Jan. 2, 1968 J. F. CHITTUM ETAL 3,361,660

REFERENCE ELECTRODE MOUNTING ASSEMBLY

Filed June 16, 1964

3 Sheets-Sheet 1

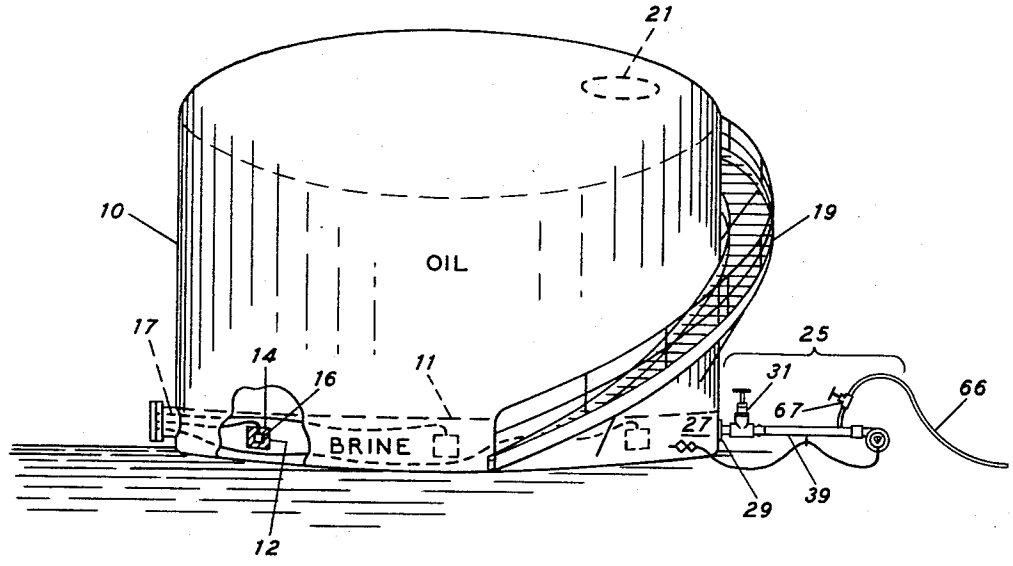


FIG. 1

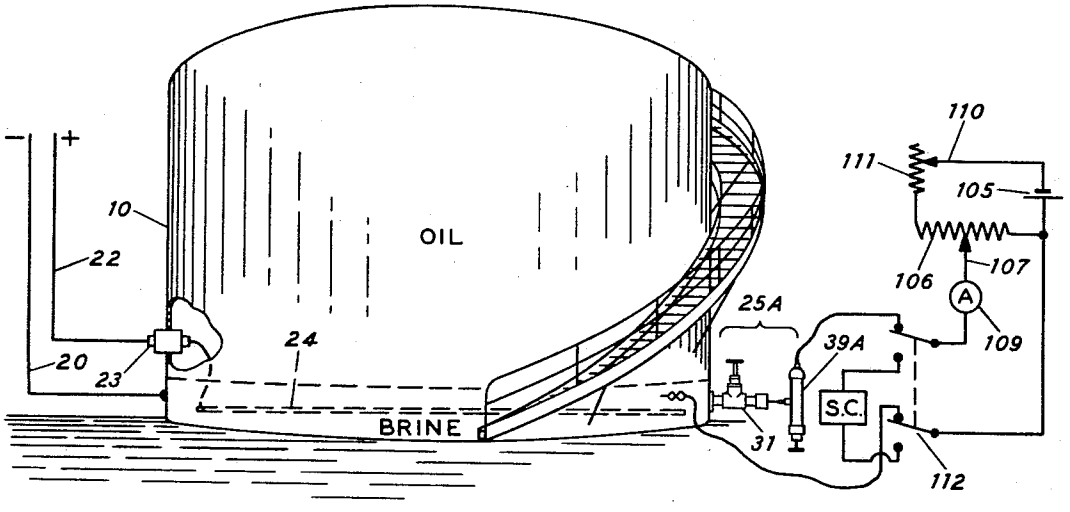


FIG. 5

INVENTORS
JOSEPH F. CHITTUM
HANK E. ENGLANDER
FREDERIC W. SCHREMP
BY J. E. Johnston
Ralph L. Freeland Jr.
ATTORNEYS

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REFERENCE ELECTRODE MOUNTING ASSEMBLY

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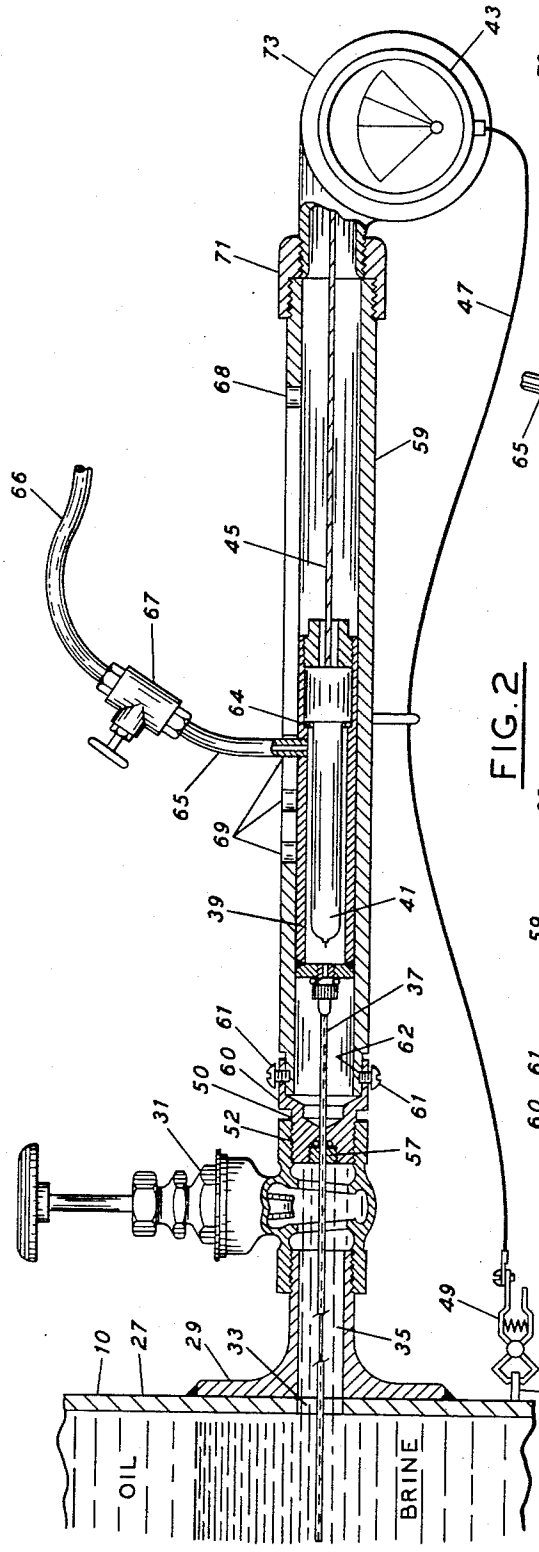


FIG. 2

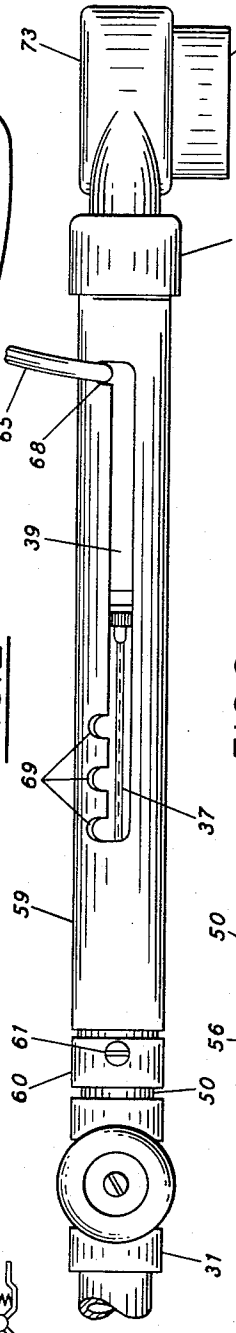


FIG. 3

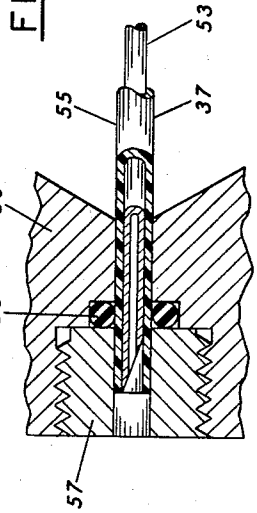


FIG. 4

INVENTORS
JOSEPH F. CHITTUM
HANK E. ENGLANDER
FREDERIC W. SCHREMP

BY P. E. Johnston
Ralph L. Freeland, Jr.
ATTORNEYS

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Filed June 16, 1964 3 Sheets-Sheet 3

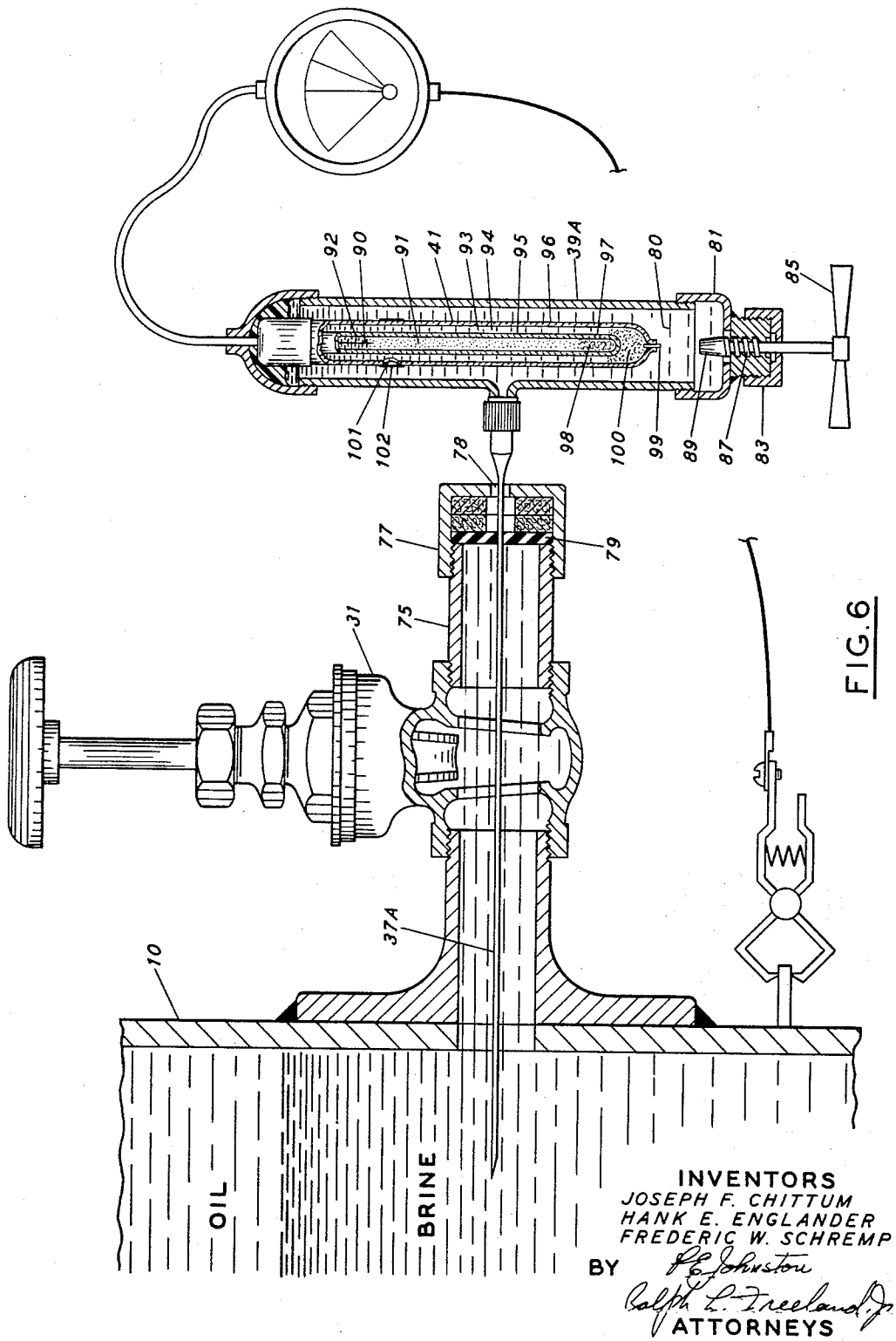


FIG. 6

INVENTORS
JOSEPH F. CHITTUM
HANK E. ENGLANDER
FREDERIC W. SCHREMP

BY H. E. Johnston
Ralph L. Freeland Jr.
ATTORNEYS

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REFERENCE ELECTRODE MOUNTING ASSEMBLY

Joseph F. Chittum, Whittier, Hank E. Englander, Costa Mesa, and Frederic W. Schremp, Fullerton, Calif., assignors to Chevron Research Company, a corporation of Delaware

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4 Claims. (Cl. 204—195)

This invention relates to electrolytic potential measuring apparatus. More particularly, it relates to a device for measuring the electrochemical potential of a steel tank in contact with a brine solution to determine the amount of cathodic protection that must be applied to the tank to prevent loss of metal by solution in the brine.

It is a primary object of the invention to provide an apparatus for measuring the electrochemical potential of the inner surface of a tank containing brine, which comprises a tubular member that can be inserted through an access opening, such as a gate valve that may be installed for such purpose or one that is already available, making electrolytic contact with the brine solution in the tank. The tubular connection permits direct electrolytic connection with the brine at a point near to, but displaced from the surface of the tank. Through this solution in the tubular member, the electrolytic connection is made to a reference electrode in a small body member connected to the tube, and this reference electrode is then connected to one terminal of a potential-indicating device. The other terminal is connected to the metal of the tank. By this arrangement, the cathodic potential then present at the inner surface of the tank can be measured.

It has long been known that it is desirable to measure the actual potential that exists between a brine solution and the inner surface of a tank, such as a crude oil storage tank or wash tank. However, this brine solution, or salt water, is usually at the bottom of the tank under the crude oil. In tanks with a capacity of several thousand barrels, the major part of the tank may be filled with oil and only the bottom few inches or few feet will contain the brine. This small amount of brine, however, frequently requires that the tank be placed under cathodic protection to prevent electrolytic solution of the tank's iron into the brine. Protection of the tank is often provided by a sacrificial anode, such as a magnesium cylinder that is installed in the brine of the tank and electrically connected by copper cable to the tank wall. The anode is consumed or dissolved to generate the current that is necessary to bring about the required protective potential on the inner surface of the tank. The tank is protected by current from a direct current source, and it is essential that the current be regulated to produce a negative potential of the correct magnitude on the surface of the tank in contact with the brine to oppose the tendency for iron to go into solution.

It has been known that this negative potential between the tank and the brine can be measured by apparatus that includes a standard reference electrode, but it has been necessary, if the cost warranted measurement at all, to lower the electrode through an access hole in the top of the tank possibly down through a body of oil on top of the brine. A particular difficulty in this procedure is that the reference electrode may become coated with crude oil unless special precautions are taken so that an erratic reading is obtained. There is also a danger of losing the reference electrode in the tank. Additionally, the reference electrode may not be properly placed in the brine to give a correct reading. To complete the measurement, the potential of the cell made up of reference electrode and the inner surface of the tank must be determined through wires running back to the top of the tank and from the tank itself to measuring instruments.

In a preferred embodiment of this invention, the foregoing problems are eliminated by connecting a gross body member into a fluid tight engagement with a gate valve that has either been specially installed in the tank below the brine-oil interface or which is already present as a part of a water drop out, or separation system, connected to the tank. The gross body member includes a small body member containing the reference electrode and forming a fluid chamber connected to the elongated tubular member forming a needle, or probe, that can be injected through the fluid tight opening in the gate valve and the interconnecting flange member on the tank so that it terminates at a point a few inches within the tank. The fluid chamber contains such standard electrode that is best adapted to be electrically connected to the brine in the tank by fluid in the probe. In said preferred form, the brine in the tank flows out through said probe to fill the fluid chamber. The inside of the tank contacting the brine, the "salt bridge" created by this fluid, and the standard electrode form a cell with a potential that is measured by a suitable high impedance voltmeter when such meter is connected across the cell. If the tank is under adequate cathodic protection, that is, a sufficient electrical current of the correct polarity is being supplied to the tank, the indicated negative potential will be a predetermined value sufficient to prevent solution of the iron. However, if direct current is connected to the tank in the wrong sense, reversed polarity, or if a sacrificial anode, such as magnesium or other metal having a more negative potential than iron, has been consumed, the potential-indicating means will indicate nonprotection. If a sacrificial anode has been consumed, this potential will be more positive than −0.78 volt when a saturated calomel electrode is used as the reference. If an external current source is used with the wrong polarity, the measured value might be several tenths of a volt less negative than the desired value because the external current acts in the same direction as the corrosion current between the steel and the brine.

In accordance with our invention, the potential of the inner surface of the tank can be measured quickly and conveniently at ground level, so that such measurements can be made often by untrained workers and with minimum hazard to the operator.

Further objects and advantages of the invention will become apparent from the detailed description taken in conjunction with the accompanying drawings which form an integral part of this application.

In the drawings:

FIG. 1 is a schematic, side elevation view of an oil storage tank to which a preferred form of the invention has been applied.

FIG. 2 is an enlarged view partially in cross section of the form of apparatus illustrated in FIG. 1.

FIG. 3 is a top plan view of the apparatus shown in FIG. 2.

FIG. 4 is an enlarged, cross-sectional view illustrating the probe, or needle, portion of the testing apparatus shown in FIG. 2.

FIG. 5 is a schematic, side elevation view of an alternate form of apparatus constructed in accordance with the present invention.

FIG. 6 is an enlarged view of the FIG. 5 apparatus in vertical cross section, and includes a detailed, cross-sectional view of a standardd, or reference, calomel cell as used in the present invention.

Referring now to the drawings, there is shown in FIG. 1 a typical oil storage tank 10 of a type frequently used for temporary storage of produced crude oil. Such tanks

normally require cathodic protection because in most oil production, salt water or brine is produced with the oil. The oil, of course, is less dense than the brine, so the brine settles as a stratum at the bottom of the tank, as indicated. The interface between the oil and the brine phases is indicated by dashed line **11**. This interface is not necessarily a sharp plane, but may be an emulsion, or diffuse layer, of oil and water. The oil, of course, is nonconductive and tank **10** requires no protection from corrosion by the oil. However, the brine forms with the iron of tank **10** an electrochemical corrosion cell that results in solution of the iron in the brine and either evolution of hydrogen or consumption of oxygen in the presence of small amounts of acid or oxygen. Acid can accompany the oil and water from the well; oxygen is also introduced inadvertently when the oil and water are pumped into the tank from the well. To prevent such corrosion, it is common to provide cathodic protection that will polarize the inside of the tank with sufficient direct current of proper negative polarity so that suitable negative electrical potential is created between the iron and brine. This potential must be about —0.770 volt when measured with the standard saturated calomel electrode as reference. Such cathodic protection can be provided by the use of a sacrificial anode **12** which usually comprises a body **14** made of magnesium surrounding a copper core **16**. Core **16** electrically contacts tank **10** through conductor **17**. The arrangement shown is schematic of one form of cathodic protection frequently used where an external direct current supply is not readily available. In some producing fields, direct current is supplied from a rectifier (not shown) by line **22** through insulator **23** to a permanent anode, such as conductor rod **24**, immersed in the brine (FIG. 5). The current is returned to the rectifier by line **20**. The rectifier in turn is connected to a public utility power line.

The only practical way to find out if the protection means is functioning, prior to this invention, has been to measure the potential between the metal surface of tank **10** and the brine from the top. To measure this potential, it was necessary to take the equipment to the top of tank **10**, for example, by stairway **19**, and then lower a potential reference electrode through an access opening (indicated in dotted outline by numeral **21**). To contact the brine phase at the bottom of the tank, the testing apparatus must pass through the oil phase. Such a procedure has generally been so inconvenient and the results undependable that it has found little acceptance as a continuing maintenance technique. At best it is used only at infrequent intervals.

As distinguished from these previously known techniques, the present invention permits simple and rapid measurement of the electrochemical potential between metal and the brine at ground level. This measuring apparatus is designated as **25** in FIG. 1 and is more specifically shown in FIGS. 2, 3 and 4.

An important feature of the apparatus shown in FIGS. 1 to 4 is that there be available an access valve from the outside of the tank and directly through wall **27** into the brine phase in tank **10**. In many field production tanks used for production metering, separation or storage of crude oil, or refined products, a water "knockout" or withdrawal line is already available at the desired level. If so, it can be fitted to include a connector, such as flange **29** welded to wall **27** near the bottom of tank **10**, and a gate valve **31** directly connected to the flange. Where such an opening is not available, it is advantageous to install gate valve **31**. This can be done when tank **10** is empty by boring access hole **33** (FIG. 2) in wall **27**. If it is not convenient to empty tank **10**, flange **29** can be installed by a technique known as "hot tapping." Briefly, this technique requires welding flange **29** to the outside of wall **27**, attaching valve **31**, and to the valve, attaching a packing gland (not shown in FIG. 2). A drill bit, proceeding through the packing gland, and the open gate valve, penetrates the tank wall. The bit is retracted through the gate valve, which is then closed. The packing gland is removed and the exterior fittings shown in FIG. 2 are attached to the gate valve.

While other forms of valves can be used, gate valve **31** is preferred so that a straight-through passageway is provided by bore **35** from the outside of tank **10** into the brine phase. This permits exact measurement of the distance that probe, or needle, **37** must be inserted into tank **10** so that the end is a few inches from wall **27** and well into the brine phase. The prime purpose of probe **37** is to form a fluid conduit path, known as a "salt bridge." A portion of the brine in tank **10** is admitted to body member **39** through probe **37** to contact reference cell **41**. Probe **37**, thus, completes an electrolytic connection from reference, or standard cell **41** to the inner surface of wall **27**. The potential difference then existing between metal and brine with respect to reference electrode **41** is indicated by high impedance voltmeter **43**. One input terminal of meter **43** is connected to electrode **41** by cable **45**; the other terminal is connected to a return circuit by lead **47** and alligator clip **49** which is clamped to any convenient metal surface connected to the tank, for example, lug **51** welded to the outside of tank wall **27**.

It is apparent that, except for flange **29** and gate valve **31**, apparatus **25** is not intended to be integral on each tank. The portable portion of measuring device **25** is best seen in FIG. 2. As indicated, it is suitably connected to the tank installation by plug **50** whose pipe threads **52** engage the internal pipe threads of valve **31**.

Plug **50**, with probe member **37**, extending through its center forms a fluid-tight seal so that the gate valve **31** can be opened to permit free access to the brine phase in tank **10**. In the embodiment of FIGS. 1–4, probe **37** comprises a stainless steel tubing **53** and an insulating cover **55** that prevents electrical contact between metal needle **53** and the metal surface of valve **31**, flange **29** and wall **27** of tank **10**. The purpose of this arrangement is to insure that the only internal electrical connection between tank and reference electrode is through the electrolytic solution that flows into the center passageway of needle **53** from tank **10**. As best seen in FIG. 4, O-ring **56** seals probe **37** to plug **50** by frictionally surrounding cover **55**. Plug **57** holds O-ring **56** in place.

To attach the measuring unit to valve **31**, tubular member **59** including annular groove **62** rotatably mounts within collar **60** or plug **50**. Screws **61** threaded into collar **60** act as keys in annular groove **62** to keep tube **59** coupled to plug **50**. By this connection, plug **50** is free to rotate but when screwed into gate valve **31**, makes a fluid-tight connection. Tubular member **59** guides body member **39** so that metal probe **37** will not touch the metal parts of the tank assembly. It also acts as a locking member for body member **39**. Standard electrode **41**, whose construction will be described more fully in connection with FIG. 6, is mounted so that it seals one end of body **39**. This seal is made fluid-tight by O-ring **64**. Tube **65** taps into the side of body **39**, and with hose **66** and valve **67**, controls the flow of brine from tank **10** into body member **39**. The flow may be continuous, but need not be. Tube **65** also serves as a means for locking body **39** in a retracted position in notch **68**, as indicated in FIG. 2, or in one of three notches **69** when probe **37** is inserted into tank **10**. Notches **69** are used to control the exact distance that the forward end of probe **37** extends into the tank. They also permit the body member to be locked against the hydraulic force of the liquid head in tank **10** acting to expel probe **37**. In the arrangement of FIG. 2, the outer end of tube **59** includes a mounting bracket **71** that suitably mounts a reel and voltmeter housing **73**. Lead **45** may be wound and unwound on a reel (not shown) when body **39** is moved in tube **59**. A unitary assembly of all the measuring system includes voltmeter **43** which also conveniently mounts on housing **73**.

FIG. 6 shows an alternate form of apparatus that may be used to carry out the present invention. In this

embodiment, pipe nipple **75** is threaded to gate valve **31** as a permanent part of the field installation. Cap member **77** mounts on nipple **75** and includes a perforation or opening **78** and a rubber or plastic diaphragm **79** that forms a fluid-tight connection with probe member **37A** when it is injected into the brine phase of tank **10**. In FIG. 6, body member **39A** forms an enclosed chamber that can be filled prior to use with a saline solution, such as potassium chloride, indicated as **80**. Body **39A** is closed by cap **81**. A rotatable piston actuator, indicated as **83**, mounts on cap **81**. Piston **83** permits solution **80** to be ejected from body **39A** through probe **37A** to complete an electrolytic solution path between calomel electrode **41** and tank **10**. As indicated, piston actuating means **83** includes a handwheel **85** and a threaded member **87**. Member **87** cooperates with threads in cap assembly **81** to move tapered member **89** inwardly to displace solution **80** through probe **37A**. The volume of member **89** is calibrated to equal the amount of fluid required to fill probe **37A**.

Reference, or standard, electrode **41** is preferably a conventional calomel electrode. It comprises a platinum wire **90** that is electrically connected to a mixture of mercury and mercurous chloride (generaly referred to as calomel) **91**. Contact between wire **90** and calomel mixture **91** is usually made through a body of mercury **92**. Mixture **91** is wetted by a potassium chloride solution **93** that fills annular space **94** between the inner tube **95** and outer tube **96**. This fluid contact is preferably through a weephole **97** and glass wool fibers **98** that hold calomel mixture **91** in place. External connection to solution **80** is then through a wood fiber **99** mounted in the lower end of cell **41**. As indicated schematically, solution **93** is normally saturated, and to assure that it remains so, crystals of potassium chloride **100** are indicated in the bottom of cell **41**. An opening **101** in the side of wall **96** permits solution **93** to be replenished or replaced. A cover of rubber tubing or electrical tape **102** covers hole **101**. It is preferably perforated with minute pin holes to assure pressure equalization between solution **80** in body **39A** and the interior of electrode **41**. Such an electrode generates a potential of +0.246 volt with respect to the standard hydrogen electrode.

FIG. 5 illustrates another way of measuring the potential between the brine and the tank. As there indicated, battery **105** and potentiometer **106** are connected to produce an IR drop whose potential will balance any potential sensed between measuring device **25A** and tank **10**. The null point is indicated by ammeter **109**. Potentiometer **106** may be calibrated by adjustment of contact **110** on slidewire resistor **111** when double-pole, double-throw switch **112** connects the potentiometer circuit to another standard cell, designated as SC. In this way, the position of slide **107** on potentiometer **106** can be used to indicate the potential between the tank and brine.

From the foregoing description it will be apparent that the primary advantage of this invention is that the actual potential existing between the metal wall of a tank and a corrosive fluid, such as brine, may be readily measured without special preparations or technically trained operators. These measurements may also be made with a minimum of risk since they are made at substantially ground level. And, a single unit is usable on a number of different tanks.

Various modifications and changes in the apparatus will be apparent to those skilled in the art. Among such changes are the materials and the form of probe member **37**. Depending upon the temperature and the condition of the corrosive solution into which the probe is inserted, certain plastics may be used as the probe member. For example, Teflon or nylon tubes have adequate rigidity at temperatures up to about 300° F. and are quite satisfactory for substitution in this arrangement. Additionally, the plastic probe member may have a reasonable amount of flexibility to pass obstructions in piping or valves that may already be available and usable as access means to reach a solution whose potential must be measured relative to a tank with apparatus constructed, as detailed in FIG. 2 or FIG. 6, and the plastic probes are naturally insulated.

It is also apparent that a solution contact can be made either by pulling brine from the tank or by adding an outside solution to the measuring probe.

Other changes falling within the terms of the appended claims are intended to be included therein.

We claim:

1. Potential-detecting apparatus for determining the potential existing between the inner surface of a tank and an electrolytic solution contained therein which comprises

a body member adapted to contain an electrolytic solution,

a reference electrode in said body member and electrolytically connected to said solution,

an elongated tubular needle member connected to said body member for establishing an electrolytic solution flow path therethrough,

a coupling member adapted to be detachably connected to a fitting on the tank, said tubular needle member being in slidable and fluid tight engagement with an opening in said coupling member,

means for extending and retracting said tubular needle member relative to said coupling member so that an end of the said tubular needle member may be extended a known distance into the electrolytic solution in said tank,

and means for detecting the potential difference between said reference electrode and said tank through said electrolytic solution to indicate the extent of cathodic protection then existing between said inner surface of said tank and said electrolytic solution.

2. Apparatus for measuring the potential between a brine solution and a steel tank to determine the extent of cathodic protection then existing on the inner surface of said tank which comprises

an elongated housing, a coupling member rotatably mounted at one end of said housing and adapted to threadably engage a fitting on said tank that opens into a portion of said tank containing brine,

an elongated tubular member slidably engaged with said coupling member,

fluid sealing means between said elongated tubular member and said coupling member,

a body member connected to said tubular member, said body member being slidable within said housing member when said tubular member is extended or retracted with respect to said coupling member, said body member forming an enclosed chamber for receiving a portion of the brine from the tank through said tubular member,

means supporting a reference electrode within said chamber, said reference electrode being electrolytically connectable to said brine in said tank through said body member and said tubular member,

and means electrically connected between said reference electrode and said tank for detecting a potential difference, said potential difference being representative of the cathodic protection of the surface of said tank in contact with said brine.

3. Apparatus in accordance with claim **2** with the addition of

conduit means connected at a substantial angle to said body member,

an elongated slot formed in said housing means for receiving said conduit,

and notch means formed in said housing adjacent said slot to lock said conduit and said body member relative to said housing to prevent extrusion of said elongated tubular member by the hydrostatic head of fluid in said tank.

4. Apparatus in accordance with claim 3, with the addition of valve means for controlling the flow of brine from said tank through said body member, said valve means being located in said conduit.

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ROBERT K. MIHALEK, *Primary Examiner.*

JOHN H. MACK, *Examiner.*

T. TUNG, *Assistant Examiner.*