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METHOD FOR PREVENTING CORROSION

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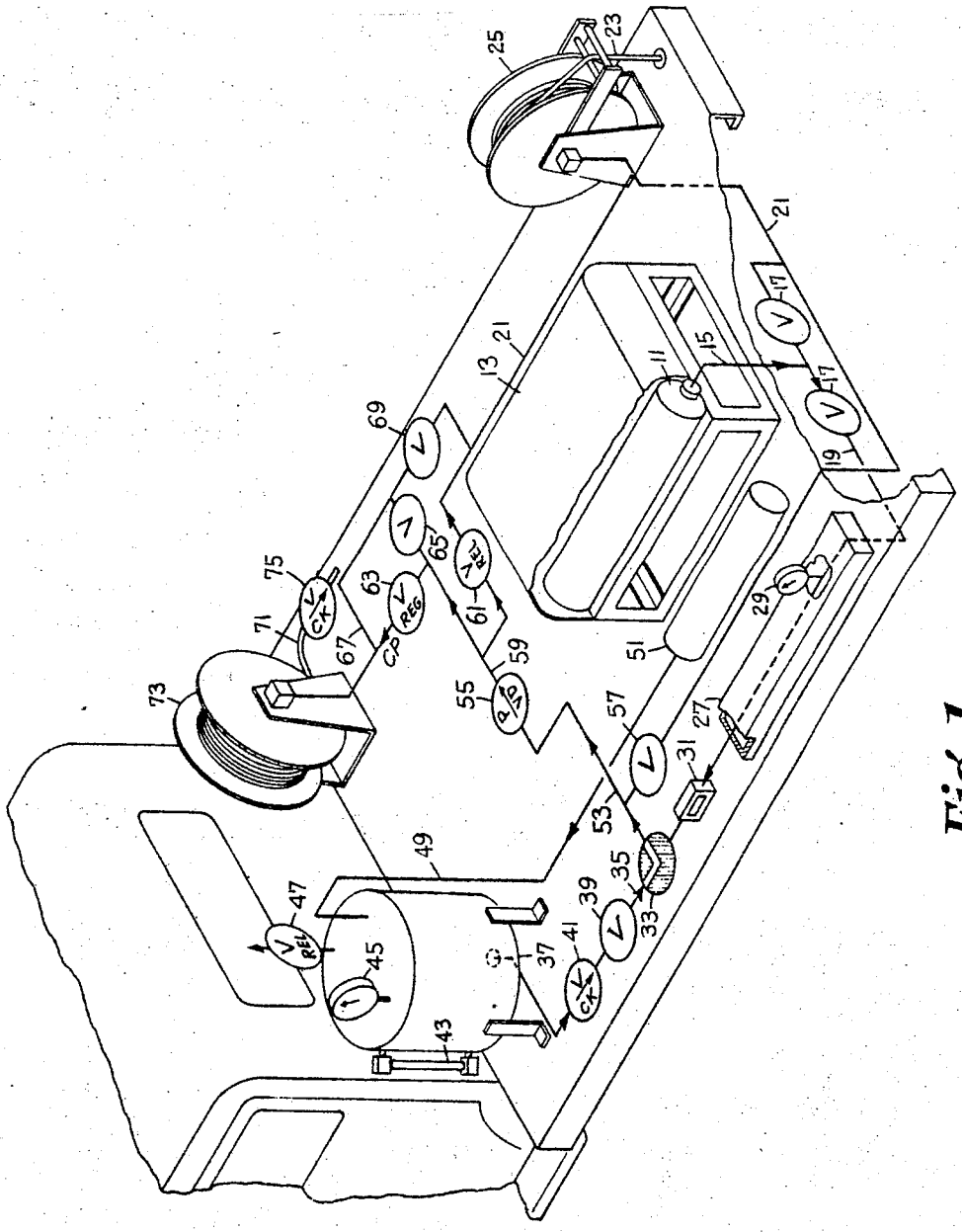



Fig. 1

ATTEST

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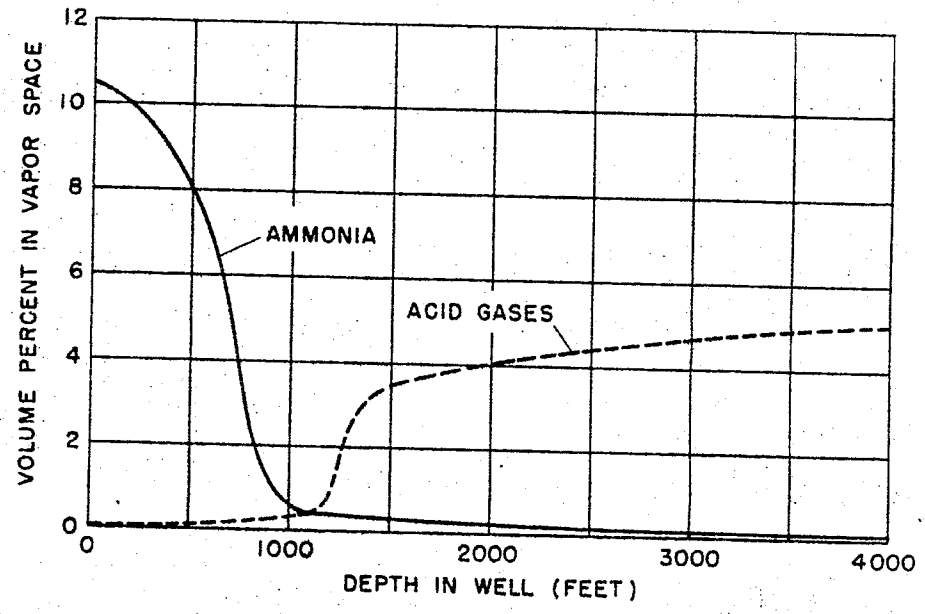



Fig. 2

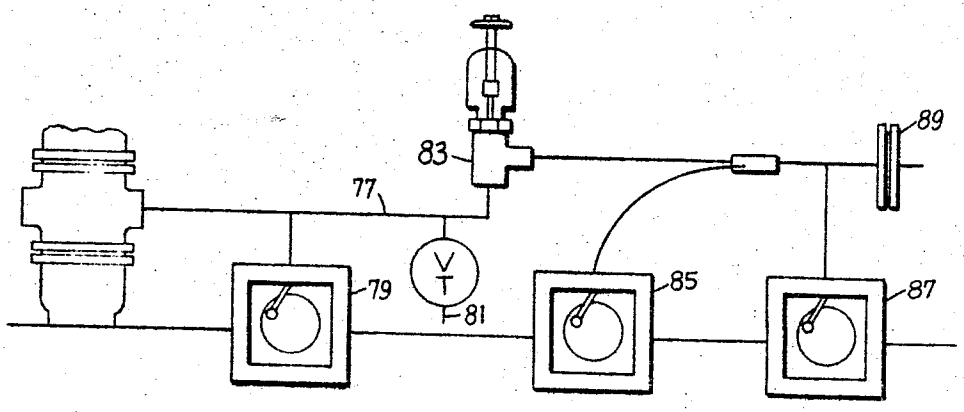



Fig. 3

ATTEST

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# METHOD FOR PREVENTING CORROSION

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This invention relates to inhibition of corrosion of metallic surfaces exposed to corrosive vapors. More specifically, this invention covers methods for injecting anhydrous ammonia or normally gaseous amines into the annular vapor space of oil, water and gas wells. In another aspect, this invention pertains to the amount of volatile inhibitor to be used. In still another aspect, this invention pertains to methods for injecting liquefied normally gaseous inhibitors.

In crude oil and natural gas production, various types of wells are used to either produce the underground fluids or to inject fluids into underground formations. Usually, these wells have an outer string of pipe called casing and an inner string of pipe called tubing. Since the tubing is smaller than the casing, there is a space between the two strings which is called the annulus or annular space. Normally, the fluids are flowed inside the tubing and a vapor space is formed in the annulus. In many instances, the entire annular space may be a vapor space and the vapor space, therefore, may extend thousands of feet into the ground. Frequently, the fluids flowing in the well contain water and acid gases like hydrogen sulfide, carbon dioxide or both. As the fluids are flowed, water vapors and acid gases collect in the annular vapor space. These gases cause corrosion of the tubing and casing exposed to the corrosive vapors. Various types of corrosion inhibition measures have been proposed to prevent this acid gas corrosion and the use of volatile inhibitors like ammonia has been suggested. But, no one has suggested a practical, safe way of introducing liquefied normally gaseous inhibitors like ammonia into this annular space especially when the pressure within the annular space exceeds the vapor pressure of the liquid inhibitor. Nor has anyone suggested effective limits on the amount of volatile inhibitor to be used in protecting the metal surfaces exposed to these corrosive vapors. In addition, the prior art does not teach an effective method of determining the depth of penetration of a volatile inhibitor into the annular vapor space. It is highly desirable to have an effective method of determining the depth of penetration of volatile inhibitors when the inhibitor is to be used in the vapor space of wells since theoretical calculations indicate that this inhibitor if injected at the surface will not readily diffuse through a long, narrow cylindrical area like that formed by the annular vapor space.

For the most part, moreover, prior art practices utilizing volatile inhibitors are designed for vapor zones where the pressure is below the vapor pressure of the liquid inhibitor and the inhibitor is added in its vaporized state or in some reacted form. These systems are impractical for high pressure equipment. Even in low pressure wells, moreover, it is undesirable to leave containers containing liquefied normally gaseous inhibitors unprotected at the wellhead since many of these inhibitors are highly toxic. In addition, whenever a large number of separate units are used to handle toxic materials and untrained personnel may be involved, the hazards are increased manyfold. It is, therefore, desirable to have a portable system for introducing the volatile inhibitor into not only high pressure systems but into low pressure systems as well. It is desirable that the injection equipment be portable



and designed to protect personnel from the hazards of handling toxic materials. Such equipment, moreover, should be capable of metering the amount of inhibitor used and lend itself to use with commercially available containers. The prior art does not provide equipment of this nature for handling liquefied normally gaseous toxic inhibitors.

Accordingly, it is the object of this invention to provide a method for preventing vapor space corrosion regardless of the pressure encountered utilizing liquefied normally gaseous inhibitors.

It is another object of this invention to provide a method for measuring the effective depth of penetration of gaseous inhibitors into the annular space of a well bore.

It is still another object of this invention to establish a method of preventing vapor space corrosion caused by acid gases like carbon dioxide, hydrogen sulfide or both.

Another object is to provide methods for preventing plugging of lines used in introducing the inhibitor and for purging such lines after use.

Another specific object of this invention is to provide such equipment especially suited to injection of liquefied normally gaseous corrosion inhibitors into the annular space of well bores.

For a better understanding of this invention, reference should be had to the accompanying drawings in which:

FIGURE 1 is a schematic, isometric view of the portable injection equipment.

FIGURE 2 is a depth of penetration curve for a typical well illustrating the amount of inhibitor required.

FIGURE 3 is a side, elevational view of the equipment utilized in obtaining data for the depth of penetration curve of FIGURE 2.

This invention relates to inhibition of corrosion of metallic surfaces exposed to corrosive vapors. This invention is divided into three sections with the first section covering methods for injecting anhydrous ammonia or normally gaseous amines into the annular vapor space of oil, water and gas wells. The second section pertains to the depth of penetration of the volatile inhibitor into the annular space of well bores and to equipment for measuring the same. The third section sets forth the amount of volatile inhibitor found necessary for protecting metallic surfaces exposed to corrosive acid gases in the annular vapor space of wells.

*Portable injection equipment*

The mobile injection equipment is designed to provide a safe, compact unit for injecting pure, volatile, toxic, liquefied normally gaseous inhibitors into high or low pressure systems. In general, the injection unit is mounted on a truck bed and comprises an inhibitor reservoir section with pump intake system, a water-miscible liquid storage section with inert gas pressurizing system and a calibrated pump section with high pressure injection and venting equipment. The mobile unit is fully equipped with safety and first aid equipment suitable to toxic inhibitors. The equipment was designed to permit operation from ground level and the high pressure system is located on one side of the truck away from the driver and most of the controls used during actual injection of the inhibitor.

While the injection equipment is suitable for all types of liquefied normally gaseous inhibitors, the following description of the injection equipment will be limited to anhydrous liquid ammonia and volatile amines like ethylamine, propylamine, isopropylamine, butylamine and all other volatile water-soluble amines.

Referring now to FIGURE 1, the mobile unit as illustrated has inhibitor reservoir 11. Covering inhibitor res-

ervoir 11 is cover 13 which permits heating of the liquid inhibitor during cold weather. Inhibitor reservoir 11 is connected by way of flexible hose 15 to manifold valves 17 interconnecting inhibitor reservoir 11 with inhibitor delivery line 19 and venting line 21. The manifold valves are located under the rear end of the truck bed so that the valves are operable from the ground and out of the way of loading and unloading the inhibitor. Moreover, in this position, the manifold valves can be covered and locked to prevent tampering while the unit is not in use.

Venting line 21 connects all the lines of the injection equipment with vent hose 23 on vent hose reel 25. Vent line 21 and vent hose 23 permit venting and draining of the injection lines to a point remote and downwind of the truck. The end of vent hose 23 is equipped with spikes (not shown) which can be driven into the ground to prevent the end of the hose from whipping.

Inhibitor delivery line 19 passes through insulated box 27 which allows cooling of the inhibitor in delivery line 19 during hot weather. On delivery line 19 is pressure gauge 29 which is used to measure the vapor pressure of the liquid inhibitor. On delivery line 19 after insulated box 27 is sight flow indicator 31 which has windows on both sides for see-through use to indicate when delivery line 19 is purged and full of liquid inhibitor, when there is flow in the line and when inhibitor reservoir 11 is empty. These features are important since the amount of inhibitor injected is measurable only so long as inhibitor delivery line 19 is full of liquid inhibitor.

Next to flow indicator 31 is two-way plug valve 33. One branch of two-way valve 33 connects with line 35 which in turn is connected to the bottom of storage tank 37. Storage tank 37 acts as a reservoir for a water-miscible liquid like glycol or alcohol, which liquid is inert to the inhibitor and acts as a purging fluid as hereinafter described. Between storage tank 37 and two-way valve 33 on line 35 are valve 39 and check valve 41. Check valve 41 acts as a safety valve to prevent liquid inhibitor from backing up into storage tank 37.

Storage tank 37 is equipped with sight gauge glass 43, pressure gauge 45 and pressure relief valve 47. Also connected to the top of storage tank 37 is line 49 which communicates with cylinder 51. Cylinder 51 contains an inert gas like helium or nitrogen of sufficient pressure to pressurize storage tank 37 to a pressure above the vapor pressure of the liquid inhibitor.

The second branch of the two-way plug valve 33 is connected to pump intake line 53 which in turn leads to inhibitor pump 55 and to vent line 21 by way of valve 57. Two-way plug valve 33, therefore, permits rapid switching from inhibitor to water-miscible fluid or vice versa without stopping inhibitor pump 55. Moreover, since the water-miscible fluid is at a pressure higher than that of the liquid inhibitor, the inhibitor does not vaporize and vapor lock inhibitor pump 55 when two-way valve 33 is used to switch pump intake line 53 from inhibitor to the water-miscible fluid in line 35.

Inhibitor pump 55 can be any suitable adjustable delivery pump capable of pumping at pressures exceeding the pressure in the equipment to be treated and capable of pumping at a rate sufficient to overcome vapor-locking tendencies of the liquefied normally gaseous inhibitor. The pump used herein was a duplex, positive displacement, single acting reciprocating plunger type pump with adjustable capacity. Inhibitor pump 55 can be motivated by a power take-off drive which is engaged from inside the truck. The truck engine r.p.m. is measured by a tachometer installed inside the truck. This allows adjusting the truck speed to correlate with the desired pump rate.

On the outlet or high pressure side of inhibitor pump 55 is injection line 59 which has three branches. One branch leads to pressure relief valve 61 which upon opening discharges the contents of line 59 to vent line 21. Pressure relief valve 61 operates as a safety valve should unusually high pressures be reached in injection line 59.

A second branch of injection line 59 leads to back-pressure regulating valve 63 which holds back pressure on the inhibitor in injection line 59 and prevents vapor-locking of inhibitor pump 55. Back-pressure regulating valve 63 also permits the injection equipment to be used for treating equipment with internal pressures below the vapor pressure of the liquid inhibitor. The valve, therefore, is set at a pressure dependent upon the material being pumped, e.g., for ammonia, it is set at 300 p.s.i.g.

The third branch of injection line 59 leads to valve 65 which is used to open by-pass line 67 around back-pressure valve 63. By-pass line 67 also has a branching line leading to valve 69 which upon being opened discharges the contents of by-pass line 67 to vent line 21.

Connected to back-pressure regulating valve 63 and by-pass line 67 is injection hose 71 which is wound around injection hose reel 73. The reel operates with an automatic rewind to facilitate handling of the injection hose. Injection hose 71 is a high pressure hose designed for this particular service.

The outlet end of injection hose 71 is equipped with check valve 75 which prevents high pressure fluids from the equipment being treated from entering the injection equipment. Check valve 75 has a manual by-pass (not shown) used to equalize pressure across the check valve to open the valve should it be closed during operation. The end of injection hose 71 is also equipped with a quick-connect union (not shown) having a double sealing feature. This allows rapid connection to the equipment to be protected and speeds operation while maintaining safety.

In operation, the mobile unit is parked from 40 to 50 feet crosswind from the equipment to be treated. Vent hose 23 is unreeled and staked down downwind from the mobile unit. Two-way valve 33 is opened to storage tank 37 containing the water-miscible liquid. All other valves are closed. The connections (not shown) on the equipment to be treated are purged of oxygen by venting some of the gas in the equipment to the atmosphere. Thereafter, injection hose 71 is unreeled and connected to these connections. After connecting injection hose 71 to the equipment to be treated, one of manifold valves 17 is opened to let liquid inhibitor from inhibitor reservoir 11 fill inhibitor delivery line 19. The operator checks sight-flow indicator 31 to note when the inhibitor delivery line 19 is full of liquid inhibitor. Inhibitor delivery line 19 must be kept full of liquid inhibitor at all times during an injection period. If the liquid vaporizes, the pump will vapor lock. In order to prevent the formation of vapors, it was discovered that the liquid inhibitor in the inhibitor reservoir 11 must be kept at a righer temperature than the liquid inhibitor in inhibitor delivery line 19. It was found that this temperature differential could be maintained by cooling inhibitor delivery line 19 on hotter days and heating inhibitor reservoir 11 on cooler days. To cool inhibitor delivery line 19, insulated box 27 is filled with ice or other refrigerant. To heat inhibitor reservoir 11, the exhaust from the truck can be piped over the reservoir or an electrical heating unit can be installed under cover 13.

After filling delivery line 19 with liquid inhibitor and insuring that the inhibitor will remain liquid, storage tank 37 is pressurized with inert gas from cylinder 51 to a pressure above the vapor pressure of the liquid inhibitor. This pressure is determinable from pressure gauge 29 in delivery line 19. Valve 39 in line 35 is opened to let water-miscible liquid flow from storage tank 37 through two-way valve 33 to pump intake line 53. The water-miscible liquid is an important feature of the injection process since water collects in the equipment connections and ammonia or volatile amines in the presence of water react with carbon dioxide to form a solid precipitate which may plug the equipment connections. The

water-miscible liquid removes water from these connections. The water-miscible liquid is also useful in purging oxygen out of the injection lines. Oxygen accelerates corrosion. The water-miscible liquid is also used to purge the equipment lines of traces of the toxic inhibitor which being hazardous could otherwise cause injury to operating personnel. Another advantage of water-miscible liquid is to insure future free operation of valves. The water-miscible liquid should be inert to the inhibitor and acid gases. Materials suggested are glycols, alcohols, and ketones.

Thereafter, the truck engine is set at the desired r.p.m. The optimum speed is predetermined to fit the type of inhibitor and pump capacity being used. For example, for ammonia, it was found that a speed of 1000 r.p.m. was optimum for a pump having a capacity of 0.52 gallon per minute at 51.1 strokes per minute. When a constant speed is used, the amount of inhibitor depends solely upon time and, therefore, an accurate means for metering the inhibitor is provided.

The pump power take-off is engaged thereby causing inhibitor pump **55** to pump water-miscible liquid from storage tank **37** until two-way valve **33** is switched to open pump intake line **53** to inhibitor delivery line **19**. Inhibitor is pumped for the desired period of time depending upon the amount to be injected. Immediately thereafter, two-way valve **33** is reswitched to line **35** and water-miscible liquid is pumped for sufficient time to purge the injection equipment of the inhibitor.

After pumping the water-miscible liquid, inhibitor pump **55** is stopped and the truck engine shut off. The valve on the equipment being treated is closed. The by-passed around check valve **75** is opened and vent valve **69** is opened to drain the injection hose and lines. Injection hose **71** is disconnected from the equipment just treated and rewound on reel **73**. All valves are then closed and the mobile unit taken to the next location. When the last injection is made, all lines are vented to vent line **21** to drain the injection equipment of toxic materials.

*Depth of penetration of the inhibitor into the annulus of the well*

As stated previously, it is highly desirable to have an effective method of determining the depth of penetration of volatile inhibitors into the vapor space of wells. Basically, the method developed herein comprises bleeding off the gas in the annular space at a measured rate and making periodic measurements of the inhibitor and acid contents. The equipment utilized in this method is illustrated in FIGURE 3.

The equipment illustrated is designed to flow the gas out of the annulus as a column at a steady rate of flow. The equipment permits collection of periodic samples of the gas and measurement of the physical conditions of the gas so as to calculate the depth at which a given sample corresponds. Communicating with the vapor space of the annulus of the well is bleed line **77** through which the gas is flowed. Near the well head, connected to bleed line **77**, are pressure recorder **79** and sampling line **81**. The flow rate through line **77** is controlled by variable choke valve **83**. Downstream of choke valve **83** and connected to line **77** are temperature recorder **85** and pressure recorder **87**. In the end of the line **77** is orifice plate **89**.

In performing a depth of penetration test, the gas is flowed out of the annulus as a column exactly as it existed in the well bore. In other words, each sample of gas analyzed can eventually be correlated with a certain depth as hereinafter described. The gas flow, therefore, once it is started should not be disrupted as this could cause mixing of the gases from various depths and give erroneous measurements. The rate of flow, moreover, should not be too rapid as this could cause turbulence in well bore and destroy the continuity of the gas column. On the other hand, the rate should not be too slow as this too could result in mixing of the gases from various depths. In addition, the rate of flow must be at least partially dependent upon the analytical techniques and the number of measurements to be taken. In the procedure used herein, the analytical equipment may include such devices as a portable chromatograph especially designed for measuring the inhibitor and acid gas contents, an Orsat designed for acid gas measurements to check the chromatograph, a Tutwiler apparatus for measuring hydrogen sulfide, a modified Nessler test for inhibitor concentrations below 2 percent, Hydrion pH papers, and lead acetate papers for hydrogen sulfide detection. Based on the above considerations, it was determined that a six hour test would be optimum for a 4000 foot well; therefore, prior to conducting a depth of penetration test, a flow rate was selected to give a six hour test dependent on the specific gravity of the gas, the length of the casing, the cross-sectional area of the annular space and the depth of the fluid level. After establishing a rate, the test procedure comprised the following method. Adjustable choke **83** was opened until the desired differential pressure was read on recorder **87**. The gas was flowed continuously for the desired period and samples of the gas were taken approximately every 20 minutes and analyzed for inhibitor, acid gas contents and pH utilizing the analytical equipment mentioned previously. Simultaneously therewith, the wellhead pressure was recorded by recorder **79** and the gas temperature was recorded by recorder **85**. After the desired period, choke **83** was closed and the depth of penetration test discontinued. The results of a depth of penetration test are illustrated in FIGURE 2 in which the analyses are plotted against depth. This figure was determined by standard gas calculations utilizing the pressure-volume-temperature relationships as shown by the recorders and the flow rate as indicated by the pressure drop across orifice **89**. Since these calculations are well known, it is felt that a more detailed discussion is unnecessary.

*Criteria for protection*

An inhibition method for protecting steel surfaces in the corrosive vapor zone of the annulus of wells utilizing liquefied normally gaseous inhibitors is only practical if an operable criterion for protection is presented. Of course, criteria are largely dependent on the type of system involved. For example, the nature of the system usually controls the conditions that can be measured to form parameters for the criterion. For example, in the vapor space of tanks, the inhibitor content adjacent the point of corrosion can easily be determined. On the other hand, to measure the inhibitor content at a point thousands of feet in the ground requires expensive tests like those described previously.

The depth of penetration tests mentioned previously have assisted in determining a workable criterion for the annuli of wells. These results have shown that sufficient inhibitor is present if the well is injected initially with at least one-fourth of the amount of inhibitor needed to react with all of the acid gases present to the depth at which protection is desired. This is illustrated by FIGURE 2 depicting the results of a penetration test on one of the wells tested. In this well, the desired depth of protection is 4000 feet. Preferably enough inhibitor should be added to react with at least one-third of the acid gases to the desired depth, but results indicate that lesser amounts will give protection to that depth as long as the amount of inhibitor used is at least one-fourth of the total acid gases present to the desired depth. Upper limits on the amount of inhibitor used are dictated by economics.

After injecting at least one-fourth of the amount of inhibitor needed to react with all of the acid gases present to the depth at which protection is desired, protection can be maintained thereafter by periodic injections of inhibitor in sufficient quantities to maintain liquid inhibitor

in the gas at the wellhead throughout the interval between injections. It was found that the rate of downward movement of the inhibitor exceeded the upward movement of the acid gases if the inhibitor concentration is maintained at this level. For example, out of 90 wells tested, most wells could be protected with a 25 pound injection of ammonia every six months and the desired concentration was more than adequately maintained. All indications were that even less amounts of inhibitor are required to maintain this concentration once the well has been injected with the quantities previously set forth.

The description herein presented has set forth preferred embodiments of methods and apparatus for injecting liquefied normally gaseous inhibitors into both high pressure and low pressure equipment, of methods and apparatus for measuring the depth of penetration of volatile inhibitors into the annular vapor space of wells and of methods for initiating and maintaining protection of steel surfaces exposed to acid gas vapors in the annuli of the wells. It will be understood that many modifications and variations may be made in the details hereinbefore set forth without departing from the scope of this invention which is limited only as defined in the appended claims.

We claim:

1. A method of injecting liquefied normally gaseous corrosion inhibitor into the vapor space of the annulus of a well when the gases in said vapor space contain carbon dioxide which method comprises connecting an inhibitor injection system to an inlet to said vapor space, pumping a first amount of water-miscible liquid into said inhibitor injection system, said first amount of said water-miscible liquid being at least sufficient to remove water from said inhibitor injection system and said inlet, cooling a liquefied normally gaseous corrosion inhibitor to a temperature sufficient to prevent vaporization of said inhibitor in said injection system, said liquefied normally gaseous corrosion inhibitor characterized by the fact that said inhibitor will react with carbon dioxide and water to form a solid salt, pumping through said inhibitor injection system a predetermined amount of said inhibitor, said inhibitor contacting said first amount of water-miscible fluid in said injection system, and pumping through said inhibitor injection system thence to said inlet and to said vapor space a second amount of water-miscible liquid, said second amount contacting said inhibitor and being sufficient to displace said inhibitor from said inhibitor injection system and from said inlet into said vapor space.

2. A method of injecting liquefied normally gaseous corrosion inhibitor into the vapor space of the annulus of a well when the gases in said vapor space contain carbon dioxide, which method comprises connecting an inhibitor injection system to an inlet to said vapor space,



pumping a first amount of water-miscible liquid into said inhibitor injection system, said first amount of said water-miscible liquid being at least sufficient to remove water from said inhibitor injection system and said inlet, heating a liquefied normally gaseous corrosion inhibitor to a temperature sufficient to prevent vaporization of said inhibitor in said injection system, said liquefied normally gaseous corrosion inhibitor characterized by the fact that said inhibitor will react with carbon dioxide and water to form a solid salt, pumping through said inhibitor injection system a predetermined amount of said inhibitor, said inhibitor contacting said first amount of water-miscible fluid in said injection system, and pumping through said inhibitor injection system thence to said inlet and to said vapor space a second amount of water-miscible liquid, said second amount contacting said inhibitor and being sufficient to displace said inhibitor from said inhibitor injection system and from said inlet into said vapor space.


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