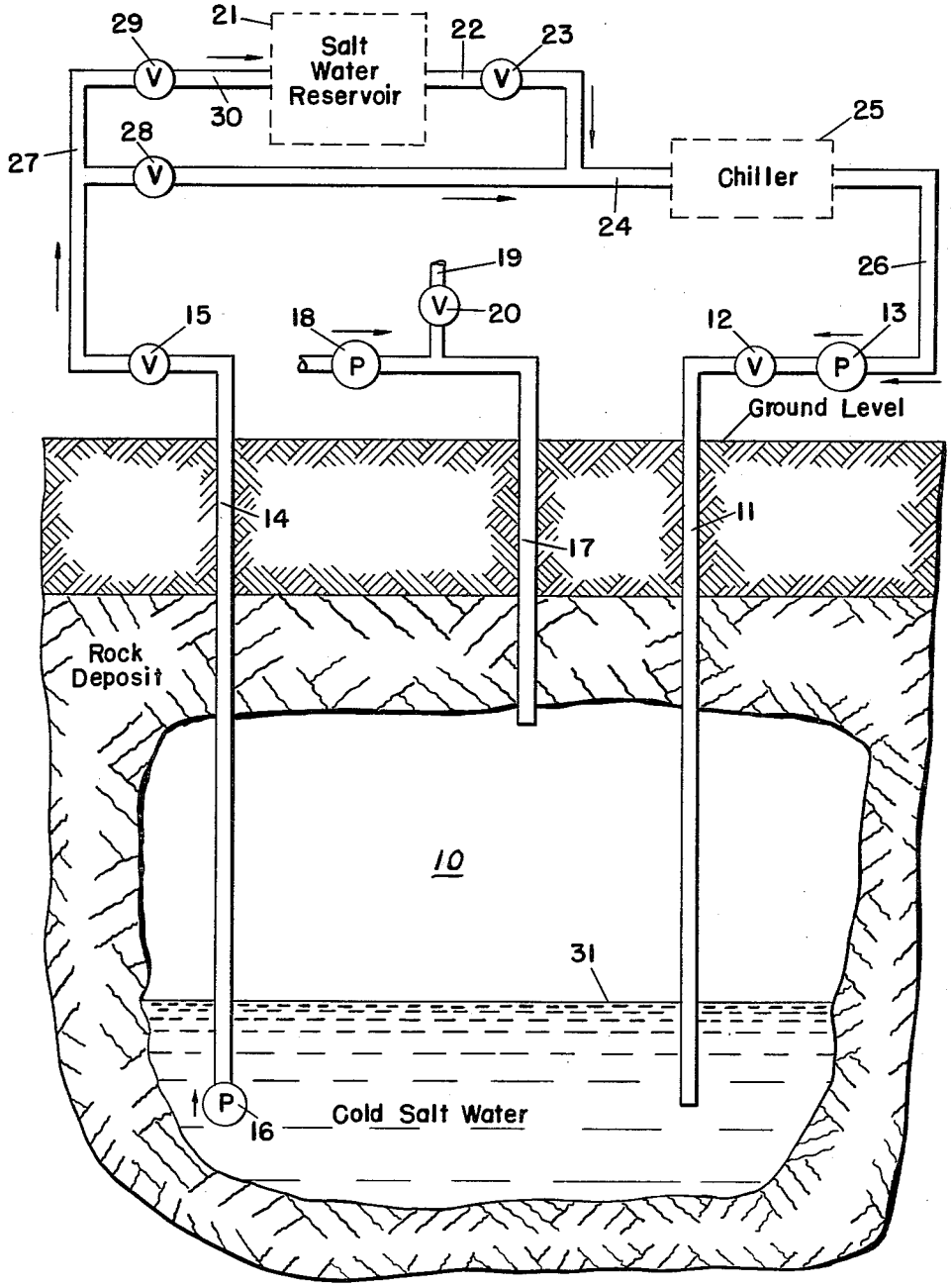
April 2, 1963 P. F. DOUGHERTY 3,083,537

STORAGE OF NORMALLY GASEOUS MATERIAL
IN UNDERGROUND CAVERNS
Filed Jan. 23, 1961



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United States Patent Office

3,083,537
Patented Apr. 2, 1963

3,083,537

STORAGE OF NORMALLY GASEOUS MATERIAL IN UNDERGROUND CAVERNS

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Filed Jan. 23, 1961, Ser. No. 83,995
4 Claims. (Cl. 61—.5)

This invention relates to the storage of normally gaseous material in underground caverns and more particularly concerns the use of underground caverns for storing in liquid phase normally gaseous water-insoluble material which has a critical temperature below the normal wall temperature of the underground cavern. The invention has particular utility in the storage of ethylene in liquid form.

Underground caverns which have been prepared by mining out rock from a solid rock formation or by washing out salt from a salt deposit have been used for the storage of hydrocarbons. Such caverns generally are produced at depths ranging from 300 to 3000 feet below the ground level and the normal temperature of the cavern wall typically is in the range of 60–85° F. depending upon the depth of the cavern. When the hydrocarbon material has a critical temperature above the normal wall temperature, it is stored in the cavern as a liquid. Thus normally gaseous hydrocarbons such as propane and butane conventionally are stored in underground caverns under sufficient pressure to maintain the hydrocarbon in liquid phase, since their critical temperatures are above the normal wall temperature. However ethylene, which has a critical temperature of about 49° F., heretofore has had to be stored as a gas, so that the amount that can be stored in a cavern of a given size is considerably less than in the case of propane or butane.

Storage caverns which have been mined in granite or other rock deposits often have fissures in the cavern wall through which water seepage occurs. In some cases where the light hydrocarbon is being stored in vapor phase, this water seepage may cause difficulties due to the formation of hydrocarbon hydrates which are solid and which may cause plugging of the hydrocarbon outlet line. It is desirable to store the light hydrocarbon under such conditions that hydrates cannot be formed.

The present invention provides a method of storing a light hydrocarbon such as ethylene as a liquid in underground caverns having a normal wall temperature which is above the critical temperature of the hydrocarbon. The conditions of storage are such that any seepage of water into the cavern is prevented and no hydrocarbon hydrates can be formed. While the invention is particularly applicable to the storage of ethylene, it can also be used for storing other water-insoluble normally gaseous materials that have a critical temperature below the normal wall temperature of the cavern, for example, silicon tetrahydride or xenon. It can also be used for the liquid phase storage of ethane where the normal cavern wall temperature is above the critical temperature of this hydrocarbon (90° F.).

The method according to the invention comprises initially filling the cavern with a cold aqueous salt solution having a freezing point substantially below the critical temperature of the material to be stored and then circulating the cold salt solution through the cavern until the wall temperature approaches that of the salt solution. Preferably the temperature of the salt solution is below 32° F. so that any water in fissures in the cavern wall will become frozen. This prevents leakage of water into the cavern which otherwise would occur when the hydrostatic head of the water is greater than the pressure in the cavern. After the cavern walls have been sufficiently chilled, the

normally gaseous substance to be stored, which has been liquefied and cooled to about the same temperature as that of the cavern wall, is pumped into the cavern thereby displacing salt solution which flows from the cavern through an outlet line. However, displacing of the salt solution is stopped before its level has reached the bottom of the cavern, so that a body of salt solution is left in the cavern. Thereafter cold salt solution is circulated into the cavern and an equivalent amount of salt solution is withdrawn therefrom. This maintains the cavern at the desired low temperature level so that the stored material will remain in liquid phase. Whenever it is desired to remove stored material from the cavern, the withdrawal of salt solution is stopped while the pumping of cold salt solution into the cavern is continued so that the stored material will be displaced therefrom.

The invention is described more specifically in conjunction with the accompanying drawing which schematically illustrates the system used in practicing the present method of storage. In the drawing numeral 10 represents an underground cavern which has been prepared either by mining out a rock formation or washing salt from a rock salt deposit. Assuming that the cavern is in a rock formation such as granite, there are apt to be small fissures in the rock which normally would allow water to seep into the cavern. An inlet line 11 having a valve 12 and connected to a pump 13 is provided for introducing cold salt solution to the cavern, and an outlet line 14 having valve 15 and connected to pump 16 is provided for withdrawal of salt solution. Another line 17 connected to pump 13 and to a branch line 19 having valve 20 also leads to the cavern and terminates adjacent its top. Line 17 is connected to an ethylene storage tank (not shown) through a chiller (not shown) adapted to reduce the temperature of the ethylene to the desired low level, e.g. −15° F.

A salt water reservoir, illustrated schematically at 21, contains an aqueous solution of a salt that reduces the freezing point of the solution to below the temperature to which the cavern 10 is to be maintained. For example, the salt water can be a 25 weight percent solution of calcium chloride in water. Reservoir 21 is connected by line 22 having valve 23 and line 24 to a chiller 25 capable of reducing the temperature of the salt solution to the desired low level, e.g. −15° F. Chiller 25 is connected through line 26 to the salt water inlet line 11.

In establishing the desired temperature conditions for cavern 10, salt water is first pumped from the reservoir 21 through chiller 25 into line 11 and the cavern is vented through valve 20 in line 19. This permits the cavern to be filled with cold salt water. When the cavern is full, valve 20 is closed and pump 16 in line 14 is started at a rate to withdraw salt water at the same rate at which it is being introduced to the cavern. The withdrawn salt water circulates through line 27, valve 28, line 24 and chiller 25, whence it returns to the inlet line 11. Circulation of the cold salt water in this manner is continued until the temperature of the cavern walls has approached the salt water temperature. The cavern then is ready for introduction of the liquefied ethylene. This is done by pumping the ethylene, chilled to a temperature of say −15° F., through pump 18 and line 17. At the same time pump 13 is stopped and the salt water which is displaced by the ethylene is passed through valve 29 and line 30 into the reservoir. Introduction of the liquid ethylene is stopped before all of the salt water is displaced from the cavern so that a body of salt water, as indicated at 31, is maintained in the cavern. Thereafter, to maintain the desired low temperature in the cavern, cold salt water is fed through line 11 into the salt water layer and an equivalent amount of salt water is removed through line 14. By heat

transfer through the liquid ethylene to the salt water layer, the desired low temperature of the cavern walls is continuously maintained. Any water in fissures in the cavern wall will become frozen so that seepage of water into the cavern will be prevented.

Whenever it is desired to remove ethylene from the cavern, pump 16 is stopped and valve 15 is closed while introduction of cold salt water through line 11 is continued. In this manner the liquid ethylene can be displaced from the cavern through line 17, valve 20 and line 19.

I claim:

1. In the storage of a normally gaseous water-insoluble material in an underground cavern the walls of which normally have a temperature above the critical temperature of said material, the method of storing said material in liquid phase which comprises filling the cavern with a cold aqueous salt solution having a freezing point substantially below said critical temperature, circulating such salt solution at a temperature between its freezing point and said critical temperature through the cavern until the temperature of the cavern walls has approached the temperature of the salt solution, displacing salt solution from the cavern by pumping in said normally gaseous material as a liquid chilled to a temperature below its critical temperature until the level of the salt solution has dropped substantially, stopping such displacement before the level of the salt solution has reached the bottom of the cavern thereby leaving a body of salt solution in the cavern, and circulating cold salt solution to and withdrawing salt solution from said body of salt solution to maintain the cavern at a temperature below said critical temperature.

2. Method according to claim 1 wherein the temperature of the salt solution in the cavern at all times is below the freezing point of water, whereby any water in fissures adjacent the cavern wall is maintained in frozen condition.

3. Method according to claim 1 wherein said normally gaseous material is ethylene.

4. Method according to claim 1 wherein the solute of said aqueous salt solution is calcium chloride.

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