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MAINTAINING CONSTANT COMPOSITION IN A VOLATILE MULTI-COMPONENT LIQUID

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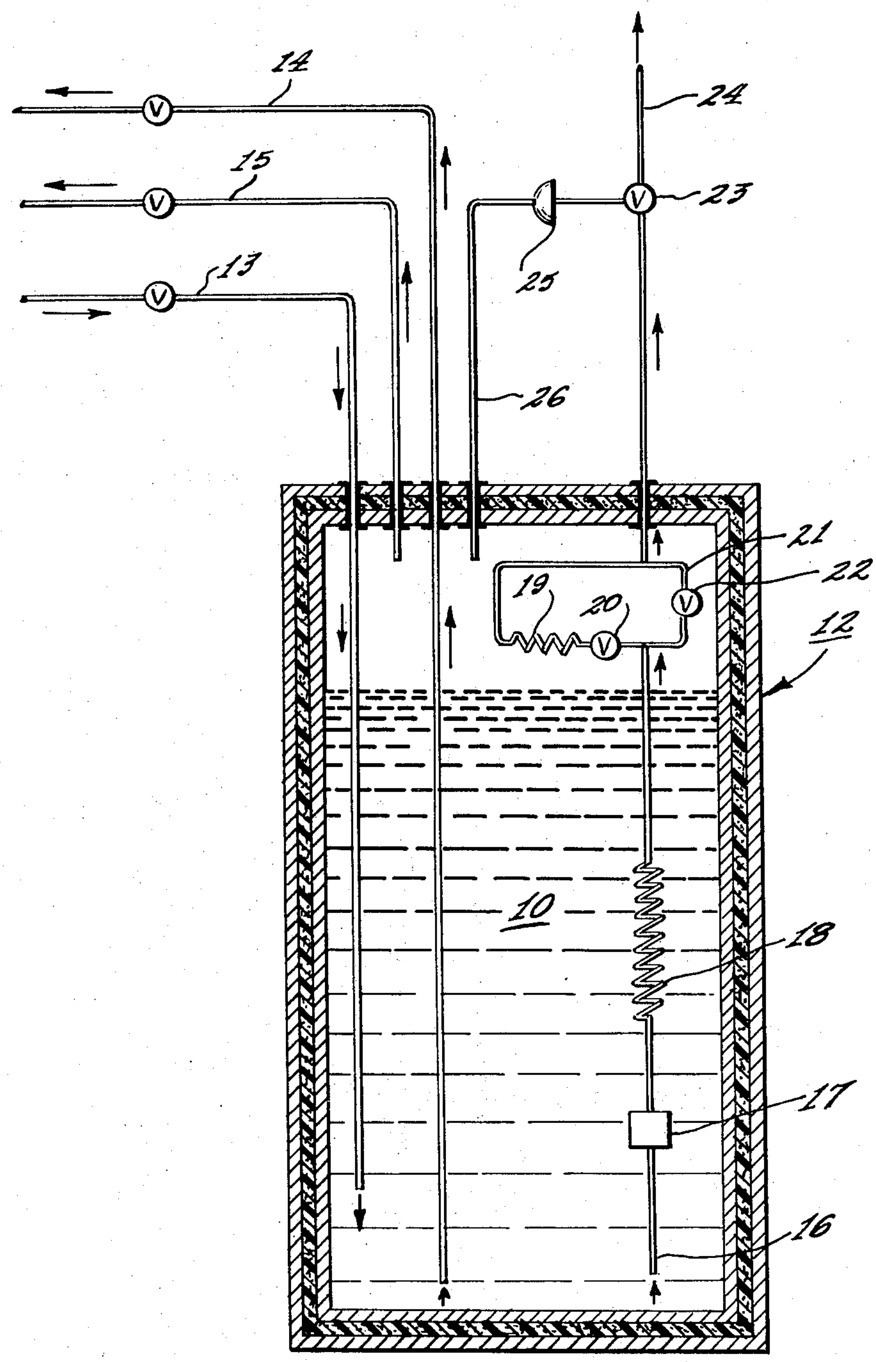

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1

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MAINTAINING CONSTANT COMPOSITION IN A VOLATILE MULTI-COMPONENT LIQUID

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ABSTRACT OF THE DISCLOSURE

A method and system is described for maintaining a multi-component cryogenic liquid of constant composition during extended periods of storage in a vessel. The system includes a pressure-responsive relief valve through which an expanded and vaporized fraction of the stored liquid is vented thereby precluding preferential vaporization of the lower boiling point component due to unavoidable heat leak into the vessel.

The present invention relates to method and apparatus for maintaining and dispensing multi-component cryogenic liquid.

In the following description, the term "cryogenic liquid" refers to a liquefied gas which is in gas-liquid equilibrium at temperatures below minus 50° C. at atmospheric pressure. However, it will be readily apparent that the present invention has utility for the storage of other less volatile gases as well.

It is recognized that space requirements and container weight can be substantially reduced for gas storage and delivery systems involving large volumes of gas by maintaining the gas in the more dense liquid phase rather than as a gas or a supercritical fluid. However, when liquefied gases are stored in insulated containers over somewhat extended periods of time at relatively low temperatures, inevitable heat leakage into the stored liquid tends to cause evaporation. If the stored liquefied gas contains multi-component gases of different boiling points, such as liquefied natural gas or liquid air, this evaporation due to heat leak will change the relative composition of the stored material. Specifically, components having the lower boiling points will tend to evaporate preferentially resulting in vapor richer in the components having the lower boiling point and liquid becoming richer in components with higher boiling points. Such preferential evaporation occurs even in predominantly single component compositions which necessarily contain minor amounts of one or more impurities, including liquid hydrogen containing a minor amount of hydrocarbons such as methane, liquid helium containing trace amounts of hydrogen, commercial liquid oxygen containing a total less than 0.4% of argon and nitrogen and liquefied ammonia containing impurities.

For example, in certain installations where a large volume of air is to be supplied as in hypersonic wind tunnels, it has been suggested that the air be stored as a liquid. However, liquid air would present a problem in that progresive vaporization of the liquid in the conventional manner would produce a gaseous mixture which would vary in composition from nitrogen-rich to oxygen-rich as the storage tanks are emptied, thereby changing the density of the gas and finally creating a hazardous oxygen-rich atmosphere. Accordingly, a system is required for such applications which insures that the withdrawn gas stream remains of the identical composition as the original liquid which is stored in the tanks.

A similar problem arises in providing breathing air for medical patients when air or other medical gas mixture is stored in liquid form. Obviously, differential vaporization such as to exceed an acceptable range of composition creates a significant and constant monitoring problem.

2

Therefore, it is an object of the present invention to provide a method and apparatus for storing cryogenic liquid over long periods of time while maintaining it at substantially constant composition.

Another object of the present invention is to provide a method and apparatus for dispensing cryogenic liquid from a storage vessel wherein the liquid is substantially identical in composition with that of the body of liquid maintained in the storage vessel throughout the storage and dispensing period.

These and other objectives will become more fully apparent from the following description when taken with the accompanying drawing which illustrates in schematic form a preferred embodiment of the present invention.

Referring now to the drawing, numeral **10** indicates a body of liquefied gas, such as liquid air or relatively pure oxygen with minor impurities, contained in an insulated vessel **12** of any suitable shape but is most often a spherical or cylindrical tank. Typically, vessel **12** has an efficient cryogenic insulation material which may be of any commercially known type, a vacuum, etc., between spaced inner and outer walls. The insulated vessel is also provided with a valved liquid fill line **13**, a valved liquid drawoff line **14** and may include a valved gas drawoff line **15**.

The present invention departs from known storage systems in providing a vapor pressure control system which includes a liquid intake line **16** connected to an expansion valve **17** and a vaporization coil **18**; all of which are immersed in the stored liquid. In addition, a preferred embodiment of the invention includes a heat exchange coil or condenser **19** and a by-pass line **21** having respective control valves **20** and **22** for regulating the flow of fluid passing from vaporization coil **18** to a pressure responsive vapor vent relief valve **23** in vent line **24**; valve **23** being purely conventional and including a pneumatic or other suitable actuator **25**, together with a pressure sensing line **26** connected to the ullage space in the storage vessel.

In the operation of the storage and dispensing system of the invention, unavoidable heat leak into the charged cryogenic storage system causes some of the stored liquid to vaporize and the pressure to rise until, at a predetermined pressure, pressure sensing line **26** and valve actuator **25** cause relief valve **23** to open. A small amount of vapor is vented through line **24**. At the same time, as pressure over the liquid is reduced, a small amount of liquid of the bulk liquid in storage is drawn into the pressure regulating system through line **16** and expanded in expansion valve **17**, producing a vapor-liquid mixture at a temperature below the bulk liquid creating a refrigeraing effect. The colder two phase mixture from valve **17** then passes through vaporization coil **18**, wherein the two phase mixture is fully vaporized by heat exchange with the warmer bulk liquid, effecting cooling of the bulk liquid **10**.

In turn, the cooled bulk liquid causes some of the vapor at the top of the vessel to condense, thereby reducing pressure inside the vessel. Vapors from the coil **18** may then be passed through heat exchange coil **19** located in the vapor space near the top of the tank (with valve **22** closed). The temperature of the vapor space near the top of a large stationary storage tank is often higher than the temperature of the liquid within the tank. Thus, the vapor produced in coil **18** is further heat-exchanged in coil **19** and this heat exchange causes an additional amount of vapor at the top of the vessel to be condensed until equilibrium conditions are restored. It is further to be noted that the temperature of the vapor produced in evaporator coil **18** can, if desired, be discharged at the saturated vapor temperature by bypassing coil **19** via bypass line **21**, and thus allow for maximum refrigeration recovery from this stream externally of the vessel. For such use, valve **20** is closed and valve **22** is opened.

Reliquefaction of the vapor in line **24** might be desirable in a cryogenic system under aerospace conditions where the materials, per se, would be of high value. However, under more normal conditions where gases for liquefaction are readily available, utilization of the residual cooling power of the gas effluent from vaporizer coil **18** in heat exchanger coil **19** is preferred to cool the vapor above the cryogenic liquid before being vented at near ambient temperatures via line **24**.

It is to be noted that, while the drawing shows the above described heat absorbing system as occupying a substantial part of the unit for purposes of illustration, in reality the drawoff tube, expansion valve, heat exchanger coils, and associated valving are very small in dimension relative to the tank and occupy only a minute fraction of container space.

In a storage tank for dispensing commercial liquid oxygen of substantially uniform composition (approximately 99.6% purity) in accordance with the invention, a 28,000-gallon unit has the following operational characteristics:

Storage tank pressure ______________p.s.i.a.__	30
Storage tank temperature ______________° F.__	—284
Vaporization coil pressure ___________p.s.i.a.__	15
Vaporization coil temperature __________° F.__	—297
Magnitude of heat leak to vessel ____B.t.u./hr.__	20,000
Liquid oxygen loss rate _____________lb./hr.__	200
Vaporization coil tubing size __________inches__	1.5
Magnitude of over-all heat transfer coefficient to vaporization coil _______B.t.u./hr./ft.^{2}/° F.__	200
Length of vaporization coil ____feet (uncoiled)__	20

In dispensing cryogenic liquid from a closed system, as the liquid level falls, the vapor space obviously increases. However, in view of the high ratio of liquid density to gas density (185/1 for air) only one part of liquid by volume is withdrawn and vaporized for about 185 to 200 parts of gas produced.

Aside from a liquid oxygen system as described above, consisting principally of one component with minor amounts of contaminants, the system disclosed is particularly applicable to storage systems for cascade refrigeration using multicomponent refrigerants. It is also applicable to liquid natural gas storage systems where concentration of heavier components in the tank due to lighter vapor boil-off is to be avoided. Thus, the unit described has broad application to any multi-component cryogenic liquid system in which it is desired to maintain or dispense liquid of constant composition regardless of the relative percentages of the intgeral components.

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.

What is claimed is:

1. A cryogenic liquid storage system comprising an insulated storage vessel, a cryogenic liquid partially filling said vessel, a vapor space in said tank above said liquid, discharge conduit means extending into said vessel for normally discharging liquid therefrom, vent conduit means extending into said vessel, a relief valve in said vent conduit, means responsive to a predetermined pressure in said vapor space for opening said relief valve, an expansion valve having an inlet in communication with said liquid, a vaporizer immersed in said liquid having an inlet connected to the outlet of said expansion valve, and conduit means connecting the outlet of said vaporizer to said vent conduit means whereby, upon opening of said relief valve, liquid is expanded, vaporized, and vented until the pressure in said vapor space is reduced to said predetermined value.

2. The system as claimed in claim **1** further including a condenser, said condenser being in heat exchange relationship with the vapor in said vapor space and being connected in said vent conduit means intermediate said vaporizer and said relief valve.

3. The system as claimed in claim **2** further including a valved bypass conduit for regulating the flow of vaporized liquid through said condenser.

4. The method of storing a multi-component cryogenic liquid in an insulated vessel at substantially constant composition and pressure throughout extended periods which comprises, absorbing heat flowing to said cryogenic liquid by (a) drawing a small fraction of liquid from the main body of cryogenic liquid in storage into an expansion system, (b) expanding and evaporizing said liquid fraction within the expansion system immersed in the main body of the liquid thus effecting cooling of the main body, (c) sensing the pressure in the vessel, and (d) venting said vaporized fraction from the insulated vessel so as to maintain a constant pressure in the vessel.

5. The method as claimed in claim **4** further including the step of heat exchanging the vaporized fraction with vapor contained in the vessel so as to warm the vaporized fraction and condense said vapor.

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