

March 29, 1960

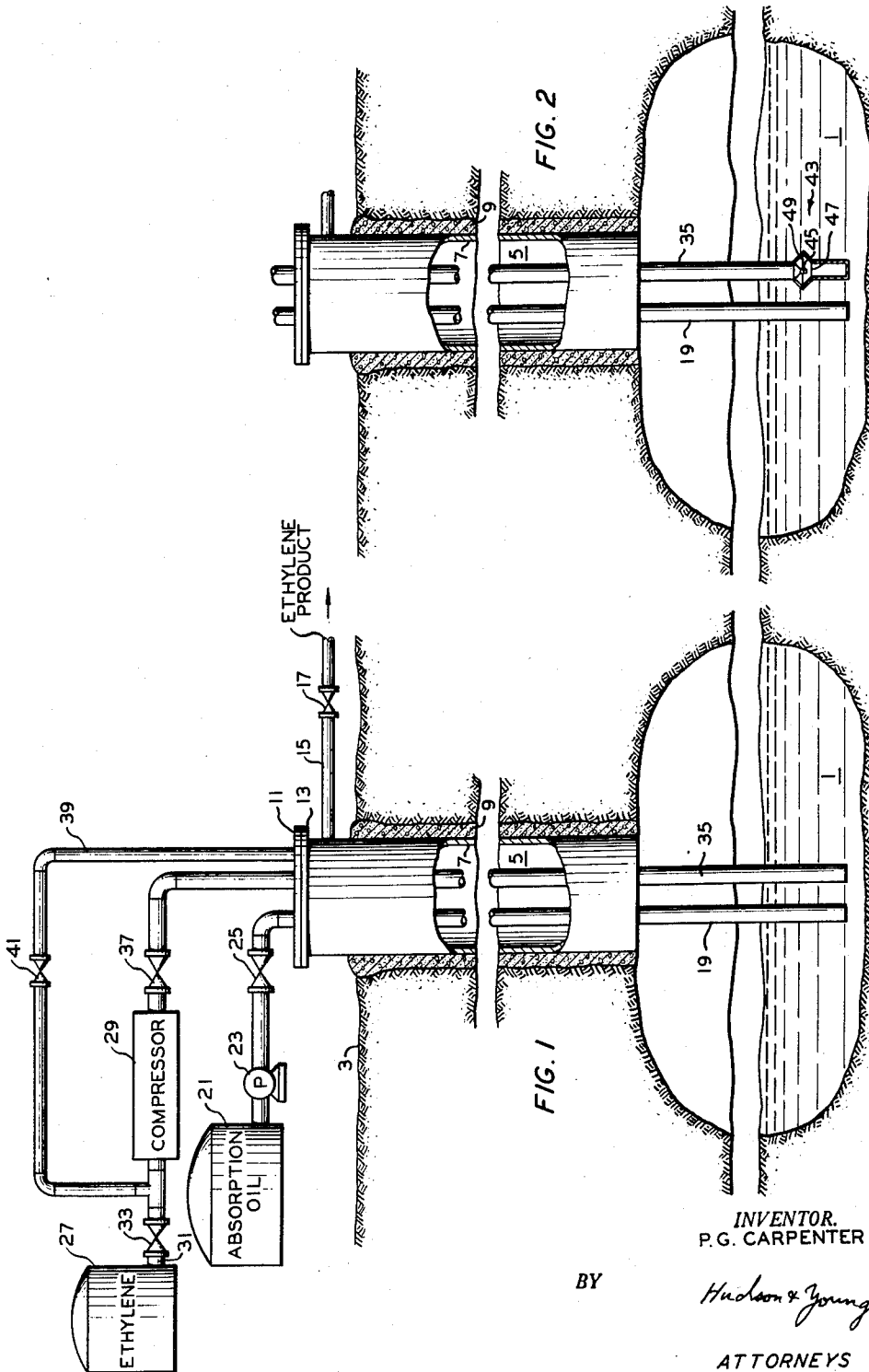
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UNDERGROUND STORAGE OF HIGH PRESSURE PETROLEUM GASES

Filed Nov. 12, 1954

3 Sheets-Sheet 1



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3 Sheets-Sheet 2

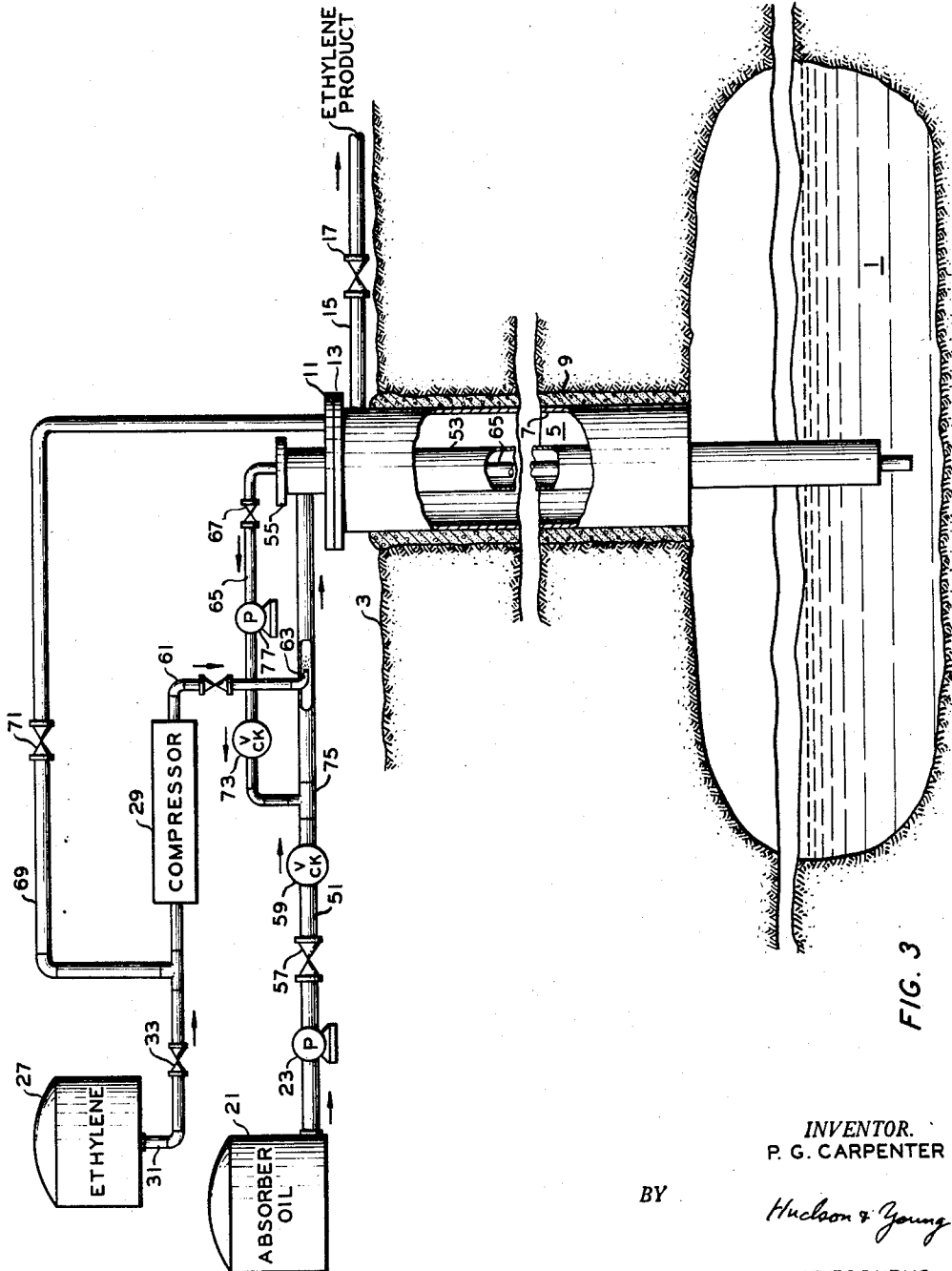


FIG. 3

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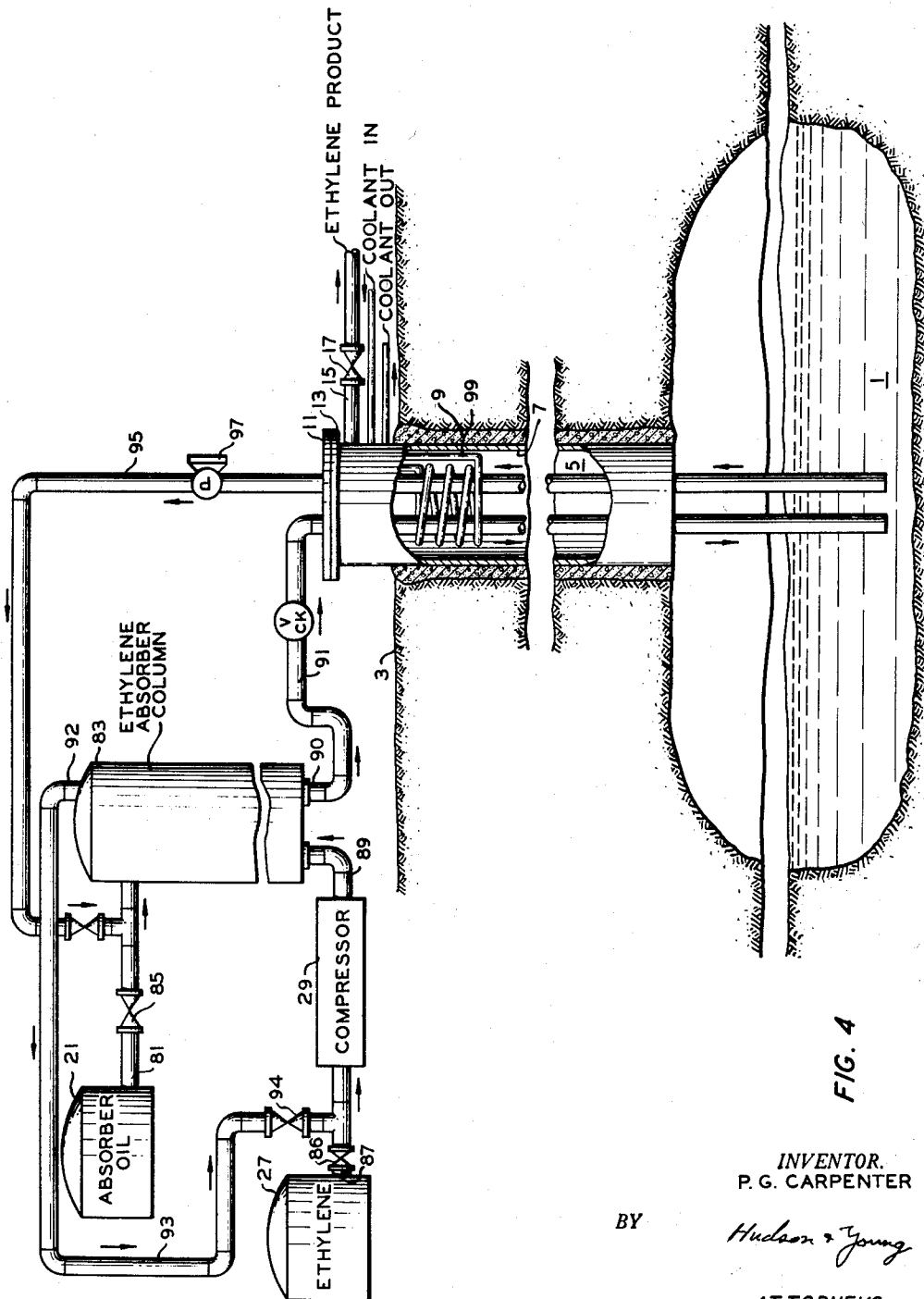


FIG. 4

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UNDERGROUND STORAGE OF HIGH PRESSURE PETROLEUM GASES

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10 Claims. (Cl. 61—5)

This invention relates to the underground storage of high pressure petroleum gases. In a more specific aspect, this invention relates to a method and apparatus for storing a high pressure petroleum gas such as ethylene, in an underground cavern.

In order to reduce the cost of storage of petroleum fluids, the petroleum industry recently has been developing underground storage facilities to handle large volumes of petroleum liquids, chiefly liquefied petroleum gases. Besides requiring a lower initial investment per unit volume of fluid stored, underground storage facilities entail a lower operating cost than do surface storage vessels, particularly in the case of liquefied petroleum gases.

To date, however, high pressure petroleum gases, for example, petroleum gases having up to 4 carbon atoms per molecule, have usually been stored in high pressure surface vessels, which are very expensive to build and operate. Some of these high pressure petroleum gases are becoming increasingly important as ingredients in chemical processes and, therefore, storage of these gases is currently a problem.

An outstanding example is ethylene, which is finding uses in a variety of chemical processes, such as alkylation and polymerization. Ethylene, as is well known, is a gas at atmospheric conditions and surface vessels for storing ethylene are exceedingly expensive. Since the critical temperature of ethylene is 49.82° F., storage of liquid ethylene requires cooling of the storage facilities to this temperature or below, which is, of course, very expensive. On the other hand, storage of ethylene at temperatures above the critical temperature either requires very large storage vessels, if stored at relatively low pressure, or relatively high pressures if stored in correspondingly smaller vessels.

A system for storing these high pressure petroleum gases at reduced cost is needed and will permit increasing expansion of new processes which require large supplies of these gases.

It is an object, therefore, of this invention to provide a system for storing high pressure petroleum gases in underground storage caverns.

A further object is to provide a method and apparatus for storing hydrocarbon gases having up to 4 carbon atoms per molecule in underground caverns.

In accordance with this invention, a high pressure petroleum gas is absorbed in an oil and the oil containing the absorbed gas is stored in an underground cavern having a vertical shaft extending upwardly to the earth's surface.

An outstanding feature of this invention is the way in which the gas is removed from the storage system. The vertical shaft connecting the cavern to the earth's surface serves as a stripping column for the absorption oil and when an outlet at the top of the shaft is opened, the gaseous product is vaporized out of the absorption oil by the heat of the earth about the cavern and shaft and is thereby fractionally distilled to provide a pure gaseous product at the shaft outlet.

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The underground caverns which can be used in accordance with this invention include those currently in use for the storage of liquefied petroleum gases which have a vertical shaft connecting the cavern to the surface and which are located sufficiently deep below the earth's surface to hold the pressure of the gases. Caverns which are formed by drilling a vertical shaft to a salt bed at depths of at least 1000 feet and thereafter by washing out a cavern in the salt are particularly well suited for use in accordance with this invention. The cavern must be located at a depth of at least about one foot per pound gauge pressure upon the fluids stored in the cavern.

It will be apparent that many systems can be utilized for carrying out this invention. High pressure gases, such as ethylene, can be absorbed in an absorption oil by releasing the gas below a pool of the oil in an underground cavern. The gas will be partially absorbed as it rises upwardly through the oil and, by recirculating the gas, the desired concentration of the gas can be absorbed in the oil.

The choice of the absorption oil, the depth of the cavern, and the optimum concentration of the gas in the absorption oil are all interdependent factors which are correlated to fit particular uses of this invention. An oil having from 5 to 20 carbon atoms per molecule can be used for absorbing a hydrocarbon gas having up to 3, inclusive, carbon atoms per molecule. Specifically, such oils as a mineral seal oil, wash oil, high-boiling absorption oil and paraffin hydrocarbons, such as heptane, octane, nonane, decane, dodecane, tetradecane, octadecane and eicosane can be used. Obviously, an oil having a higher molecular weight will reduce the vapor pressure of the combined gas and oil for storage in the cavern but the higher molecular weight oil has the disadvantage of absorbing a smaller volume of the gas. An oil having from 7 to 16 carbon atoms per molecule, therefore, represents the preferred oil for use as the absorbing medium in accordance with this invention, since an oil in this range will provide satisfactory reduction of the vapor pressure as well as provide the maximum absorption of the gas to be stored.

A preferred embodiment of this invention concerns the storage of ethylene and the data presented below in Table I demonstrate the advantages which are afforded by this invention when ethylene is stored in accordance therewith. The important advantage which accrues from using this method for the storage of ethylene is that a greater weight of ethylene per cubic foot of fluid in the cavern can be obtained by absorbing the ethylene in an absorption oil such as normal heptane, than if pure ethylene were stored under the same conditions of temperature and pressure.

TABLE I

Ethylene stored in n-heptane at 100° F.

1	2	3	4	5
Ethylene-n-heptane compositions, weight percent ethylene	Reservoir Pressure, ethylene-n-heptane compositions, p.s.i.a.	Density of ethylene-n-heptane compositions, lbs./cu. ft.	Pounds ethylene per cubic foot of ethylene-n-heptane composition	Pounds per cubic foot of pure ethylene at 100° F. at reservoir pressures of column 2
20-----	480	37	7.4	2.6
30-----	600	34	10.2	3.6
50-----	820	30	15.0	5.9
70-----	970	24	16.8	8.0

In Table I above, it will be observed that four ethylene-n-heptane compositions are shown in column 1. The pressures shown in column 2 are the reservoir pressures

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of the corresponding ethylene-n-heptane compositions of column 1 at 100° F. A comparison of the data in columns 4 and 5 shows that at a temperature of 100° F., which is below the critical temperature of the ethylene-n-heptane compositions in column 1, more ethylene can be stored per cubic foot of fluid in the presence of normal heptane than can be stored in the absence of normal heptane.

As was indicated above, many systems can be devised for carrying out this invention. Specific embodiments which can be used are illustrated in the accompanying drawings, in which:

Figure 1 is a diagrammatic sketch, partially in section, of an embodiment of this invention wherein the gas to be stored is bubbled through an absorption oil in an underground cavern;

Figure 2 is a partial view of a modification of the embodiment in Figure 1, showing a jet-mixing device installed therein to increase the efficiency of the absorption of the gas in the system of Figure 1;

Figure 3 is a diagrammatic sketch of a further modification of the embodiment of my invention shown in Figure 1 wherein absorption of the gas in the oil occurs in a pipe conveying both the gas and absorption oil into the cavern; and

Figure 4 is a diagrammatic sketch, partially in section, of a further embodiment of my invention wherein the gas is absorbed in the absorption oil in an absorber column at the surface.

Referring now to Figures 1 through 4, there is shown an underground cavern 1 connected to the surface 3 of the ground by a vertical shaft 5. Shaft 5 is lined throughout its length by a casing 7 which is sealed to shaft 5 by cement 9. Shaft 5 is sealed at the top by a casing head 11 secured to a flange 13 on the upper end of casing 7.

Cavern 1 is at a depth below the surface of the ground of at least about one foot per pound gauge pressure exerted by fluids stored in the cavern. Such a cavern is provided by drilling shaft 5 to the level of a salt bed at the depth desired for cavern 1. The cavern is then washed out by solution mining methods well known to those skilled in the art.

Referring further to Figures 1 through 4, a pipe 15 communicates with the interior of shaft 5 above the surface 3 of the ground and a valve 17 controls pipe 15.

Referring now to Figure 1, a pipe 19 connects a source of absorption oil 21 to a region near the bottom of cavern 1. Absorption oil 21 is pumped into cavern 1 by a pump 23 and a valve 25 controls pipe 19 downstream of pump 23.

A source of ethylene gas 27 is connected to the inlet of a compressor 29 by a pipe 31 which is controlled by a valve 33. Ethylene gas is discharged from the outlet of compressor 29 through a pipe 35 to a region near the bottom of cavern 1. Pipe 35 is controlled by a valve 37 located downstream of compressor 29.

A pipe 39 connects the top of the interior of shaft 5 to pipe 33 and the inlet to compressor 29. A valve 41 controls pipe 39.

To operate the embodiment of my invention shown in Figure 1, the absorption oil is pumped from source 21 into cavern 1 until the cavern is filled to the maximum operating depth. Ethylene is withdrawn from source 27 by compressor 29 and is discharged into the bottom of the pool of oil in cavern 1 via pipe 35. The discharged ethylene gas bubbles upwardly through the oil, thereby being at least partially absorbed therein. The unabsorbed ethylene gas rises to the top of shaft 5 and is recirculated through pipe 39 to pipe 33 and into the inlet to compressor 29 to be again discharged at the bottom of the pool of oil in cavern 1. A valve 41 in pipe 39, which can be a pressure control valve, controls the flow of recirculated ethylene therein. This recirculation of the ethylene gas is continued until the optimum concentra-

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tion of ethylene in the particular absorption oil being used is reached.

When it is desired to withdraw ethylene from the storage system illustrated in Figure 1, valve 17 is opened and ethylene gas is produced through pipe 15. The increased temperature of the earth at the depth of the cavern supplies the energy for expelling the ethylene from the absorption oil when the pressure at the top of the shaft 5 is reduced by opening valve 17. Shaft 5 acts as a stripping column and the cooler earth near the surface of the ground causes any absorption oil which is vaporized by the heat of the earth about the cavern to be condensed in shaft 5 and thereby removed from the ethylene gas.

Referring now to Figure 2, a modification of the apparatus in Figure 1 is shown. A jet-mixing device 43 is installed at the lower end of pipe 35. Jet-mixing device 43 can be any of the conventional devices used for mixing fluids, comprising a restricted diameter opening 45 which discharges into the throat of a venturi 47, as shown. As ethylene gas passes through opening 45 into venturi 47, absorption oil in the cavern is drawn into venturi 47 through the open end 49 of venturi 47, mixed with the ethylene, and discharged into the cavern out of the bottom of mixing device 43. The modification shown in Figure 2 causes the ethylene gas to be absorbed in the oil more efficiently due to the mixing of the gas and the oil provided by the jet-mixing device 43. This results in less recirculation of the ethylene gas being required in order to obtain the optimum concentration of ethylene in the absorption oil.

Referring now to Figure 3, a further modification of the embodiment in Figure 1 is shown. Absorption oil from the source 21 is conveyed by pump 23 through a pipe 51 into the top of a vertical tubing 53. Tubing 53 extends from above casing head 11 through shaft 5 to a region near the bottom of cavern 1 and is sealed at the top by a tubing head 55. The pipe 51 is controlled by a valve 57 and by a check valve 59 downstream of pump 23.

As in Figure 1, ethylene source 27 is connected to the inlet of a compressor 29 by a pipe 31, controlled by a valve 33. However, in Figure 3 the outlet of compressor 29 is connected to a pipe 61 which is connected to pipe 51 downstream of check valve 59. The discharge end of pipe 61 carries a jet or nozzle 63 having a reduced diameter opening which ejects the ethylene gas into pipe 51 in the direction of flow of the oil therein at a high velocity.

A pipe 65, having a smaller diameter than tubing 53, is concentrically placed within tubing 53 and extends from below the lower end of tubing 53 upwardly through tubing head 55 to connect into pipe 51 at a point 75 intermediate to the position of check valve 59 and jet or nozzle 63 in pipe 51. A pump 77 is connected into pipe 65 and a check valve 73 is connected into pipe 65 intermediate to point 75 and pump 77. A valve 67 is connected into pipe 65 intermediate to pump 77 and tubing head 55.

A pipe 69 connects the top of shaft 5 to pipe 31 and the inlet to compressor 29. A valve 71, which can be a pressure control valve, controls pipe 69.

In the operation of the modification shown in Figure 3, absorption oil from source 21 is pumped via pipe 51 and tubing 53 into cavern 1. Ethylene gas is withdrawn from source 27 via pipe 31 by compressor 29 and is passed via pipe 61 and jet or nozzle 63 into pipe 51. The ethylene jets out of nozzle 63 into the stream of oil in pipe 51, thereafter breaking up into bubbles of ethylene which travel downwardly through tubing 53 into cavern 1. The absorption oil from source 21 is pumped through this jet stream and bubbles of ethylene in pipe 51 and tubing 53 which forms films of oil on the inner surface of tubing 53 contacting the ethylene gas. This contact-

ing of the oil films and ethylene in pipe 51 and tubing 53 affords excellent mixing of the oil and gas, thereby effecting very efficient absorption of the ethylene in the absorption oil.

As the cycle of these operations is continued, the concentration of ethylene is increased until the optimum concentration for the particular absorption oil being used is reached.

Liquid absorption oil from cavern 1 is recirculated via pipe 65 by means of pump 77 to pipe 51 to be further mixed with ethylene until the optimum concentration of ethylene in the oil is obtained. Unabsorbed ethylene is withdrawn from cavern 1 via pipe 69 to pipe 31 and the inlet to compressor 29.

Ethylene is removed from the cavern in Figure 3 by opening valve 17 in pipe 15 as was described above in connection with Figure 1.

Referring now to Figure 4, there is shown a further embodiment of my invention utilizing an absorber column at the surface for absorbing ethylene in the absorption oil.

Absorption oil 21 flows by gravity, or is pumped by means not shown, through a pipe 81 into the top of an absorber column 83. A valve 85 controls pipe 81.

Ethylene 27 is connected by a pipe 87 to the inlet of the compressor 29. A valve 86 is connected into pipe 87. The outlet of compressor 29 is connected by a pipe 89 to the bottom of absorber column 83. The downwardly flowing oil in absorber column 83 contacts the upwardly rising ethylene gas, thereby absorbing the gas in the oil. The absorber column 83 can be any of the conventional columns for absorption of gases and liquid, having contacting plates or trays.

The ethylene-enriched absorption oil leaves an outlet 90 at the bottom of column 83 and passes to a lower region of cavern 1 via a pipe 91 which connects the lower region of cavern 1 through shaft 5 to the oil outlet 90 in column 83. The unabsorbed ethylene leaves the top of absorber column 83 through an outlet 92 and is conveyed to compressor 29 by a pipe 93 which connects into pipe 87 and the inlet to compressor 29. A valve 94, which can be a pressure control valve, in pipe 93 controls the flow of ethylene in pipe 93.

Ethylene is removed from storage by opening valve 17 in pipe 15 as has been described in connection with the other embodiments of the invention.

To increase the concentration of ethylene in the absorption oil in the cavern, the absorption oil is removed from cavern 1 via a pipe 95 and pump 97. Pipe 95 extends from a lower region of cavern 1 through shaft 5 to connect into pipe 81 and the oil inlet at the top of absorber column 83. The oil is then further contacted with fresh ethylene gas to be stored under conditions such as to produce the optimum concentration of ethylene in the absorber oil.

The following data constitute a specific operating example of the embodiment of my invention shown in Figure 4, wherein ethylene is absorbed in normal heptane in an absorption column of 6 theoretical plates to obtain the optimum concentration of ethylene in normal heptane given hereinbefore in Table I, i.e., 70 weight percent ethylene at 100° F.

With a normal heptane temperature of 100° F. and an ethylene pressure of 1000 p.s.i.a. from the outlet of compressor 29, the K constant for ethylene is 1.0, according to "Liquid-Vapor Equilibrium Relations in Binary Systems" by W. W. Kay, Industrial and Engineering Chemistry, volume 40, August 1948, pp. 1459-1464. The material balance and theoretical plate calculation for this system, following the method of T. K. Sherwood, "Absorption and Extraction," First Edition (1937), p. 119, McGraw-Hill Book Company, are as follows:

Ethylene feed rate=280 lbs./min.=10 lb. mols/min.
n-Heptane feed rate=90 lbs./min.=0.9 lb. mol/min.

Assume 75 percent absorption of ethylene,

$$\Sigma X_1 = \frac{10}{0.9}(0.75) = 8.33 \text{ mols ethylene/mol n-heptane}$$

Since $K=1.0$,

$$\frac{L'(1+\Sigma X_1)}{KG'} = \frac{0.9}{10}(1+8.33) = 0.84$$

Since a 6 theoretical plate column is being used,

$$\frac{(0.84)^6 - 0.84}{(0.84)^6 - 1} = \text{percent ethylene absorbed}$$

$$= \frac{.351 - .84}{.351 - 1} = \frac{.489}{.649} = 75.3 \text{ percent ethylene absorbed}$$

thus the foregoing assumption was correct.

lb. mols ethylene absorbed=10(.753)=7.53 lb. mols
ethylene absorbed=211 lbs. ethylene absorbed

Composition of ethylene-enriched n-heptane,

$$\text{weight percent} = \frac{211}{211+90} = 70.1 \text{ wt. percent ethylene}$$

and 29.9 wt. percent n-heptane

Lean gas out=2.5 lb. mols ethylene/min.

Thus, I have described the preferred embodiments of my invention as shown in Figures 1 through 4. A feature of my invention is that the high vapor pressure of the gas to be stored is reduced by absorbing the gas in an oil, thereby permitting storage of the gas-enriched oil in underground storage caverns at depths which are not uneconomical. The outstanding advantage of my invention is that substantially absorber oil-free gas can be easily withdrawn from such a storage system due to the stripping action of the vertical shaft which connects the cavern to the earth's surface. This stripping action is induced by the natural temperature gradient which exists in the earth about the cavern and shaft.

As has been indicated above, storage caverns in salt beds are readily adaptable to use in accordance with my invention. Many of these salt well storage caverns are located in the State of Texas and the natural temperature gradient for different locations along the Gulf Coast of Texas ranges from 1.6 to 2.2° F. per 100 feet of depth. These values and others are given in "Secondary Recovery of Oil in the United States," Second Edition, pp. 118-119, published by American Petroleum Institute, 50 West 50th Street, New York, New York, which also states that the estimated temperature of a subsurface formation, assuming a mean surface temperature of 74° F., is equal to the depth of a formation times the gradient, plus 74° F.

It will be readily appreciated by those skilled in the art that many variations, additions and substitutions can be made in the specific embodiments of my invention shown in the accompanying drawings without departing from the scope of the invention. For example, the stripping action of the vertical shaft can be aided by placing a packing material in the upper portion of the shaft, thereby to further insure that the absorber oil is removed from the ethylene gas and returned to the cavern when the gas is withdrawn from storage. Also, the temperature gradient existing in the earth can be enhanced and, thereby, the stripping action of the vertical shaft improved by installing cooling coils 99 in shaft 5 as is illustrated in Figure 4.

My invention is broadly applicable to the storage of high pressure petroleum gases, i.e., hydrocarbon gases having up to 3, inclusive, carbon atoms per molecule. Methane, ethane, ethylene, propane and propylene are specific operating examples of such gases which can be used in accordance with this invention. Mixtures of these gases can also be absorbed in an oil and stored in accordance with this invention.

I claim:

1. A method for introducing and subsequently withdrawing a high pressure petroleum gas from an underground storage system which comprises, absorbing said gas in an absorption oil, passing the mixture of the oil containing the absorbed gas into the underground storage system, and utilizing the natural temperature gradient in the earth to fractionally distill the oil and gas mixture to thereby withdraw said gas alone from said storage system.

2. A method according to claim 1 wherein said gas is methane.

3. A method according to claim 1 wherein said gas is ethane.

4. A method according to claim 1 wherein said gas is ethylene.

5. A method according to claim 1 wherein said gas is propane.

6. A method according to claim 1 wherein said gas is propylene.

7. A method for storing a high pressure petroleum gas underground which comprises, forming a shaft downwardly into the earth, forming a gas impermeable cavern in the earth which communicates with the lower end of said shaft, absorbing said gas in an oil, and passing said oil containing said absorbed gas into said cavern.

8. A method for storing a high pressure petroleum gas underground which comprises, forming a shaft downwardly into the earth to a depth of at least one foot per pound gauge pressure on fluids stored underground, forming a cavern in the earth which is connected to the lower end of said shaft, absorbing said gas in an oil having from 5 to 20 carbon atoms per molecule, at least partially filling the mixture of the cavern with said oil containing said absorbed gas, and utilizing the natural temperature gradient existing in the earth about said cavern and shaft to fractionally distill said oil and gas

mixture to thereby withdraw said gas alone from said cavern.

9. In a storage system comprising an underground cavern connected to the surface of the earth by a generally vertical shaft, a method of storing and subsequently withdrawing gas which comprises disposing an absorption oil in the cavern, passing gas to be stored into the cavern to a region below the surface of the oil so that the gas is absorbed by the oil, and subsequently fractionally distilling the oil-gas mixture in the shaft so as to withdraw gas alone from the storage system.

10. In a storage system comprising an underground cavern connected to the surface of the earth by a generally vertical shaft, a method of storing and subsequently withdrawing gas which comprises disposing an absorption oil in the cavern, passing gas to be stored into the cavern to a region below the surface of the oil so that the gas is absorbed by the oil, passing gas not absorbed by the oil from the region above the surface of the oil back to the region below the surface of the oil, and subsequently fractionally distilling the oil-gas mixture in the shaft so as to withdraw gas alone from the storage system.

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