

# UNITED STATES PATENT OFFICE 

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# METHOD OF STORING VOLATILE LIQUIDS 

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This invention relates to a method of operating a storage vessel, and particularly to a method of operating a storage vessel for liquid such as gasoline which has a substantial vapor pressure which is normally substantially below atmospheric pressure.
The problem of storing such a volatile liquid has been dealt with in the past in many ways. When stored in ordinary vessels, there is no problem so long as the vessel is completely full. Upon emptying and refilling, however, there is evaporation into the vapor space. Normally the vapor space is left open to atmosphere so that air enters and is forced out carrying with it a substantial quantity of gasoline.
In order to overcome this difficulty, a large number of mechanical expedients have been suggested, including floating roofs, breather roofs, lifter roofs, and the like. All of these present mechanical difficulties and are expensive to operate.

The present invention permits the operation of a storage vessel with fixed walls. In accordance with it, a storage vessel is made sufficiently strong to withstand substantially full atmospheric pressure directed inwardly and to withstand an internal gauge pressure substantially equal to atmospheric. The vessel, when filled the first time, is permitted to vent to atmosphere to remove substantially all air, and the tank is preferably filled to the top. After filling, about $2 \%$ of liquid is withdrawn to allow for expansion but no air is vented into the space thus vacated. Furthermore on removal of liquid from the vessel, no air is admitted thereto, liquid being removed by means of a pumping system capable of operating against full vacuum (or full vacuum less the vapor pressure of the liquid). On filling the vessel no venting is contemplated. However, venting may be required whenever the safety limit of the tank is exceeded. Normally such venting will not be required, but excessive pressure may be developed in three ways: (1) by excessively high temperatures; (2) too rapid filling; and (3) by reason of the additive vapor pressure of air entrapped or entrained in the liquid.
When the vessel is filled it is obvious that vapors therein will be compressed. Theoretically, these vapors will condense when they reach a pressure exceeding maximum vapor pressure, but this does not always follow immediately, and particularly is not necessarily true where the vessel is filled with extreme rapidity and in the presence of air. Normally I prefer to fill the vessel in a manner so that pressure generated in the gasoline vapors will remain low, the excess pressure generated by compression being taken up by condensation in the liquid.

It is of course impossible to remove all air entrapped or entrained by the liquid and, therefore,

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air will accumulate slowly within the vessel. This air not only adds its vapor pressure to that of the gasoline vapors, but it interferes with the proper condensation of the gasoline during filling and ultimately requires removal. For this reason I provide a vent which operates at nearly the safety limit of the tank for removing excessive air. The air obviously carries with it vapor, the loss of which is undesirable. This loss is kept to a minimum by venting when the safety limit of the tank has been approximately reached, and may further be reduced by cooling or refrigerating the vented air in any suitable manner and returning condensate to the tank.
The use of a vent valve operating at the safety limit of the tank is not only important because venting is limited to the minimum, but because it insures that the concentration of air in the gas vapor will normally have been markedly increased prior to venting. This increase in concentration of air occurs for two reasons. In the first place the vapor pressure of the gasoline is fixed at any temperature. Therefore, if the tank is set to vent at 12 lbs . and the vapor pressure of the gasoline is, say 5 lbs. absolute, air will have to represent approximately 22 lbs . of the total pressure before any venting occurs. Therefore, increase in pressure represents air, and the higher the pressure of venting, the greater is the proportion of air, other things being equal.
Furthermore, venting will nearly always occur during filling of the tank and seldom while the tank is quiescent. During filling of the tank, the pressure will rise, as any residual air is compressed, but at the same time gasoline vapors within the vapor space will condense because their condensation pressure is exceeded the minute the tank begins to fill. Therefore, the vapors gradually become more concentrated in air as the filling operation goes on, and by making the venting pressure as high as possible, the concentration of air increases and less gasoline vapors are lost upon venting.

It is preferred, as stated before, to fill the tank completely full whenever it is filled, and then to withdraw some liquid and leave about $2 \%$ of vapor space. This, however, is not customary refinery practice, the ordinary practice being to fill about $98 \%$ full. In order to conform to this practice, it is, therefore, desirable in some instances to include a second valve which is sealed against operation until the tank is substantially $98 \%$ full, and then opens slightly below the safety limit of the tank and preferably at a pressure very slightly below the first valve, and which then stays open to vent all of the gases contained within the $2 \%$ space until atmospheric pressure has been reached. Such a valve is of value because it vents gases at a time when the concentration of air therein is at a maximum. This maximum
content of air is due to the fact that gasoline vapors have been condensing during all of the filling of the tank, the air concentration increasing during all of that time. By venting as much as possible when the air concentration is at its maximum, vapor losses are reduced.

A typical storage system for storing volatile liquids according to the method of this invention is shown in the accompanying drawings. Of the drawings Fig. 1 is an elevation of the storage system; and Fig. 2 is an enlarged fragmentary vertical section through the valves on the top of the storage vessel.

The storage system shown in the accompanying drawings comprises a storage vessel 10 , a pump 11, a valve i2 set at a desired pressure such as 12 lb . per sq. in., and a second valve 13 preferably set at a slightly lower pressure than the first valve 12. The second valve 13 is designed to open at, for example, $113 / 4 \mathrm{lb}$. per sq. in., and to close at substantially atmospheric pressure.

The storage vessel 10 comprises vertically aligned intersecting spheres 14 supported by a steel rim 15 which rests upon a concrete foundation 16. This intersecting spherical vessel is oi the type shown and described in the copending application of Harry C. Boardman, Serial No. 608,884, filed August 4, 1945.

The first valve 12 at the top of the storage vessel comprises a valve seat 16 held in closed position by a spring 17 resting against cross bars 18. This valve may be set at any desired pressure, such as 12 Ib . per sq. in.
The second valve 13 at the top of the storage vessel includes a first valve seat is connected by means of a rod 20 to a second valve seat 21 of larger area than the first valve seat 13. Both valve seats are held in place by means of a spring 22 bracing against cross bars 23. The opening 24 leading to the second valve 13 is normally kept closed by means of a gate 26 . This gate is opened only when the vessel is slightly less than full, for example, $98 \%$ full, and is opened by means of a float 25, which turns the gate 25 about hinge 27 , When the vessel is almost silled.

The outlet from the valves may be joined to a pipe 28 , where the vapors may be conducted to a refrigerating unic to recover the volatile liquid carried off by the vapors.

An important part of the storage system is a means for filling and emptying the vessel. This filing and emptying means may be a pump 11 which must be of sufficient power to fill the vessel against internal pressure and to empty the tank against full vacuum (or full vacuum less the vapor pressure of the liquid). Liquid is led to the pump by means of an intake line 28 and exhausted to the vessel through a line 3 C . When the pump is used to withdraw liquid from the vessel these lines serve as an outlet.

Having described my invention in considerable detail, it is my intention that the invention be not limited by the details of description unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

I claim:

1. The method of filling and emptying a storage vessel for storing volatile liquids having a substantial vapor pressure normally substantially below atmospheric pressure which comprises introducing such liquid to a storage vessel capable
of withstanding substantially a full vacuum and also an internal gauge pressure substantially equal to atmospheric pressure, continuing the filling of said vessel substantially to completion to compress the entrapped air and condense the vapors, and venting the entrapped air when the vessel is slightly less than full at a pressure not exceeding the safety limit of the vessel, the venting being continued until the absolute pressure within the vessel above the top of the liquid has fallen to slightly above atmospheric pressure.
2. The method of claim 1 wherein the liquid is introduced into the vessel at such a rate that the pressure of the volatilized gases within the vessel is substantially the same as the vapor pressure of the liquid during the filling operation.
3. The method of claim 1 wherein the liquid is withdrawn from the vessel at such a rate that the pressure of the volatilized gases within the vessel is substantially the same as the vapor pressure of the liquid during the emptying operation.
4. The method of claim 1 wherein the liquid is introduced into and withdrawn from the vessel at such a rate that the pressure of the volatilized gases within the vessel is substantially the same as the vapor pressure of the liquid during the flling and emptying operations.
5. A storage system for storing volatile liquids having a substantial vapor pressure substantially below atmospheric pressure comprising a storage vessel capable of withstanding substantially a full vacuum and also an internal gauge pressure substantially equal to atmospheric pressure, a vent connected to the vessel and having a pressure responsive valve closure therein adapted to open in response to the build up in the vessel of an internal pressure slightly less than the safety limit of the vessel and to remain open only while said internal pressure is maintained, a second vent connected to the vessel and having a pressure responsive valve closure therein adapted to open in response to the build up in the vessel of an internal pressure slightly less than the safety limit of the vessel and to remain open until a pressure slightly greater than atmospheric is reached, a gate closing said second vent and having operating means for placing the vent in communication with the interior of the vessel only when the vessel is slightly less: than full, and means for introducing liquid into and withdrawing liquid from the vessel.
6. A storage system as set out in claim 5 wherein said second vent is adapted to open at a pressure slightly less than that required to open the first vent.

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