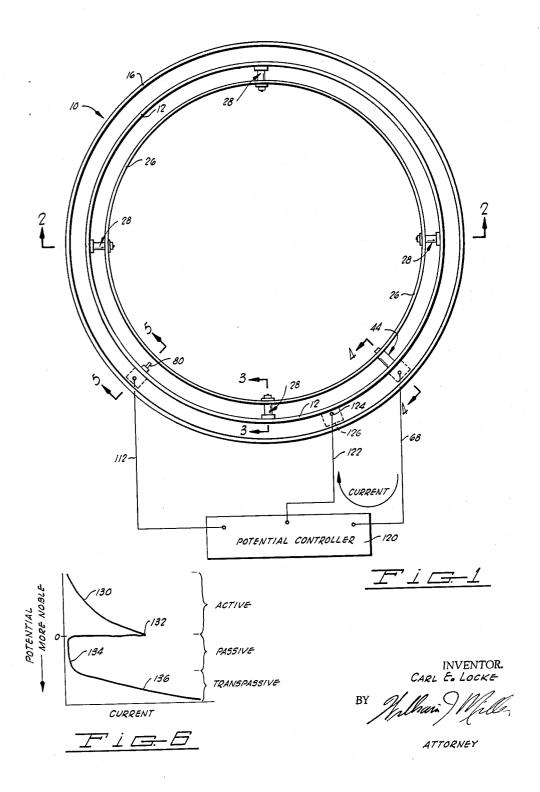
ANODIC PASSIVATION OF WETTED WALL VESSELS

Filed Nov. 13, 1962

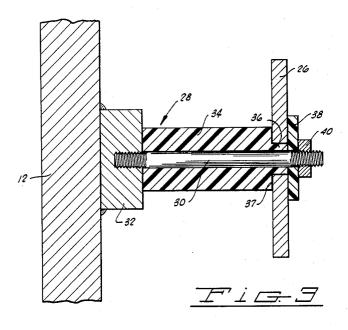
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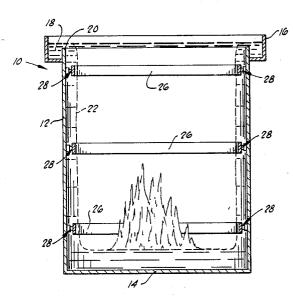


ANODIC PASSIVATION OF WETTED WALL VESSELS

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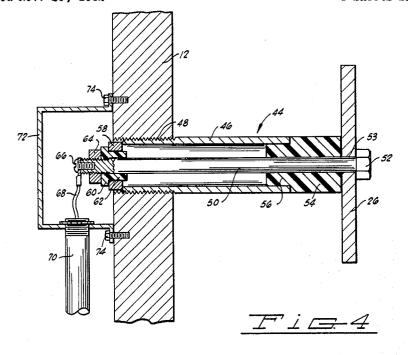
BY Milham Mills

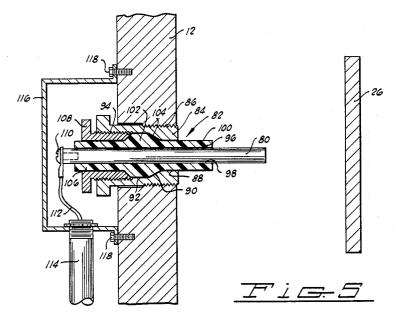
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ANODIC PASSIVATION OF WETTED WALL VESSELS

Filed Nov. 13, 1962

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United States Patent Office

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3,216,916 ANODIC PASSIVATION OF WETTED WALL VESSELS

WALL VESSELS
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The present invention relates to anodic passivation of 10 corrosible metals and more particularly, but not by way of limitation, relates to the anodic passivation of vessel walls over which a corrosive fluid is flowing.

In industry there are frequently instances in which a corrosive fluid flows over a metallic surface. For ex- 15 ample, in one particular commercial application phosphor is burned in the center of a relatively large tank to produce desired chemical products. The heat of combustion is severe and the walls of the tank must be protected from the high temperatures. One of the best methods found 20 for cooling the tank involves flowing phosphoric acid downwardly over the interior surface of the tank walls at a substantially uniform depth of a few inches around the entire periphery of the tank. Since the phosphoric acid will then be heated substantially above room temperature, corrosion of the walls of the tank will be greatly accelerated, even if fabricated from stainless steel, and the tank will soon be corroded beyond usefulness. In order to combat the corrosion, the tank could possibly be coated with a highly resistance ceramic or the like. However, in commercial applications the tanks may be as large as 20-25 ft. in diameter and perhaps 35 ft. tall, and special coatings and other types of construction become economically unfeasible.

It is known in the art that so-called anodic passivation methods can be used to greatly retard corrosion in cases where a fluid is standing in a vessel. When using this method, the metallic surface to be protected is maintained at a constant potential with respect to a reference half-cell or electrode by passing a current from the metallic surface to a cathode disposed in the corrosive fluid. In this case, the metallic surface corresponds to an anode, from which the system gets its name, and the corrosive fluid serves as an electrolyte for conducting the current from the anode to the cathode. However, anodic passivation systems have heretofore been applicable only in cases wherein a vessel is either completely filled, or partially filled to a constant level, with the corrosive fluid such that the fluid is continually in contact with the entire surface of the vessel which is subjected to corrosion. The cathode is then merely a single, elongated rod of conductive material disposed at some convenient point within the fluid standing in the vessel.

In accordance with the present invention, a method and apparatus are provided for passivating a metallic surface against corrosion by a fluid flowing over the surface. In general, the method comprises the steps of disposing an elongated cathode generally parallel to and spaced from the metallic surface a distance less than the depth of the fluid flowing over the surface such that the cathode will be disposed within the flowing fluid, disposing a reference electrode within the fluid and in close proximity to that portion of the metallic surface which is nearest the reference electrode, and then maintaining the metallic surface at a potential with respect to the reference electrode that is within the passive region by passing a controlled, direct current from the metallic surface to the elongated cathode. The present invention also contemplates in combination with the wetted wall vessel, a novel cathode construction comprising, in its more specific form, a horizontally disposed conductive cathode ring uniformly spaced

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from and extending around the walls of the vessel. The cathode ring is electrically insulated from the walls of the vessel by novel connection means and is connected to an electrical source by a novel connector which passes through the wall of the vessel. A reference electrode is then located in such a manner as to monitor the maximum potential of the vessel wall and is passed through the vessel wall and insulated therefrom by a novel coupling. Therefore, it is an important object of the present invention to provide a method for passivating a metallic surface over which a corrosible fluid is flowing.

It is also an important object of the present invention to provide a wetted wall tank which is protected from corrosive fluid flowing down the walls of the tank.

Another object of the present invention is to provide a novel cathode construction for providing anodic protection to a vessel having vertically disposed walls and a corrosive fluid flowing down the surface of the walls.

Another object of the present invention is to provide a novel cathode for use in anodic passivation systems for protecting the walls of a tank against corrosion.

Yet another object of the present invention is to provide an improved and economical device for passing a reference electrode through the wall of the vessel.

Another object of the present invention is to provide a device for passing an electrical lead through the wall of a tank and connecting the lead to a cathode disposed within the vessel.

Another object of the present invention is to provide a device for coupling a ring cathode within a vessel and maintaining the ring cathode electrically insulated from the vessel.

Another very important object of the present invention is to provide apparatus of the type described and having the objects and advantages herein set forth which may be economically manufactured and assembled, and which has a long service life.

Many additional objects and advantages of the present invention will be evident to those skilled in the art from the following detailed description and drawings wherein:

FIG. 1 is a plan view of a device constructed in accordance with the present invention;

FIG. 2 is a sectional view taken substantially on lines 2—2 of FIG. 1;

FIG. 3 is a sectional view taken substantially on lines 3—3 of FIG. 1;

FIG. 4 is a sectional view taken substantially on lines 4—4 of FIG. 1;

FIG. 5 is a sectional view taken substantially on lines 5—5 of FIG. 1; and,

FIG. 6 is a plot of the potential of the anode against the current flowing from the anode to the cathode of a typical anodic passivation system.

Referring now to the drawings, and in particular to FIGS. 1 and 2, a tank constructed in accordance with the present invention is indicated generally by the reference numeral 10. The tank 10 has cylindrical, vertically disposed walls 12 and a bottom 14. An annular fluid channel 16 or other suitable means is disposed around the upper end of the tank for distributing a fluid 18 in such a manner that the fluid 18 will spill over the upper edge 20 of the tank and flow downwardly over the interior surface of the walls 12 at a substantially uniform depth, as illustrated in FIG. 2 at 22. As in the particular commercial application heretofore described, the fluid 18 may be phosphoric acid and is used to cool the walls 12 as phosphor is burned generally at bottom center of the tank 10 to produce desired products of combustion. The specific manner in which the fluid 18 is flowed downwardly over the interior surface of the tank walls 12 and the manner in which the combustible materials are combined 0,010,01

and combustion supported, as well as the manner in which the desired products of combustion are removed, do not constitute a significant part of the present invention and accordingly are not illustrated in detail.

A plurality of cathode rings 26 are generally horizontally disposed and uniformly spaced from the walls 12 of the tank 10 around the entire circumference. The cathode rings may be fabricated from any of the metals found suitable for this purpose by the various workers in the art, such as platinum or stainless steel. In most cases the latter metal will be preferred because of economic considerations. The cathode rings 26 are vertically spaced one from the other in accordance with considerations hereafter discussed in greater detail. However, each of the cathode rings 26 is of substantially identical construction and each is supported by a plurality of electrically insulated support mounts, indicated generally by the reference numeral 28.

Referring now to FIG. 3, each of the support mounts 28, which are of identical construction, is comprised of a 20 stud 30 which may be threaded into a plate 32 which in turn is welded to the interior surface of the tank walls 12. A Teflon insulating spacer 34 is disposed around the stud 30 and between the plate 32 and the cathode ring 26. The spacer 34 has a reduced diameter sleeve portion 25 36 to form an annular shoulder 37, and the sleeve portion 36 is inserted in an aperture (not referenced) in the cathode ring 26 until the shoulder 37 abuts the cathode Thus it will be noted that the spacer 34 both physically supports and electrically insulates the cathode 30 ring 26 from the stud 30 and the tank walls 12. A Teflon insulating washer 38 is then disposed around the innermost end of the stud 30 and a nut 40 is threaded onto the end of the stud 30 to securely hold the cathode ring 26 in place. Thus it will be noted that the cathode ring 26 is 35 completely insulated from the electrically conductive stud 30 and from the tank walls 12 by the Teflon spacer 34 and the Teflon washer 38.

Each cathode ring 26 is electrically connected to a D.C. electrical power source by an electrical connection indi- 40 cated generally by the reference numeral 44. The electrical connection 44 may best be seen in FIG. 4 and is comprised of a tubular sleeve 46 which is threaded into a tapped bore 48. The tapped bore 48 extends through the wall 12 of the tank and an electrically conductive bolt 50 having a head 52 is passed through an aperture 53 in 45 the cathode ring 26, through an inner Teflon insulating spacer 54, through the tubular sleeve 46 to a point beyond the exterior surface of the tank walls 12. The inner Teflon insulating spacer 54 preferably has a reduced diameter portion 56 which is inserted into the end of the 50 tubular sleeve 46 to insure that the bolt 50 remains centered within the tubular sleeve 46. The Teflon insulating spacer 54 also provides a means for sealing off the fluid 18 from entering the tubular sleeve 46, although in most cases there will be no fluid pressure, as will hereafter be 55 described in greater detail. A suitable metallic washer 58 is inserted in the outer end of the tapped bore 48 and abuts against the outer end of the tubular sleeve 46. An outer Teflon spacer 60 is disposed around the bolt 50 and has a reduced diameter sleeve insert portion 62 which is 60 inserted into the metallic washer 58 substantially as illustrated.

A nut 64 is threaded onto the bolt 50 and when securely tightened, the head 52 of the bolt 50 will be drawn tightly against the cathode ring 26 to insure a good electrical connection. The inner Teflon spacer 54 will be drawn tightly against the inner end of the tubular sleeve 46 to insure a fluid tight seal. The threaded connection between the tubular sleeve 46 and the tapped bore 48 provides a fluid tight coupling to insure that the fluid 18 cannot seep through the wall 12 of the tank 10. At the same time, the conductive bolt 50 is electrically insulated from the tank wall 12 by the Teflon inner spacer 54 and the Teflon outer spacer 60.

The outer end of the bolt 50 is preferably provided with a small tapped bore which receives a screw 66. An electrical lead 68 may then be securely clamped by the screw 66 against the bolt 50 to insure a good and permanent electrical connection. The electrical lead 68 may then extend through a suitable conduit 70 to the source of electrical power, hereafter described, and a weathertight housing 72 may be provided around the entire electrical connection and secured to the tank wall 12 by bolts 74 in the conventional manner.

A reference electrode 80 is passed through the tank wall 12 adjacent each cathode ring 26 and is electrically insulated therefrom by a coupling, which is indicated generally by the reference numeral 82 and illustrated in detail in FIG. 5. The coupling 82 comprises a metallic insert 84 which is threaded into a tapped bore 86 extending through the tank wall 12. A bore 38 extends through the insert 84 and a tapered shoulder 90 is formed within the bore 83 by a counterbore 92 which is tapped at 94. A Teflon insulating sleeve 96 has a center bore 98 for closely receiving a suitable reference electrode 80. The external diameter of the insulating sleeve 96 at the inner end 100 is such as to be snugly received within the bore The Teflon sleeve 96 also has an enlarged center portion 102 which forms an annular shoulder 104 which is tapered to a degree corresponding to the taper of the shoulder 90 formed by the counterbore 92. The diameter of the enlarged center portion 102 is such as to be snugly received in the diameter of the counterbore 92. The outer end portion 106 of the Teflon sleeve 96 has a diameter corresponding approximately to the diameter of the inner end portion 100. A second, inner metallic insert 108 is then placed around the outer end portion 106 and is threaded into the threads 94 of the tapped counterbore 92. When the second inner insert 108 is tightened, the tapered shoulder 104 of the Teflon sleeve 96 will be wedged against the tapered shoulder 90 of the insert 84 to clamp the relatively resilient Teflon sleeve 96 tightly around the reference electrode 80 and thereby provide a mechanically secure, fluid tight, electrically insulated coupling.

The outer end of the reference electrode 80 is preferably provided with a small tapped bore for receiving a screw 110 which connects an electrical lead 112 to the reference electrode 80. The lead 112 may be housed within the conventional electric conduit 114 which is connected to a suitable electrical housing 116 which is in turn connected to the tank wall 12 by bolts 118.

Referring once again to FIG. 1, a conventional and commercially available potential controller is represented schematically by the reference numeral 120. The electrical lead 68 from the several cathode rings 26 and the electrical lead 112 from the reference electrode 80 are connected to the potential controller 120. The tank wall 12 is also connected by a suitable electrical lead 122 to the potential controller. The lead 122 may be connected to the wall 12 by any suitable coupling means, indicated generally by the reference numeral 124, at almost any point, and the coupling means may be protected by a conventional housing 126. The potential controller 120, and indeed the broad concept of anodic passivation, is well known in the art and does not comprise, per se, a part of the present invention. However, it should be noted that the reference electrode 80 must be so disposed as to be continually covered by the fluid 18, which must be an electrolyte. The reference electrode 80 and fluid 18 then form the conventional half cell which will produce a standard potential at reference conditions. The reference electrode 80 may be fabricated from any one of several suitable materials which are known in the art, such as for example, Cr2C3, Pt-PtO2, or stainless steel, depending upon which is more economical in view of initial cost and service life.

Referring now to FIG. 6, the potential of the anode is 75 plotted against the current flowing between the anode and

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cathode in a typical anodic passivation system. It will be noted that as the potential of the anode becomes more noble and is changed from a negative potential to a positive potential along the region 130 of the curve, the current increases rapidly until the Flade point 132 is reached. The region 130 is highly active and the anode will be corroded rapidly. However, as the potential of the anode is made more noble, i.e., more positive in the conventional current sense, the current drops sharply to a relatively low value in the passive region 134. If the anode is made still more noble, so that the passive region 134 is exceeded, the current will increase sharply once again in the active region 136 and the anode will again be corroded at an accelerated rate.

In operation, the potential controller 120 compares 15 the potential of the reference electrode 80 with the potential of the tank wall 12 and maintains the tank wall 12 at a constant potential within the passive region 134 by supplying a direct current, in the conventional sense, through a circuit comprised of the lead 122, the tank 20 wall 12, the electrolyte fluid 18, the cathode ring 26, the coupling 44 and the lead 68. The tank wall 12, which then constitutes an anode, should be quickly lowered to and maintained at the potential within the passive region. Then as the current is passed from the tank wall 25 12 to the cathode ring 26, corrosion will occur at a very rapid rate on the tank wall 12 until a very thin film of protective oxide is formed over the entire surface of the tank. During this phase, a current of considerable magnitude is required. However, the protective film formed 30 by the process has a relatively high resistance to electrical currents such that the desired potential of the tank wall 12 can thereafter be maintained by a relatively low current. The high resistivity of the protective film results in a high so-called "throwing power" of the system. 35 In other words, each of the cathode rings 26 may be spaced a substantial distance apart and the surface of the tank walls still maintained at the desired potential because the resistance of the protective film is relatively high with respect to the resistance of the fluid electrolyte 40 and the tank wall. Of course the exact vertical spacing of the cathode rings will vary with each type of installation.

Several important features of the present invention should be noted. First, each of the cathode rings 26 should be spaced from the wall 12 around its entire periphery at a distance which is less than the depth of the fluid 18 flowing downwardly over the wall 12 so as to insure constant and uniform electrical contact between the cathode rings 26 and the fluid 18. Further, the 50 cathode rings 26 should be uniformly spaced from the wall 12 at all points in order to insure that the potential of any particular spot on the wall 12 will not be less than the minimum potential at the Flade point 132 nor exceed the potential in the passive region 134 and enter 55 the transpassive region 136 which is highly active and accelerates corrosion. In this respect, it will be noted by referring to FIG. 5 that the reference electrode 80 is disposed within the fluid 18 which flows over the tank wall 12. The reference electrode 80 should also be po- 60 sitioned such that it is in close proximity to that portion of the tank wall 12 which is nearest to a cathode ring 26. This will greatly reduce the possibility of creating so-called "hot spots" where the potential of the tank wall exceeds the passive region and enters the transpassive 65 region so that accelerated corrosion of the "hot spot" occurs.

It will be appreciated by those skilled in the art that a highly useful tank construction has been disclosed for utilizing anodic passivation methods to retard corrosion of the walls of the tank. Also, novel cathode and electrically insulated support constructions have been disclosed which can be economically fabricated and installed. Novel electrical connections have also been disclosed for passing electrical current through the walls of the tank 75

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and through the electrolyte fluid to the cathode rings within the tank. Also, a novel insulating mount has been provided for passing an elongated reference electrode through the wall of the tank and positioning the electrode in the electrolyte fluid.

Having thus described preferred embodiments of the method and apparatus in accordance with the present invention, it is to be understood that various changes, substitutions and alterations can be made therein without departing from the spirit and scope of the invention as defined by the appended claims.

What is claimed is:

1. In combination with a fluid vessel having inclined metallic walls adapted to have

a conductive, corrosive liquid film flow downwardly over the walls at a depth;

a continuous cathode ring;

nonconductive support means interconnecting the walls and the cathode ring for supporting the cathode within the flowing liquid film, said means also supporting the cathode ring in uniformly spaced relation to the walls around substantially the entire periphery thereof;

a reference electrode disposed in the liquid film and electrically insulated from the walls and from the cathode ring except through the liquid film; and,

electrical circuit means connected to the cathode, the reference electrode and the metallic walls for maintaining the potential of the walls at a predetermined value with respect to the reference electrode by passing a convenional direct current from the walls through the liquid film of the cathode ring,

whereby the potential variation of the metallic surface detected by said reference electrode is used to control by means of the electrical circuit means, the potential of the conductive surface within the passive region and corrosion of the surface of the walls by the fluid retarded.

2. In combination with a cylindrical fluid vessel having vertically disposed metallic walls and adopted to have

a conductive corrosive liquid film flow downwardly over the interior surface of the walls at a depth; a continuous cathode ring;

a plurality of electrically insulating mounts connected to the walls and to the cathode ring for supporting the cathode ring uniformly spaced from the walls and within the liquid film;

a reference electrode extending through the vessel wall and disposed in the liquid film in close proximity to a point on the interior surface of the walls which is nearest the cathode ring;

electrically insulated support means for the reference electrode for supporting and insulating the reference electrode from the wall except through the liquid film; and.

electrical circuit means connected to the cathode ring, the reference electrode and the walls for maintaining the potential of the walls at a predetermined value with respect to the reference electrode by passing a conventional direct current from the walls through the liquid film to the cathode ring,

whereby the potential variation of the metallic surface detected by said reference electrode is used to control by means of the electrical circuit means, the potential of the conductive surface within the passive region and corrosion of the surface of the walls by the fluid retarded.

3. The combination as defined in claim 2 wherein each of the plurality of electrically insulating mounts is com70 prised of:

a stud member connected to the wall of the vessel and extending radially inwardly therefrom, the inner end of the stud member being threaded;

a nonconductive spacer member disposed around the stud member, the spacer member having a portion

of reduced diameter adjacent the inner end to form an annular shoulder;

an aperture in the cathode ring for receiving the portion of reduced diameter;

a nonconductive washer around the stud member and 5 abutting the inner surface of the cathode ring; and,

a nut threaded onto the inner end of the stud member for clamping the washer against the cathode ring, the cathode ring against the shoulder formed on the spacer member, and the spacer member against the 10 wall of the tank,

whereby the cathode ring will be supported in spaced, electrically insulated relationship to the vessel walls.

4. The combination as defined in claim 2 wherein the reference electrode is a cylindrical rod and the electrically 15 insulated support means for the reference electrode comprises:

a threaded bore extending through the walls of the

a first insert member threaded into the threaded bore, 20 the first insert member having a bore extending therethrough, a counterbore to the bore forming an outwardly facing tapered shoulder, and internal threads in the counterbore;

a nonconductive sleeve member disposed in the first 25 insert member and extending therethrough, the sleeve member having a bore extending therethrough for receiving the reference electrode, an inner end portion having an external diameter to be received in the bore in the first insert member, a center por- 30 116. tion of enlarged diameter to be received in the counterbore in the first insert member, and an outer end portion of smaller external diameter than the external diameter of the center portion to form an outwardly facing shoulder on the sleeve member; 35 and,

a second insert member disposed around the outer end portion of the sleeve member and threaded into the first insert member, the inner end of the second insert member engaging the outwardly facing shoulder of the sleeve member,

whereby as the second insert member is tightened against the shoulder, the center portion of the sleeve member will be wedged against the tapered shoulder in the first insert member and the sleeve member will be seated against both the reference electrode extending therethrough and the first insert member disposed therearound.

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