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ELECTROLYTIC BRIDGE ASSEMBLY

Filed March 9, 1961 2 Sheets-Sheet 1

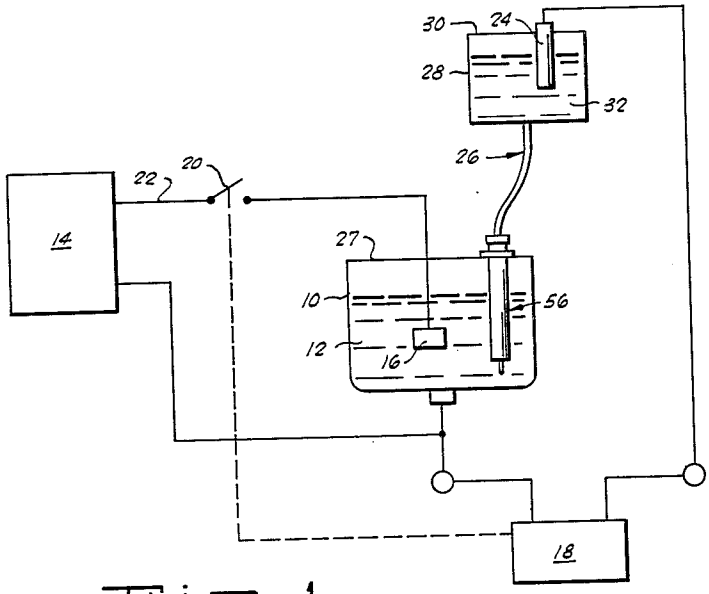


Fig. 1

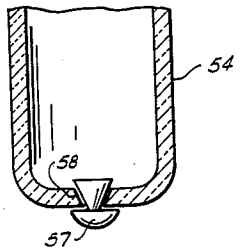


Fig. 4

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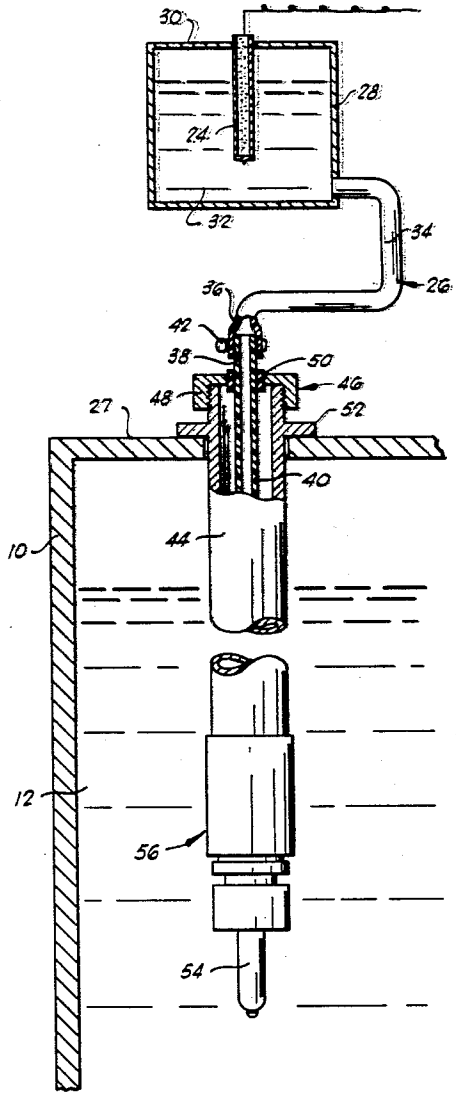


Fig. 2

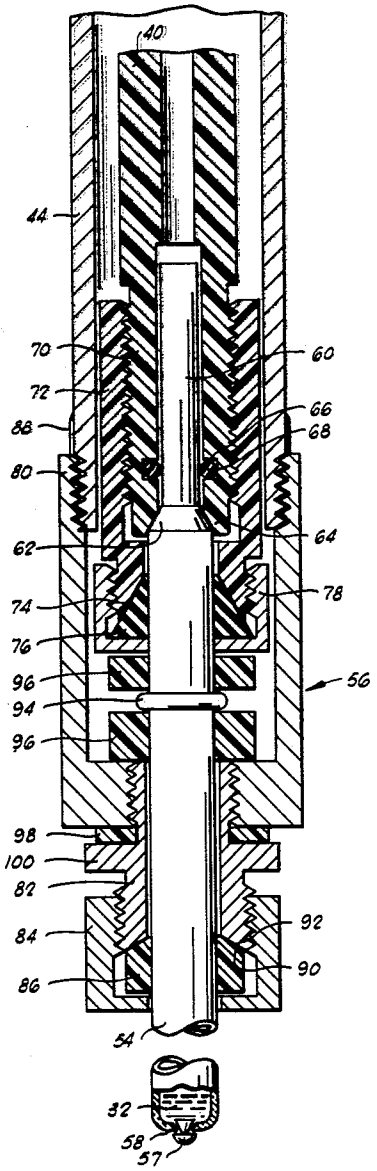


Fig. 3

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ELECTROLYTIC BRIDGE ASSEMBLY

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7 Claims. (Cl. 204—195)

This invention relates to an electrolytic bridge assembly which may be utilized to provide a liquid, electrically conductive path between a standard electrode and a corrosive solution which is maintained under pressure. More particularly, but not by way of limitation, the present invention relates to an electrolytic bridge assembly which may be utilized in systems for inhibiting the corrosion of metal containers by the passage of an anodic current through an electrolyte held in the container when such electrolyte is maintained under pressure.

In co-pending United States application Serial No. 797,986, filed March 9, 1959, a novel electrolytic bridge assembly which is especially well adapted for use in anodic corrosion control systems is disclosed. The electrolytic bridge assembly described in said co-pending application is utilized to provide a liquid, electrically conductive bridge between the standard electrode which is used in such systems and the corrosive solution contained in the vessel which is to be protected. A bridge of this type is required in such systems because the corrosive solutions which are frequently encountered are harmful to most standard electrodes and, moreover, it is necessary that contamination of the corrosive solution by contact with the electrode be avoided.

In previously known electrolytic bridges of the general type described in said co-pending application, it has been the practice to employ a tubular member which extends into the corrosive solution and provides a liquid junction between the electrolyte in the bridge and the corrosive solution. The tubular member which extends into the corrosive solution is frequently termed a weeping glass bridge and is usually provided at its lower end with a minute passageway to permit the electrolyte inside the bridge to be gradually dripped from the lower end thereof into the corrosive solution. A conduit of some type extends from the upper end of the weeping glass bridge to a reservoir located outside of the vessel containing the corrosive solution, and the reservoir is filled with an appropriate electrolyte so that a fresh supply of electrolyte is constantly available at the liquid junction for making electrical contact with the corrosive solution. The standard electrode is suspended in the electrolytic solution in the reservoir and is thus insulated by the intervening column of electrolyte from contact with the corrosive solution in the vessel.

Although electrolytic bridges of the type described have functioned quite well when the vessel containing the corrosive solution is relatively shallow, substantial difficulty has been encountered in using such bridges when the depth of the vessel is relatively large, say, in the order of five to twenty feet. The alternative is then presented of extending the conduit connected to the upper end of the glass bridge below the level of the corrosive solution in the tank, or of making a single glass tubular member which is long enough to extend the necessary distance below the surface of the liquid. The latter alternative is, of course, not a satisfactory solution to the problem since any agitation of the corrosive solution is likely to break the elongated glass tube with the result that the corrosive solution becomes contaminated with an excessively large amount of the electrolyte. On the other hand, if the joint between the tubular glass member and the conduit intervening between the glass member and the reservoir is located beneath the surface of the corrosive solution, an opportunity is thereby afforded for leakage of electrolyte or corrosive solution to occur between the conduit and glass tubular member, thus contaminating the corrosive solution. Moreover, the conduit which is utilized must then be constructed of a material which is not subject to attack by the corrosive solution, since such attack would also permit the solution to become undesirably contaminated.

Serious problems have also arisen in the use of previous types of electrolytic bridges in anodic control systems when the solution contained in the vessel to be protected has been maintained under superatmospheric pressure. One of these problems is the difficulty of maintaining a constant flow of a minute amount of electrolyte through the bridge and into the solution in the vessel. Since the reservoir containing the electrolyte is open to atmospheric pressure, it is apparent that the imposition of superatmospheric pressure upon the solution in the vessel will interfere with the constant flow of a minute amount of fresh electrolyte through the bridge and into the solution, and may, in some cases, even result in some of the corrosive solution being forced upwardly through the glass tube and the conduit and into the electrolyte reservoir where it may then attack the standard electrode. When attempts have been made to maintain the constant flow of electrolyte into the corrosive solution by the imposition of pressure upon the electrolyte contained in the reservoir, it has been found that the connection or joint between the glass tube and the conduit has not afforded a sufficient seal to prevent undesirable leakage of electrolyte through the connection and into the solution contained in the vessel. This situation is, of course, highly undesirable since it is of the utmost importance that the highest purity of the solution in the vessel be preserved consistent with the establishment of an electrolytic path between the standard electrode and the solution by means of the minute seepage of the electrolyte through the tiny orifice in the bottom of the weeping glass bridge.

The present invention contemplates a novel electrolytic bridge assembly which is especially well adapted for use in a vessel containing a corrosive solution under pressure. In a preferred embodiment of the invention, the electrolytic bridge assembly employs an electrolyte reservoir of a type similar to those which have previously characterized electrolytic bridge assemblies, but modified to facilitate the imposition of a superatmospheric pressure upon the electrolyte contained in said reservoir. A suitable glass tube of the weeping glass bridge type is provided at the lower end of the bridge assembly for immersion in a corrosive solution contained in a vessel to be protected. The glass tube is connected at its upper end by means of a novel sealing means to a tubular member constructed of a plastic material which is relatively inert to chemical attack and is characterized by high melting point and high mechanical strength. Materials of construction of the tubular member which have been found to be especially suitable are the fluorocarbon resins. A length of flexible tubing connects the upper end of the plastic tubular member to the reservoir to facilitate the flow of electrolyte from the reservoir into the plastic tubular member and the weeping glass bridge.

For the purpose of affording protection to the weeping glass bridge and the elongated plastic tubular member connected thereto against violent agitation of the corrosive solution, an elongated metallic sleeve of high mechanical strength is telescoped over the plastic tubular member and a portion of the weeping glass bridge, and is utilized to vertically support the bridge assembly in the corrosive solution from the top of the vessel in which it is contained. The metal of the sleeve is preferably formed of the same material as the vessel containing the corrosive solution in order to avoid contamination of the

solution and improper function of the anodic corrosion control system due to erroneous potential readings. A novel seal is provided between the lower end of the metallic sleeve and the weeping glass bridge in order to prevent the corrosive solution from infiltrating the sleeve and attacking the seals between the plastic tubular member and the weeping glass bridge.

The sealing means which is provided between the plastic tubular member and the weeping glass bridge is an important feature of the present invention and is in effect a triple seal assuring that none of the electrolyte will be permitted to seep through the joint between the plastic tubular member and the glass bridge and come in contact with the metallic sleeve surrounding the joint. It is highly desirable to avoid such contact resulting from leakage of the electrolyte, since the effect of the establishment of a conductive path between electrolyte contained in an intermediate portion of the bridge and the internal wall of the metallic sleeve is an erroneous potential measurement by the standard electrode.

An important object of the present invention is to provide an electrolytic bridge which may be effectively utilized to establish a conductive path between a corrosive solution which is maintained under pressure and a standard electrode.

An additional object of the present invention is to provide an electrolytic bridge which may be utilized in an anodic corrosion control system of the type employed to protect vessels and tanks of relatively large depth against attack from corrosive solution contained therein.

An additional object of the present invention is to provide an electrolytic bridge between a standard electrode and a corrosive solution which functions efficiently when the corrosive solution, the electrolyte, or both, are maintained under superatmospheric pressure.

An additional object of the present invention is to provide an electrolytic bridge which may be utilized at relatively great depth in a body of corrosive solution without sustaining mechanical damage or undergoing chemical attack.

Yet another object of the present invention is to provide an electrolytic bridge between a standard electrode and a corrosive solution maintained under pressure, which bridge is constructed to prevent excessive leakage of the electrolyte into the corrosive solution, and to prevent infiltration of the corrosive solution into the electrolyte contained within the bridge.

An additional object of the present invention is to provide an electrolytic bridge assembly which may be effectively utilized in a system for controlling corrosion by the use of anodic current even when the corrosive solution with which the bridge is in contact is maintained under pressure.

A further object of the present invention is to provide an electrolytic bridge assembly which is of rugged construction and which functions efficiently over long periods of operation.

Additional objects and advantages of the invention will be evident from the following detailed description, when read in conjunction with the accompanying drawings which illustrate our invention.

In the drawings:

FIGURE 1 is a schematic illustration of an anodic corrosion control system in which the present invention is incorporated.

FIGURE 2 is a view in elevation of the electrolytic bridge assembly of the present invention with parts broken away to show certain details of construction.

FIGURE 3 is a vertical sectional view through the portion of the electrolytic bridge which is immersed in the corrosive solution.

FIGURE 4 is a detail view showing in section the lower end of the weeping glass bridge.

Referring now to the drawings in detail, and particularly to FIG. 1, reference character **10** designates a vessel to be protected from attack from a corrosive solution **12** by an anodic current control system. The corrosive solution **12** is an electrolyte and may be either acidic or alkaline. A source **14** of direct current energy is connected to the vessel **10** and to an electrode **16** positioned in the solution **12** to pass an anodic current through the solution **12** and passivate the exposed inner surfaces of the vessel **10** against corrosive attack by the solution **12**.

The anodic current is controlled by a suitable type of controller **18** connected to the energy source **14** in any suitable manner, such as by means of a switch **20** interposed in the conductor **22** leading from the source **14** to the electrode **16**. The controller **18** is connected across the vessel **10** and a standard electrode **24** which communicates with the solution **12** through the electrolytic bridge **26** of the present invention to monitor the potential difference between the vessel **10** and the standard electrode **24**. For an efficient operation of the current controller **18**, the standard electrode **24** must communicate electrically with the solution **12** under all operating conditions, such as during variation in the level of the solution **12** in the vessel **10** and during rather violent agitation of the solution **12**, such as occurs in many processes utilizing corrosive solutions. It should also be noted at this point that the vessel **10** is closed by a suitable top member **27** to facilitate the imposition of pressure upon the corrosive solution **12** when this is desirable. The standard electrode **24** may take any desired form such as a calomel electrode, a copper-copper sulphate electrode, a silver-silver chloride electrode or a hydrogen electrode.

A preferred embodiment of the electrolytic bridge **26** of the present invention is illustrated in detail in FIGS. 2, 3 and 4. The assembly comprises a reservoir **28** which is provided with a top wall **30** permitting the reservoir to be closed and facilitating the imposition of superatmospheric pressure upon an electrolyte **32** contained therein. The reservoir **28** is supported above the vessel **10** in any suitable manner so that the electrolyte **32** may gravitate downwardly through the tubular portions of the bridge assembly into the corrosive solution **12**. The electrolyte **32**, which may be any suitable electrolytic solution, such as potassium chloride, is stored in the reservoir **28** at a level sufficient to contact the standard electrode **24** suspended from the top wall **30** of the reservoir.

A flexible tubular conduit **34** communicates with the interior of the reservoir **28** near the bottom thereof and extends downwardly from the reservoir toward the vessel **10**. The tubular conduit **34** may be made of any suitable material which is flexible and insoluble in the electrolyte, such as a commercially available plastic sold under the trade name Tygon. The lower end **36** of the tubular conduit **34** is pressed over the upper end **38** of a plastic tubular member **40** and is secured thereto by means of a clamp **42**. The plastic tubular member **40** extends downwardly into the vessel **10** and is constructed of plastic having properties of high mechanical strength, high melting point and a high degree of inertness to chemical attack. When highly corrosive solutions such as oleum are contained in the vessel **10**, we have found that the fluorocarbon resins, such as those sold under the trade names Teflon and Kel-F, are especially well suited for the construction of the plastic tubular member **40**. A metallic sleeve **44** constructed of the same material as the vessel **10** is telescoped over the plastic tubular member **40** and is provided at its upper end with a fitting **46**. The fitting **46** comprises a metallic cap **48** having a resilient bushing **50** therein for the establishment of a seal with the plastic tubular member **40**. The metallic sleeve **44** is vertically supported in the vessel **10** by means of a circumferential flange **52** adjacent its upper end.

At its lower end, the plastic tubular member **40** is connected to a weeping glass bridge **54** which is shown in

FIG. 2 as it projects from the lower end on the metallic sleeve 44. At the lower end of the metallic sleeve 44, a novel fitting designated generally by reference character 56 is employed to facilitate the establishment of a seal between the sleeve 44 and the glass bridge 54. At the lower end of the glass bridge 54, a liquid junction between the electrolyte 32 contained within the bridge and the corrosive solution 12 in the vessel 10 is established by the employment of a small plug 57 which is fitted in an aperture 58 formed in the bottom of the bridge to permit a minute amount of electrolyte to constantly seep into the corrosive solution 12. This construction is best illustrated in FIGS. 3 and 4.

As has been previously indicated, two of the important features of the present invention are the connection which is formed between the plastic tubular member 40 and the glass bridge 54, and the seal which is provided between the metallic sleeve 44 and the glass bridge 54. The construction employed in these features may be best understood by referring to FIG. 3. In this figure it will be perceived that the lower end of the plastic tubular member 40 is telescoped over the upper end 60 of the glass bridge 54. A tapered shoulder 62 is formed on the body of the glass bridge and mates with a tapered portion 64 of the internal walls of the plastic tubular member 40. The glass bridge 54 is thus precluded from moving upwardly into the plastic tubular member 40 under the influence of pressure exerted by the corrosive solution 12. The internal wall of the plastic tubular member 40 is provided with an annular groove 66 for the reception of a resilient sealing ring 68 which seals against the periphery of the glass bridge 54.

The external periphery of the plastic tubular member 40 is threaded adjacent its lower end as indicated by reference numeral 70, and a tubular fitting 72, which is also constructed of plastic, threadedly engages the lower end of the plastic tubular member 40 and extends downwardly therefrom. The plastic of which the tubular fitting 72 is constructed has the same properties as the material of construction of the tubular member 40 and is preferably identical in chemical composition. As indicated by reference character 74, the internal walls of the tubular fitting 72 are tapered outwardly adjacent the lower end of the fitting so that the internal walls define with the external periphery of the glass bridge 54 a conical space adapted to accommodate a conical sealing member 76 of resilient material. The sealing member 76 extends below the lower end of the tubular fitting 72 and is biased into sealing engagement with the internal walls of the fitting 72 and the external periphery of the glass bridge 54 by means of a lock nut 78 which is threaded upon the lower end of the fitting 72. The lock nut 78 is preferably of metallic construction.

The novel sealing means 56 which is utilized for the establishment of a seal between the lower end of the metallic sleeve 44 and the glass bridge 54 comprises a generally cup-shaped fitting 80 which is threaded upon the lower end of the metallic sleeve 44, a fistular insert member 82 threaded into an aperture in the lower end of the cup-shaped fitting 80, a lock nut 84 on the lower end of the fistular member 82, and a plastic sealing member 86. In order to assure tight sealing engagement between the cup-shaped fitting 80 and the metallic sleeve 44, a section of tape 88 impregnated with a fluorocarbon resin is inserted between the threads of the fitting 80 and the sleeve 44. The interior of the cup-shaped fitting 80 is further sealed against the ingress of the corrosive solution by means of the fistular member 82 which is slidingly telescoped over the glass bridge 54, and also by means of the sealing member 86. The plastic sealing member 86 is characterized by a conically tapered upper end portion 90 which mates with a tapered surface 92 formed in the lower end of the fistular member 82 so that tightening of the lock nut 84 forces the plastic sealing member into tight sealing engagement with the periphery of the glass bridge 54 and the tapered portion 92 of the fistular member 82.

In order to prevent the weeping glass bridge 54 from being forced downwardly out of the plastic tubular member 40 when pressure is exerted upon the electrolyte 32 in the reservoir 28, the glass bridge 54 has formed thereon a circumferential protuberance or rib 94 which is located between a pair of plastic spacing washers 96. The spacing washers 96 bear against the lock nut 78 and the cup-shaped fitting 80 to prevent vertical movement of the glass bridge 54 with respect to the tubular member 40 and metallic sleeve 44 under the influence of a pressure differential applied to the inside or outside of the glass bridge. To assure against the infiltration of the corrosive solution into the interior of the cup-shaped fitting 80 by way of the threaded connection between the fistular member 82 and the cup-shaped fitting 80, an annular sealing washer 98 of plastic material is inserted between a flange 100 formed on the periphery of the fistular member 82 and the lower end of the cup-shaped fitting 80. The sealing washer 98 is slidingly fitted around the fistular member 82 with a relatively tight fit, and when the fistular member 82 is screwed upwardly into the cup-shaped fitting 80, the sealing washer 98 is expanded into tight sealing engagement with the periphery of the fistular member 82 as well as the lower surface of the cup-shaped member 80. The sealing washer 98 also functions as a cushion preventing the fistular member 82 from being threaded too far into the cup-shaped fitting 80 and thereby causing excessive pressure to be exerted upon the rib 94 of the glass bridge 54 by the lowermost spacing washer 96.

Operation

When the reservoir 28 of the electrolytic bridge assembly of the present invention is mounted over the vessel 10 in the manner shown in FIG. 2, the electrolyte 32 contained in the reservoir 28 flows downwardly through the flexible conduit 34 into the plastic tubular member 40 and the glass bridge 54. When neither the electrolyte in the reservoir 28 nor the corrosive solution 12 in the vessel 10 are under pressure, the electrolyte 32 seeps at a very slow rate through the liquid junction at the lower end of the glass tube of the weeping glass bridge 54. The same action must be maintained when the corrosive solution 12 is stored in the vessel 10 under a superatmospheric pressure. The reservoir 28 is therefore closed by a top member 30 to facilitate the imposition of a sufficient amount of pressure upon the electrolyte 32 to assure a positive flow of electrolyte through the orifice 58 in the bottom of the glass bridge 54 at all times. As has been previously explained, it is essential that the electrolyte 32 contained within the electrolytic bridge not be permitted to seep through the joint between the plastic tubular member 40 and the weeping glass bridge 54 and thus come into contact with the internal walls of the metallic sleeve 44. To this end, the novel sealing means between the plastic tubular member 40 and the glass bridge 54 is provided. In referring to FIG. 3, it will be perceived that three areas of sealing contact exist between these two elements. Thus, the resilient sealing ring 68 constitutes one of the seals, the mating surfaces of the tapered shoulder 62 and the tapered internal walls 64 of the tubular member 40 provide a second seal, and the third seal is constituted by the conically shaped, resilient sealing member 76 located at the lower end of the fitting 72. In a preferred embodiment of the invention, the sealing ring 68 and the conical sealing member 76 are constructed of rubber or a similar material to allow them to be compressed tightly between the adjacent structural elements.

In order to further assure against possible infiltration of the corrosive solution into the electrolyte contained within the electrolytic bridge, as well as to provide means for vertically supporting the plastic tubular member 40 and weeping glass bridge 54 in the vessel 10, the metallic sleeve 44 is telescoped over the plastic tubular member

40 and a portion of the glass bridge 54, and a tight seal 56 is established between the tubular member 44 and the periphery of the glass bridge 54. Infiltration of the corrosive solution 12 into the interior of the fitting 80 where it might attack the rubber sealing member 76 is thus prevented by the plastic sealing member 86 located in the lock nut 84, by the sealing washer 98, and also by the tape 88 interposed between the threads of the fitting 80 and the sleeve 44. Sealing member 86, sealing washer 98 and the tape 88 are all constructed of a plastic material which is inert to attack by the corrosive solution 12. In a preferred embodiment of the invention, the plastic utilized is one of the fluorocarbon resins. The resin sold under the trade name Teflon and referred to above has been found to function well in practice.

From the foregoing description it will be understood that the present invention provides an electrolytic bridge of sufficient mechanical strength to permit it to be used in tanks and vessels of considerable depth without danger of damage resulting from agitation of the corrosive solution contained in the vessel. The possibility of malfunctioning due to undesired leakage of electrolyte from the bridge at points intermediate its length is avoided, as is the possibility of infiltration of the corrosive solution into the electrolyte under the influence of a superatmospheric pressure.

Changes may be made in the combination and arrangement of parts or elements as heretofore set forth in the specification and shown in the drawings, it being understood that changes may be made in the embodiments disclosed without departing from the spirit and scope of the invention as defined in the following claims.

We claim:

1. An electrolytic bridge assembly for use in a vessel containing a corrosive solution under pressure comprising:

(*a*) a first elongated tubular member of an electrically insulating and chemically inert material;

(*b*) a weeping glass bridge means having a first and second end, said first end adapted to allow electro-chemical communication with said corrosive solution, said second end having a reduced diameter and telescoped within said first tubular member;

(*c*) cup-shaped sealing means surrounding the weeping glass bridge means and attached to said first tubular member;

(*d*) a second tubular member telescoped over said first tubular member;

(*e*) a peripheral ribbed means formed around the external diameter of said glass bridge intermediate the ends of said bridge;

(*f*) sealing means on each side of said peripheral ribbed means;

(*g*) a second cup-shaped sealing means surrounding said glass bridge and secured to said second tubular member in a manner to bias said ribbed portion sealing means against first cup-shaped means;

whereby said weeping glass bridge is sealed against high internal or external pressures thereby preventing corrosive solution from seeping into and damaging the operation of said bridge.

2. An electrolytic bridge as claimed in claim 1 wherein said second tubular member includes means for supporting said bridge in said vessel containing said corrosive solution.

3. An electrolytic bridge assembly for use in a vessel containing a corrosive solution under pressure comprising:

(*a*) a first and second elongated tubular member, said first tubular member having electrically insulating and chemically inert properties, said first tubular member telescoped within said second tubular member;

(*b*) an electrochemical bridge means having an electrochemical communicating means on one end and a reduced diameter adapted to telescope within said first elongated tubular member;

(*c*) a first sealing means between said bridge and said first tubular member and a second sealing means between said first tubular member and said second tubular member;

(*d*) an annular rib extending concentrically around the outer periphery of said electrochemical bridge;

(*e*) a pair of resinous washers around said bridge on opposite sides of said rib and means attached to said second tubular means for biasing said washers and said rib against said second sealing means;

whereby vertical movement of said glass bridge relative to said tubular member is limited by contact of said rib with said resinous washers.

4. An apparatus as described in claim 3 wherein said second tubular member is made of the same material as the vessel containing the corrosive solution.

5. An electrolytic bridge as claimed in claim 1 wherein said weeping glass bridge means is provided with a tapered annular shoulder adjacent said one end of said first tubular member; and wherein the internal walls of said first tubular member are tapered outwardly at said one end to mate with said tapered annular shoulder whereby said weeping glass bridge means is prevented from moving farther into said first tubular member.

6. An electrolytic bridge as claimed in claim 3 wherein said washers, said fitting, and said first tubular member are constructed of a plastic having properties of chemical inertness, high melting point, and high mechanical strength.

7. A reference potential assembly as claimed in claim 3 wherein said reservoir is closed whereby the electrolyte in said reservoir may be placed under pressure.

References Cited in the file of this patent

UNITED STATES PATENTS

2,289,589	Pomeroy	July 14, 1942
2,289,687	Stuart	July 14, 1942
2,343,885	Coleman	Mar. 14, 1944
2,764,427	Andrus	Sept. 25, 1956
2,918,420	Sabins	Dec. 22, 1959

FOREIGN PATENTS

695,776	Great Britain	Aug. 19, 1953

OTHER REFERENCES

Edeleanu: "Metallurgia," September 1954, pages 113–116.