is therefore seen that the liquefied gases have temperatures at least as low as about -50° F. However, it is preferred to attain ambient temperatures within the chamber or about at least -150° F. to quickly and efficiently solidify the petroleum fractions of the type described. To illustrate a particular embodiment, kerosene, which starts to boil at about 350° F., is a flowable liquid at room temperature and solidifies to the consistency of wax at about -260° F. when liquefied natural gas is introduced into the subterranean chamber.

The process of conditioning the subterranean chamber for storing liquefied gases provides that the selected petroleum fraction is introduced into the chamber, and then applied against at least a major area of the internal walls of the chamber. The petroleum fraction, which is a relatively economical material, may be introduced in a variety of ways, such as filling the cavern and then exhausting the excess liquid petroleum fraction by suction pumps or the like. The interior walls of the chamber may also be coated by spraying the selected petroleum fraction in a pressurized stream against the walls until such walls are desirably coated. The mixture of heavier and liquid hydrocarbons may be applied by troweling on the upright walls, heating to lower the viscosity and then spraying, and in still other ways.

The petroleum fraction which is applied to the walls is then solidified by introducing into the chamber the liquefied gas which will be stored in that chamber. The temperature of the liquefied gas is, of course, sufficiently low so that the ambient temperature within the chamber is low enough to solidify the petroleum fraction coated on the walls. Practitioners will appreciate that a more rapid solidification with lower ambient temperatures will be obtained by introducing greater volumes of the liquefied gas into chamber of a given volume. It will be further appreciated that liquefied gases with lower boiling points need be present in smaller volumes than liquefied gases having higher boiling points to attain a desired ambient temperature for solidification.

Referring to the diagrammatic representation of FIG. 1, a subterranean chamber formed as a natural cavern is indicated at 10. A shaft 12 communicates the chamber with the area above ground surface 14. A concrete superstructure 13 is shown closing the shaft opening. A line 16 is shown for delivering a petroleum fraction, which is liquid at room temperature, under pressure to a spray head 18 which may deliver the petroleum fraction in a circular spray pattern. Such a spray head may be rotatable to centrifugally eject streams or droplets of the petroleum fraction onto the walls 19 of the cavern. A box is shown at 20 for housing means to raise and lower line 16 so that a pressurized stream of the petroleum fraction, which is discharged from the end of line 16, may coat upper and lower portions of the cavern walls. Valve means are shown at 22 to control the flow, and a pump is indicated at 24 to deliver the petroleum fraction from a source (not shown) at selected pressure levels.

Liquefied natural gas is adapted to charge the cavern from a source 26 through a line 27. Pump and valve means are shown at 28 and 29, respectively. The liquefied natural gas may be discharged or withdrawn from the cavern through line 30 under the force of means such as a pump indicated at 32. In the illustrated embodiment, the liquefied natural gas is shown pooled at the bottom of the cavern at 34 and the petroleum fraction is shown solidified as the layer or coat 36 on the walls of the cavern.

The storage system may be constructed by initially depositing a porous thermal layer in the cavern against

at least a portion of the walls thereof. Such a porous thermal layer will, of course, have insulating properties which advantageously help to retard heat transfer into the cavern. Such a porous thermal layer may be deposited in the cavern and impregnated with the liquid petroleum fraction before introducing the liquefied gas to solidify the petroleum fraction. The remaining portions of the cavern walls may then be coated in a variety of ways, followed by introducing the liquefied gas in sufficient volumes to lower the ambient temperature in the chamber to solidify the petroleum fraction on the walls. The porous thermal layer may take many recognized forms and may include aggregates of prefoamed polyurethane or polystyrene particles blown into and against the floor of said cavern as a roll or in a collapsed form, and then extended against the floor of the cavern. Also, curable synthetic resin mixtures may be introduced as a fluid into the cavern and then cured in situ.

Referring to FIG. 2, the subterranean chamber is shown as an excavated strip mine or pit 41, and the communication with the ground level 43 is indicated as the upper part 42 of the strip mine. A superstructure 44 covers the shaft opening or the top of the strip mine. A petroleum fraction charging line 45 is shown with a spray head 46, box 47 to lower and raise the line valve control means 48 and pump 49, similarly as in FIG. 1. A liquefied natural gas line 50 conveys liquefied natural gas from a reservoir 51. The line is provided with valve control means 52 and pump 53.

A further line 54 conveys a curable synthetic resin mixture under the force of a pump 55. The resin mixture is delivered from a mixing container 56 which receives the flowable resin from communicating container 57 and further receives a chemical hardener from another communicating container 58. The resin may be an isocyanate and the hardener may be a diamine. The pot life mixture is dispensed upon the floor of the strip mine, whereupon it cures to form a foamed porous layer 60. If the foamed porous layer does not adhere to the floor of the strip mine, or if a prefoamed synthetic layer is placed on the floor of the strip mine, anchoring weights such as gravel 61 is dropped through the communicating shaft to hold the porous thermal layer on the floor.

The porous thermal layer is then impregnated with the petroleum fraction, which impregnant is diagrammatically indicated as at 62. The bottom of the strip mine is then flooded with the liquefied gas to solidify the impregnant and partially cool the pit. The walls of the strip mine are then coated with the petroleum fraction, after which, the mine is charged with a liquefied natural gas 63. The cold ambient temperature within the strip mine will then solidify the petroleum fraction into a waxlike coat 64 to efficiently seal the cavern and protect the deposited liquefied gas against undesirable boiloff losses through heat leak.

FIG. 3 illustrates an embodiment wherein a petroleum fraction is a mixture containing 10% by weight of gasoline in a solid hydrocarbon which has a pour point at about 85° F. The mixture is applied to the upright walls of a pit mine. A source of liquid gas 70 is urged through pump 72 and valve 74 through line 76 into the chamber. The floor or bottom wall 77a and upright walls 77b of the chamber 77 are covered with the petroleum fraction mixture 78 which may be applied by manual troweling, or by equivalent mechanical means. A thermal layer 80 is cut to fit the floor and upright walls, and pressed against the mixture. The concrete superstructure 82 is mounted with gas inlets and outlets and LNG is introduced until a desired level 84 is deposited. The LNG solidifies the petroleum fraction 78 which retains sufficient flexibility to provide improved sealing. Such sealing is enhanced by the porous thermal layer 80. Other means may be selected to introduce the mixture, such as an angularly extensible conduit with an extruder which may be positioned proximate to the walls. The heavy mixture may be

applied to the walls by the extruder moving over substantially the total area of such walls. Further, the mixture may be heated to render same more flowable, and then introduced through a conduit with an affixed spray head. The viscosity of the mixture will increase as it cools on the walls to enhance retention thereof, particularly on upright walls.

It is required that the sealant not be solidified into a very hard physical state because ruptures will develop in the coat as a result of brittleness. The prescribed petroleum fraction may be conveniently handled for application and also can be solidified to the desired non-brittle state. If in a particular system or method, a given petroleum fraction tends to solidify to an undesirable degree of hardness, then the practitioner may add paraffins such as propane or butane to soften the solidified petroleum fraction. The actual concentration of a particular paraffin in a given petroleum fraction will depend on the degree of hardness desired by the practitioner. The practitioner will readily make such determination in view of the nature of the petroleum fraction employed, and the ambient cooling temperatures which are expected to be attained in the subterranean chamber. The amount of the particular paraffin which will be added to a given volume of a petroleum fraction may be readily determined on a small scale pilot level or in actual field conditions.

The advantages of the system and method may be illustrated by considering the filling of a cavern having a substantially cylindrical configuration, said cavern having a diameter of about 135 feet and a depth of about 180 feet. The walls of the chamber are covered with a liquid petroleum fraction and the floor of the chamber is provided with a porous thermal layer of about ten inches in thickness. The thermal conductivity of the ground formation may be considered as being about 2.3 B.t.u. per hour, per foot. Adding liquefied natural gas to the chamber at the rate of about 18,000,000 cubic feet per day would lead to the filling of the chamber in about 125 days. Maintaining the chamber filled for about 110 days reduces the boiloff loss from about 7,500,000 cubic feet per day to about 5,070,000 cubic feet per day. By the fourth year, the boiloff loss falls to a level of about 3,700,000 cubic feet when maintaining the cavern at full levels. If the chamber is not conditioned according to the teachings of this invention, the chamber is not expected to be filled within one year because of boiloff loss. In general, the boiloff would increase several fold without the pretreatment or conditioning, say two to three times the foregoing estimated levels.

The invention may now be practiced in the various ways which will occur to practitioners, and all such practice is intended to comprise a part of the invention so long as it comes within the terms of the appended claims which are given further meaning by the language of the preceding specification.

What is claimed is:

1. A system wherein liquefied gas is storable in a chamber, said system including a flexibly solidified petroleum fraction substantially coating the interior walls of said chamber said petroleum fraction at least including a minor portion of a hydrocarbon which is a liquid at room temperature and at atmospheric pressure, said hydrocarbon liquid boiling at temperatures from about 100° F. to about 600° F., and a charge of liquefied gas in said chamber which provides an ambient temperature in the chamber sufficiently low to have solidified said petroleum fraction.

2. A system as in claim 1 wherein the liquefied gas is liquefied natural gas in an underground chamber.

3. A system as in claim 1 wherein the petroleum fraction is gasoline boiling from about 100° F. to about 230° F. at atmospheric pressure.

4. A system as in claim 1 wherein said petroleum fraction is kerosene boiling between about 350° F. to about 600° F. at atmospheric pressure.

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5. A system as in claim 1 wherein said petroleum fraction is present as a solid layer over substantially the entire interior walls of the chamber, and said solid layer is maintained at the general consistency of wax by ambient temperatures of at least about -150°F .

6. A system as in claim 1 wherein there is further included a porous thermal layer in proximate location to a portion of the interior walls of a subterranean chamber, and said porous thermal layer being charged throughout a substantial portion thereof with said solid petroleum fraction.

7. A system as in claim 1 wherein the petroleum fraction is a mixture of a heavy hydrocarbon having a pour point greater than room temperature, and from about 10% to about 40% by weight of a liquid hydrocarbon boiling between about 100°F . and 600°F .

8. A system as in claim 7 wherein said petroleum fraction mixture is applied at least to the upright walls of the chamber, and further including a porous thermal layer covering said applied mixture.

9. A method for conditioning a chamber so that said chamber may be used to store liquefied gases, including the steps of delivering a petroleum fraction into said chamber, applying said petroleum fraction to the interior walls to substantially coat said walls, said petroleum fraction at least including a minor portion of a hydrocarbon which is a liquid at room temperature and atmospheric pressure, said liquid hydrocarbon boiling at temperatures of about 100°F . to about 600°F ., and charging said chamber with a liquefied gas having a temperature sufficiently low to flexibly solidify said petroleum fraction and thereby seal said walls.

10. A method for conditioning a chamber as in claim 9 wherein the gas is liquefied natural gas in an underground chamber.

11. A method for conditioning a chamber as in claim 9 wherein the petroleum fraction is entirely a liquid at room temperature and atmospheric pressure, said hydrocarbon fraction being applied to substantially the entire area of the chamber walls.

12. A method for conditioning a chamber as in claim 11 wherein said petroleum fraction is gasoline which

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boils at atmospheric pressure from about 100°F . to about 230°F .

13. A method for conditioning a chamber as in claim 11 wherein said liquid petroleum fraction is kerosene boiling at atmospheric pressure from about 350°F . to about 600°F .

14. A method for conditioning a chamber as in claim 11 which further includes the step of first depositing a porous thermal layer on the floor of said chamber, impregnating said porous thermal layer with said petroleum fraction, delivering said petroleum fraction to coat any remaining areas of the chamber walls, and then charging said chamber with a liquefied gas to solidify the petroleum fraction in said porous thermal layer.

15. A method for conditioning a chamber as in claim 11 which further includes applying said liquid petroleum fraction to at least a portion of the chamber walls, and then mounting a porous thermal layer to said applied petroleum fraction prior to charging said chamber with said liquefied gas.

16. A method for conditioning a chamber as in claim 9 wherein said petroleum fraction is a mixture of a heavy hydrocarbon having a pour point greater than room temperature, and from about 10% to about 40% by weight of said liquid hydrocarbon, and wherein said mixture of heavy hydrocarbon and liquid hydrocarbon is applied to at least the upright walls of the chamber.

17. A method for conditioning a chamber as in claim 11 which further includes the step of covering said applied mixture with a porous thermal layer.

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U.S. Cl. X.R.

62—45; 166—302; 175—17

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,526,095

Dated September 1, 1970

Inventor(s) Ralph E. Peck

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

LIQUID GAS STORAGE SYSTEM

Ralph E. Peck, Chicago, Ill., assignor to Gas Developments Corporation, Chicago, Ill., a corporation of Illinois
Filed July 24, 1969, Ser. No. 845,940
17 Claims.

**SIGNED AND
SEALED
NOV 1 1970**

NOV. 17, 1970

(SEAL)

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Commissioner of Patents