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M. HUTCHISON ET AL
ANODIC PROTECTION AGAINST CORROSION

3,208,925

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3 Sheets-Sheet 1

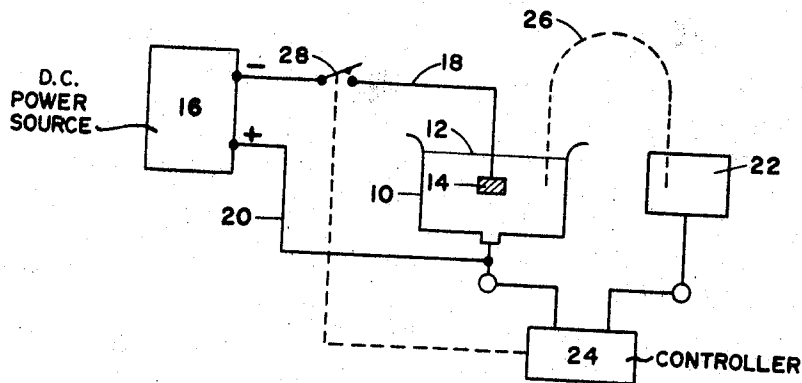


FIG. 1

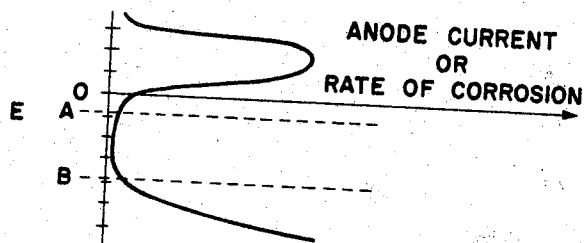


FIG. 2

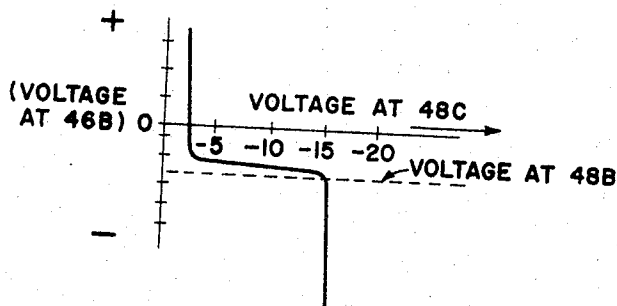


FIG. 4

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3 Sheets-Sheet 2

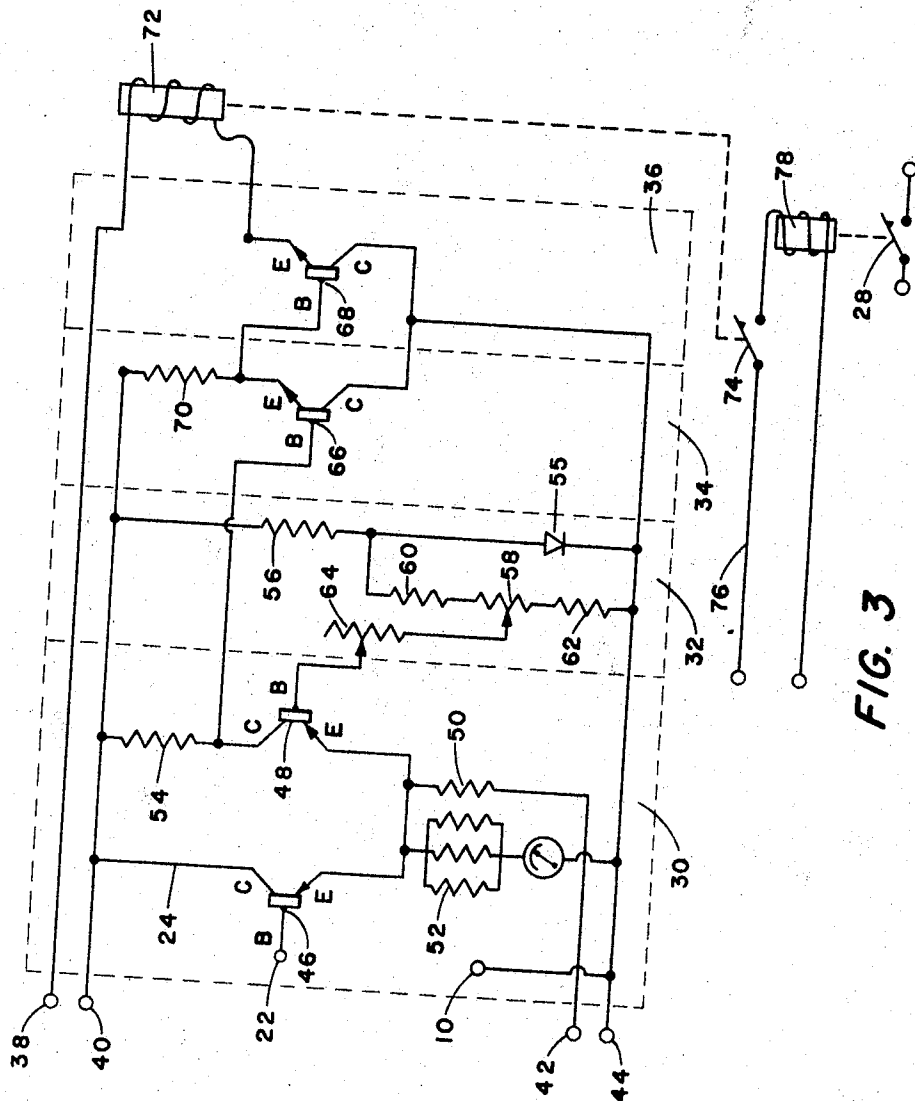


FIG. 3

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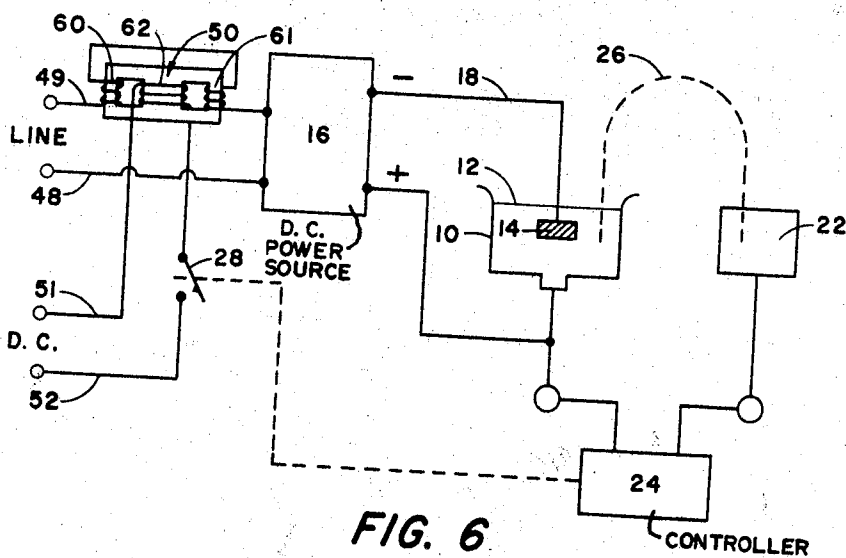
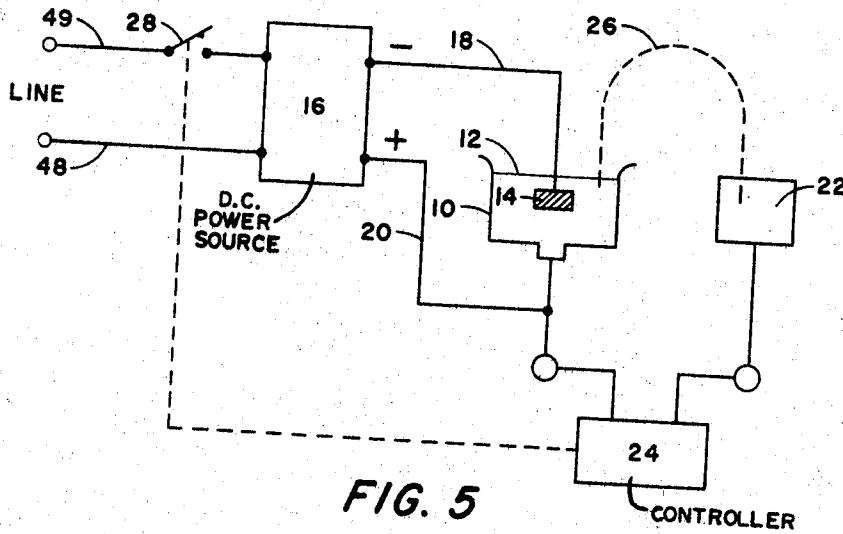
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ANODIC PROTECTION AGAINST CORROSION
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Filed Jan. 7, 1960, Ser. No. 1,136
28 Claims. (Cl. 204—147)

This is a continuation in part of co-pending application, Serial No. 777,499, filed December 1, 1958, now abandoned.

This invention relates to an improved method and apparatus for the protection of metals against corrosion by anodic passivation.

As it is well known in the art of corrosion control, the corrosion of many metals may be prevented or seriously curtailed by cathodic polarization. For example, in the oil industry many pipelines are protected against corrosive action of the soil in which they are laid by cathodic polarization. Cathodic protection is very useful in the case of iron in near neutral solutions, but it is of no practical value in the protection of stainless steel in acid environments, because of the high current requirements.

It is also known that anodic polarization can prevent or seriously limit corrosion by inducing passivity, as set forth in an article by Dr. C. Edeleanu, pages 113—116, *Metalurgia*, September 1954. However, the application of an anodic current can easily lead to an increase in corrosion rate rather than a decrease if not properly applied, and anodic systems have not been used commercially to any appreciable degree. Heretofore, and as noted in the above article, it has been believed necessary to provide a substantially constant adjustment of the anodic current, which in turn requires complicated and expensive control apparatus.

When dealing with anodic polarization, it is generally believed that passivity depends upon the presence of an insoluble film on the exposed surface of the vessel or specimen being protected, and that the solubility of the film in acid, in turn, depends on potentials. In any event, it has been found that the potential of the vessel or specimen is sufficiently indicative of the rate of corrosion for practical purposes. The above-mentioned article also discloses that these potentials may be measured against a standard electrode, but teaches the use of a substantially constantly changing anodic current, as previously indicated.

The present invention contemplates a method and apparatus for anodic polarization wherein the anodic current is applied only periodically. More specifically, the present invention contemplates the initial establishment of protection for a metallic vessel containing a corrosive solution (which solution will conduct current) by the use of an anodic current passing from the vessel to an inert electrode positioned in the solution. The protected condition is indicated by the potential difference between the vessel and a standard electrode communicating electrochemically with the solution. This potential difference is monitored and when a pre-determined potential difference is reached, depending principally upon the materials of construction of the vessel and the type of solution, the anodic current is discontinued. When the above-mentioned potential difference reaches a predetermined value, indicating the approach of an increased rate of corrosion, the anodic current is again passed from the vessel to the inert electrode to again decrease the rate of corrosion. This stepwise process is repeated as long as the vessel is exposed to the solution, and no appreciable corrosion results.

Metals which may be protected by the method of this

invention include, by way of example and not by way of limitation, mild steel, all types of stainless steel, titanium or alloys of titanium, hafnium and zirconium.

Examples of a few of the corrosive liquids for which this invention is adaptable include tap water, liquid fertilizers, such as ammonium nitrate; caustic solutions such as sodium and lithium hydroxide; aluminum sulfate solution; organic acids; and inorganic acids such as sulfuric (including oleum), nitric, and phosphoric acids.

An important object of this invention is to reduce corrosion of metallic vessels containing acid solutions, without diluting the acid solutions by use of conventional corrosion inhibitors.

Another object of this invention is to provide a novel method of, and apparatus for, controlling the anodic current in a corrosion control system using anodic polarization.

A further object of this invention is to reduce the complexity and cost of equipment required in an anodic polarization system of corrosion control.

Another object of this invention is to handle corrosive solutions containing chlorides.

And another object of this invention is to improve product quality in processes involving the handling of corrosive solutions by eliminating emulsion and color problems.

A still further object of this invention is to provide a system for anodically reducing corrosion of a metallic vessel containing a corrosive solution which is simple in construction and operation and which will have a long service life.

Other 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.

FIG. 1 is a schematic drawing illustrating a practice of this invention.

FIG. 2 is a curve illustrating variations of anodic current, or of the corrosion rate of a stainless steel subjected to an acid solution at various potentials of the stainless steel.

FIG. 3 is a schematic wiring diagram of a suitable anodic current controller of this invention.

FIG. 4 is a curve illustrating the response of the voltage amplifier of the suitable anodic current controller at various potentials of a vessel being protected.

FIGS. 5 and 6 are schematics illustrating other methods of switching the anodic passivation circuit.

Referring to the drawings in detail, and particularly FIG. 1, reference character 10 designates a vessel, such as a tank, containing an electrolytic corrosive solution 12 and which is to be protected against corrosive action of the solution 12. The vessel 10 is constructed of metal, normally stainless steel in view of the required service. The solution 12 may be, for example, sulfuric, phosphoric, or nitric acid. Examples of processes wherein an acid is usually processed in a stainless steel vessel, and hence processes wherein the present invention is particularly useful, are acid storage and transportation, phosphorizing, nitriding, the manufacture of sulfonic acids and sulfonates in chemical industries, and uranium ore processing using phosphoric acid. In each of these processes the stainless steel vessels have relatively short service lives under present operating conditions; furthermore, the presence of iron in the product as a result of corrosion may result in off-color products and troublesome emulsions.

In accordance with the present invention an inert electrode 14 is suspended or otherwise supported in a solution 12 and is connected to the negative side of a source 16 of direct current energy by a conductor 18. The electrode 14 may be any material which is inert to solution 12. Preferable electrode materials are platinum or carbon. It will be understood that D.C. power supply 16 may take

any desired form, such as an A.C. power supply and a rectifier, or a battery, providing the necessary power is available. The positive side of power supply 16 is connected by a conductor 20 to vessel 10. It will thus be seen that vessel 10 functions as an anode and electrode 14

functions as a cathode. As it is well known in the art, and as previously indicated, the rate of corrosion of the type being considered varies with the potential of the specimen being corroded, and the corrosion may be prevented, or at least minimized, by anodic polarization. The potential of the specimen is determined with respect to a reference electrode located in the E.M.F. table at a lower or more noble position than the material of the specimen. When the specimen is made the anode of an electrochemical cell, the potential of the specimen shifts in the more noble direction. When this shift is of sufficient magnitude, the corrosion stops and it is said that the specimen has become passive. In this connection it should be noted that the sign of the potential difference between the specimen and the standard electrode is of no consequence insofar as the nobility (the relative position in the E.M.F. table) of the specimen is concerned, i.e., the sign of this potential difference may be positive or negative or change as the specimen is made more noble. We have found that when the anodic current is stopped, the potential very slowly shifts in the less noble direction and that the passivity of the specimen remains for an appreciable period after the anodic current is stopped.

It can be shown that the rate of corrosion varies with the potential between the specimen and one type of standard electrode (calomel cell) in the manner illustrated in FIG. 2, wherein E is the potential of the calomel cell with respect to the specimen. This potential will be sometimes hereinafter referred to as the noble potential or voltage. As shown in this drawing, the rate of corrosion increases at a substantial rate and then decreases as the noble voltage approaches zero. As the noble voltage increases in a negative direction, the corrosion rate decreases to a low level for an appreciable range of noble voltages and then increases rapidly again. Thus, as long as the noble voltage is maintained in the range between points A and B of FIG. 2, which may be referred to as the positive minimum potential area, a minor amount of corrosion takes place.

To measure and control the potential of vessel 10 (FIG. 1) we provide a standard electrode 22 communicating with solution 12, along with a suitable controller 24 connected across electrode 22 and vessel 10. Standard electrode 22 may be of any suitable type, such as a calomel cell, a silver-silver chloride cell, a copper-copper sulfate cell or a hydrogen cell, and is connected to the solution 12 by a suitable electrolytic bridge 26 to prevent the cell from coming into direct contact with solution 12 and either affecting operation of the cell or dilution of solution 12. While an electrolytic bridge 26 is shown communicating the standard cell 22 with the solution 12, it is to be understood by those skilled in the art that any well known means may be used to electrically couple the standard cell to solution 12. Bridge 26 must be an ionic conductor and may be either a liquid, such as a KCl solution, or a solid, such as silver chloride. Controller 24 functions to operate a switch 28 in conductor 18 to periodically impose a uniform potential between vessel 10 and cathode 14 in accordance with the potential between vessel 10 and standard electrode 22, i.e., the noble voltage.

In accordance with the method of this invention, switch 28 is closed to pass a current from vessel 10 through solution 12 to inert electrode 14 until vessel 10 becomes pacified and the rate of corrosion has decreased to a low level. It may be noted that this initial passage of anodic current varies the rate of corrosion in the manner illustrated in FIG. 2 until the potential between vessel 10 and standard electrode 22 reaches a level between points A and B in FIG. 2, and preferably on the flat minimum

portion of the curve midway between points A and B. At this time it is believed that an insoluble film has formed on that portion of the inner surface of vessel 10 opposite solution 12 and no appreciable corrosion is taking place. Controller 24 then opens switch 28 and removes the potential between vessel 10 and the cathode 14. Upon cessation of the anodic current, the potential between vessel 10 and standard electrode 22 gradually changes (decreases in a negative direction in the example illustrated) and vessel 10 becomes less noble, probably by a gradual deterioration of the insoluble film on the inner surface of vessel 10.

Controller 24 monitors variations in the potential between vessel 10 and standard electrode 22. When this noble voltage reaches a level close to point A in FIG. 2, controller 24 closes switch 28 to again impose a potential between vessel 10 and cathode 14 and induces another anodic current. Whereupon, the potential between vessel 10 and standard electrode 22 again increases to within the vicinity of the flat minimum portion of the curve between points A and B of FIG. 2, and the controller again opens switch 28. This step-wise procedure is repeated to provide a minimum of corrosion of vessel 10. The lasting power of the corrosion protection (when the anodic current is stopped) ranges from a few seconds immediately following formation of passivity to several days when passivity has been established from eight to twenty-four hours.

It can also be shown that the current density required to obtain and to maintain passivity varies in substantially the same manner as the corrosion rate illustrated by the curve in FIG. 2. In other words, as the specimen or vessel is being passivated, rather high current densities are required. However, once the specimen is passivated, the passivity may be maintained with a very small current density. Thus, the power or energy required to maintain corrosion protection by the present invention is at a minimum. The data in the following table illustrate the various current densities required before and after passivity is established when various steel samples are immersed in a 65% solution of H_2SO_4 .

It should be noted that current requirements may vary with the particular system involved, and may increase with increasing temperatures or alteration of other variables.

Steel Type and No. A.I.S.I.	Current Density		Weight Losses in Grams ³	
	(a) ¹	(b) ²	Before Passivity	After Passivity
302-----	6.0	2.2	0.2605	0.0007
304-----	5.0	3.8	0.2533	0.0010
316-----	0.5	0.1	0.2748	0.0001
405-----	163.0	2.7	0.1939	0.0057
446-----	27.3	0.7	0.6060	0.0064

¹ (a) Current density to passivate sample (milliamperes/cm.²).

² (b) Current density to maintain passivity (microamperes/cm.²).

³ Test conducted for 24 hour duration. Sample size 17 sq. cm. surface area.

In a preferred embodiment of this invention, and as shown in FIG. 3, controller 24 generally comprises a voltage amplifier 30 controlled by a reference section 32; and an isolation section or buffer 34 for operating a power amplifier 36 without affecting amplifier 30. Power is supplied to the preferred controller 24 at various potentials through junctions 38, 40, 42 and 44. In one embodiment, junction 38 is at -12 volts D.C., junction 40 is at -15 volts D.C., junction 42 is at +2 volts D.C. and junction 44 is at ground.

Voltage amplifier 30 comprises two transistors 46 and 48 having their emitter contacts 46E and 48E connected through a resistor 50 to junction 42 and through a resistor 52 to junction 44. Collector contact 46C of transistor 46 is connected directly to junction 40 and collector contact 48C of transistor 48 is connected through a resistor 54 to junction 40. The base contact 46B of trans-

sistor 46 is connected to standard electrode 22, and vessel 10 is connected to the ground junction 44, such that amplifier 30 is energized by the potential between standard electrode 22 and vessel 10. Base contact 48B of transistor 48 is connected to reference section 32 to control the operating point of amplifier 30, as will be described.

The reference section 32 comprises a diode 55 connected across junctions 40 and 44 in series with a resistor 56 and shunted by a potentiometer 58 having two series resistors 60 and 62. Another potentiometer 64 is connected to the contact of potentiometer 58 and the contact of potentiometer 64 is in turn connected to the base contact 48B of transistor 48. Potentiometers 58 and 64 are manually adjustable and may be used to position the operating point of amplifier 30 to any desired level. Potentiometer 58 is used to adjust the voltage at contact 48B and potentiometer 64 is used to adjust the amount of change required at contact 46B to result in (in one embodiment) a zero to -15 volt change at contact 48C.

The response of amplifier 30 is illustrated by the curve in FIG. 4 wherein the vertical axis indicates the voltage at contact 46B and the horizontal axis indicates the voltage at contact 48C. The dashed horizontal line indicates the voltage level at contact 48B and hence the voltage level desired to be maintained at contact 46B. It will be observed that the voltage at contact 48C remains near zero until the voltage at 46B reaches a level near the voltage at 48B. At this time the voltage at 48C begins to increase and so increases until the voltage of junction 40 is reached, that is, -15 volts D.C. Any further increase of voltage at contact 46B has no effect on the voltage at 48C; however, when the voltage at 46B reaches the level of the voltage at 48B, the anodic current is stopped, as will be described, and the voltage at 46B again decreases.

Voltage variations at contact 48C of amplifier 30 are fed to base contact 66B of a buffer transistor 66 of isolation section 34, and transistor 66 in turn drives a power amplifying transistor 68. The emitter contact 66E of transistor 66 is connected to base contact 68B of transistor 68 and both of these contacts are connected to junction 40 through resistor 70. The collector contacts of both of the transistors 66 and 68 are connected to junction 44. Thus, transistor 66 furnishes the necessary power to operate transistor 68 and isolates amplifier 30. Transistor 66 is constructed in such a manner as not to alter the voltage swing available from contact 48C of amplifier 30; hence (in the embodiment disclosed) a zero to -15 volt change occurs at contact 68B of the power amplifier. Emitter contact 68E of transistor 68 is connected in series with the coil of a primary relay 72 and junction 38 to supply the current necessary to operate relay 72. It will be apparent that when the voltage at contact 68E is equal to the voltage at junction 38, no current will flow through the coil of relay 72. However, when the voltage at contact 68E is varied, current will flow through the coil of relay 72.

Primary relay 72 is provided to operate a switch 74 interposed in a secondary power circuit 76 having the coil of a secondary relay 78 therein. Power circuit 76 may be easily constructed to derive energy from the common D.C. power source 16 illustrated in FIG. 1. Secondary relay 78 in turn controls the operation of switch 28 in conductor 18 leading from power source 16 to the cathode 14 (see FIG. 1). It will be understood that a single relay may be used if sufficient power is available for operating the switch 28.

In analyzing and summarizing the operation of preferred controller 24 illustrated in FIG. 3, let it be assumed that it is desired to retain the voltage between standard electrode 22 (a calomel cell) and vessel 10 (a stainless steel vessel) at about -500 millivolts D.C., which is somewhere between points A and B of FIG. 2. Potentiometer 58 is adjusted to provide a voltage of about -500 millivolts D.C. at contact 48B, and potentiometer 64 is adjusted to make the voltage at contact 48C about zero when the voltage at 46B is below -450 millivolts

D.C. Assume further that when controller 24 is first placed in operation the potential between standard electrode 22 and vessel 10 is -200 millivolts D.C. At this last voltage (being below -450 millivolts) the voltage at 48C, and therefore at 66B, 66E, 68B and 68E will be zero, and current will flow through the coil of relay 72 to close switches 74 and 28 and provide an anodic current from vessel 10 to cathode 14. This anodic current continues, as described previously, to further increase (in a negative direction) the potential between standard electrode 22 and vessel 10.

When the potential between standard electrode 22 and vessel 10 reaches -500 millivolts, the voltage at contact 48C will reach -15 volts D.C. This voltage will also appear at contact 66E of the buffer transistor 66 and result in a voltage of -12 volts D.C. at the emitter contact of transistor 68. Under these conditions, no current will flow through the coil of relay 72, such that switch 28 will be opened and the anodic current will be discontinued.

The potential between the standard electrode 22 and the vessel 10 will then again decrease in a negative direction as previously indicated. When this potential reaches approximately -450 millivolts D.C., the voltage at contact 48C will again become zero and the anodic current will again be passed from vessel 10 to cathode 14. This step-wise operation is repeated to discontinue the anodic current when the potential between the standard electrode 22 and the vessel 10 reaches -500 millivolts, and to generate the anodic current each time the potential between standard electrode 22 and vessel 10 reaches -450 millivolts D.C., whereby the corrosion rate is maintained between points A and B on FIG. 2.

Referring to FIG. 5, D.C. source 16 is of the type which requires an external power source such as alternating current. A pair of conductors 48 and 49 are connected from a source of power such as a line to power source 16. Switch 28 may be interposed in either or both lines, however, for simplicity it is shown in line 49. As described in conjunction with FIG. 1 controller 24 likewise operates switch 28.

The operation of the current is substantially identical with the embodiment shown in FIG. 1, however, switch 28 was interposed in the input side of the power supply to prevent the necessity for breaking large currents that would normally be present in controller 18. Further, as is well known by those skilled in the art, it is more difficult to break a high current D.C. line than it is a low current A.C. line, therefore, the embodiment shown in FIG. 5 presents many advantages over the embodiment shown in FIG. 1.

FIG. 6 shows another method of substantially switching the power on or off between the line and D.C. power source 16. In place of switch 28 in conductor 49, a saturable reactor 60 is inserted. The particular form of saturable reactor disclosed comprises two windings 60 and 61 which form the primary and a winding 62 which forms the secondary or control winding. Primary windings 60 and 61 are connected in series, and in series with conductor 49. The secondary, or control, winding is connected to any suitable D.C. source, such as a battery, through a pair of conductors 51 and 52. Switch 28 is interposed in one of the conductors 51 or 52 and serves to interrupt the flow of D.C. through control winding 62.

In operation, with switch 28 open, reactor 50 presents a very high impedance to the flow of alternating current. Therefore, the majority of the voltage will be dropped across reactor 50, leaving only a small portion to be applied to D.C. power source 16. With switch 28 closed, reactor 50 presents a very low impedance to the flow of alternating current. Thus, a very small voltage drop will appear across reactor 50 and a very high voltage will be applied to D.C. power source 16. An additional advantage is obtained by this embodiment. Normally switch 28 (see FIG. 1 and FIG. 5) must break a substantial

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amount of current and oftentimes it must break this current at an extremely rapid rate. Further, it must operate at many times a second. This tends to seriously reduce the overall life of switch 28. The saturable reactor on the other hand provides a delaying action to the circuit. Thus, when switch 28 operates such that power is supplied to D.C. power source 16, the applied power will not build up instantaneously, but will require a finite period of time. This period of time tends to prevent rapid, and oftentimes, destructive operation of switch 28. The saturable reactor then tends to stabilize the circuit and substantially improve the overall operation and reliability of the circuit.

While a similar form of saturable reactor is disclosed, it should be obvious to those skilled in the art that other forms of saturable reactors may be interposed between or in series with lines 48 and 49. It should also be apparent to those skilled in the art that switches such as thyratrons or ignitrons or semi-conductor switches could easily be substituted for the disclosed embodiments. Semi-conductor devices or vacuum tubes or their equivalent, could also be substituted for switch 28 within the teaching and scope of this invention.

The following examples are given to illustrate our invention. It will be understood that these examples are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims:

EXAMPLE 1

A 500-gallon tank clad with 304 stainless steel was equipped with the anodic polarization system as shown in FIG. 1, using a 6-volt lead storage battery as the source of D.C. current, a platinum electrode as the inert electrode, and a calomel cell as the standard electrode (electrochemically communicating with the tank by an agar-KCl bridge). The controller was of the type illustrated in FIG. 3.

The corrosive solution employed was a 67 percent aqueous solution of sulfuric acid. The current required to passivate this tank (having a surface area of 70 sq. ft. or approximately 10,000 sq. in.) was 4.2 amperes applied for about $\frac{1}{30}$ of a second. The current required to maintain passivity was approximately 142 milliamperes, which amounted to a current density of about 2 milliamperes per square foot (or about 2 microamp. per cm.²).

Without application of the anodic passivation technique, the build-up of metal in a 67 percent H₂SO₄ solution in this tank, in 41 hours, was 560 parts per million of iron, 93 p.p.m. of chromium, and 58 p.p.m. of nickel. When a fresh 67 percent solution of H₂SO₄ was placed in this tank, and the tank was passivated anodically, there was no detectable build-up of iron, chromium, or nickel, after over 120 hours. Thus, it is apparent that application of this anodic passivation technique reduced corrosion to a negligible amount.

EXAMPLE 2

A 60-gallon pfaudler, lined with 316 stainless steel, was charged with a 115 percent solution of phosphoric acid and nonene in the ratio of 1:4 by weight. (Nonene is a mixture of olefinic hydrocarbons in the C₈-C₁₂ range. This material is most economically derived as a by-product of the polymerization of propene using a phosphoric acid-kieselguhr catalyst, as illustrated in the patent to Grote et al., U.S. Patent No. 2,457,146, the nonene being described in the patent as a "low boiling polymer.") Nonene was used for the purpose of simulating the conditions under which olefin polymerization can be carried out utilizing a liquid phosphoric acid catalyst.

The system of FIG. 1 was employed, using a platinum electrode, a solid reference electrode consisting of silver coated with silver chloride, and a controller of the type shown in FIG. 6.

At a temperature of about 350° F., a pressure of 50 p.s.i., and under conditions of moderate agitation, the

system was passivated using 5 volts and a current of 5 amp. Less than 2 volts and 0.6 amp. were required to maintain passivity. The passive potential range was selected at 45-175 millivolts with respect to the reference electrode. The system was maintained in a passive condition for a period of four days, with only 5 p.p.m. of iron dissolved during this period. Without protection the same environment caused an iron pick-up of 100 p.p.m. in one day.

EXAMPLE 3

The method and apparatus of this invention was successfully used to prevent corrosion in a petrochemical plant manufacturing water-soluble xylene and toluene petroleum sulfonates suitable for the formulation of detergents. In this plant the hydrocarbon is sulfonated with oleum, and the sulfonic acid product is then neutralized with sodium hydroxide to form a neutral sulfonate.

In the absence of anodic polarization, the equipment is subject to rather severe corrosion, particularly the 304 stainless steel neutralizer tank, which is subject to severe pitting resulting in the necessity for frequent shut-down for repairs. The mild steel oleum storage tank is subject to mild corrosion due to the presence therein of a small amount of water resulting from condensation of moisture. An oleum measuring tank, hereinafter referred to as a "blowcase," is subject to corrosion of a more severe degree than the oleum storage tank.

Oleum storage tank

The oleum storage tank was passivated using the basic system of FIG. 1 utilizing a platinum electrode, a controller of the type shown in FIG. 3, and a calomel cell as the standard electrode (electrochemically connected to the liquid oleum by means of a weeping glass bridge assembly).

Prior to installation and operation of the anodic passivation system, iron content in the oleum tank had been as high as 1273 p.p.m., the average being about 500-600 p.p.m. At the time of installation of the passivation system, the tank contained about 450 p.p.m. of iron. The oleum as charged to the tank contains on the average of from 30-50 p.p.m., the additional iron content resulting from corrosion during storage. In less than one week after anodic protection was commenced the iron concentration dropped to 39-41 p.p.m., a value which was maintained continuously for a period of over one year.

Blowcase

The system of FIG. 1 was also employed to passivate the blowcase, using a platinum electrode and a reference (standard) electrode consisting of silver coated with silver chloride. The same controller was used for both the oleum tank and the blowcase, the controller being connected to the oleum tank at all times except when the blowcase was being filled. By means of a switching arrangement the controller was connected to the blowcase while it was being filled, during which time the oleum tank did not lose its passive condition.

Oleum samples from the blowcase had contained about 550 p.p.m. dissolved iron prior to start-up of the anodic passivation system. Following start-up the iron concentration was reduced to 125 p.p.m. after three batch runs. Following an initial two-week period, the iron concentration in the blowcase did not exceed 50 p.p.m.

Neutralization tank

The neutralization of sulfonic acid with caustic involves a multi-pH system, which subjects the metal to a range of corroding potentials. Since the anodic polarization technique depends upon the existence of a positive minimum potential area (as shown in FIG. 2) in which a minimum of corrosion occurs, it was necessary to determine the polarization curves for both the sulfonic acid and the caustic. It was found that the two curves overlapped to afford a safe operating range in which the poten-

tial could be maintained prior to and during actual neutralization.

The system of FIG. 6 was employed, using a platinum electrode, a solid silver-silver chloride reference electrode, and a control system of the type shown in FIG. 3.

The tank was initially passivated using a current density of about 4 amp. per sq. ft. at about 75° F., which was the temperature of the caustic in the tank just prior to addition of the sulfonic acid thereto. Upon addition of the sulfonic acid, the temperature began to rise, and rose to a maximum of about 190° F. At the latter temperature, the peak current density required to maintain passivity was about 7.5 amp. per sq. ft.

Prior to installation of the anodic passivation system, the neutralizer was down for an average of about 4 days per two-week period, for repairs due to corrosion. After the system was installed, the down-time was substantially reduced, and was only 4 days out of one 3-month period of time.

Just prior to installation of this system, a decision had been made to replace the tank, in view of the fact that it was badly in need of repair due to extended use over a long period of time coupled with severe corrosive damage. Fifteen months after installation of this system, the tank was still in condition for use. Thus, it is apparent that the passivation system extended the life of this tank for a period of 15 months beyond the originally-contemplated replacement time.

Other benefits resulting from the anodic passivation of the above-mentioned oleum tank, blowcase, and neutralizer were as follows:

(1) Prior to passivation, the hydrocarbon layer was not readily distinguishable from the sulfonate layer, since a high percentage of both hydrocarbon and product were retained in the undesirable stable emulsion formed, known as "cuff" (resulting from formation of iron soaps). After passivation, more distinct breaks in product separate occurred.

(2) After passivation the amount of cuff formation was greatly decreased.

(3) Prior to passivation, the sulfonate product was loaded with a fluffy white flocculant matter. After passivation, the product was bright and clear.

(4) The amount of iron in three batches of sulfonate prepared prior to installation of the passivation system was 230 p.p.m., 240 p.p.m., and 310 p.p.m., the total iron in the charges to the neutralizer having been 30 p.p.m., 24 p.p.m., and 55 p.p.m., respectively. After the passivation system was placed into operation, the iron content of three batches of sulfonate was 19 p.p.m., 16 p.p.m., and 20 p.p.m., the total iron in the charges having been 20 p.p.m., 19 p.p.m., and 17 p.p.m., respectively.

Another truly significant aspect of this invention is the ability of the system to passivate remote portions of the vessels and even attendant equipment. This throwing power is believed to be due to formation of an oxide film of high resistance. Once this film has been formed to render the metal surface passive, only small increments of additional current are required to patch the tiny pinholes which inevitably form in these remote places.

From the foregoing it will be apparent that the present invention will reduce corrosion of metallic vessels containing corrosive solutions without diluting the solutions by use of conventional corrosion inhibitors. With anodic protection, small amounts of chlorides can be tolerated. Also, no appreciable iron will enter a corrosion solution to affect the color of the product or provide an emulsion. An anodic current is passed from the vessel to an inert electrode in the acid solution periodically to reduce the power required in protecting the vessel against corrosion and to permit the use of simplified control apparatus. It will also be apparent that the present invention provides a novel and simple anodic current control apparatus which is simple in construction and operation and which will have a long service life.

Changes may be made in the combination and arrangement of parts or elements, as well as steps and procedures, as heretofore set forth in the specification and shown in the drawings, without departing from the spirit and scope of the invention as defined in the following claims.

We claim:

1. A method of anodically minimizing corrosion of a metallic vessel containing a corrosive solution, said metallic vessel and corrosive solution system having an anodic polarization curve wherein the metallic vessel and corrosive solution shows a minimum current region comprising passing direct current from the vessel to an inert cathode in the solution until the potential difference between the vessel and a standard electrode which is in electrochemical communication with the corrosive solution reaches a level corresponding to a predetermined maximum nobility of the vessel, then stopping the flow of said current until said potential difference reaches a level corresponding to a predetermined minimum nobility of the vessel, then again passing said current from the vessel to the cathode in the solution until said potential difference again reaches said first-mentioned level.

2. A method of anodically minimizing corrosion of a metallic vessel containing a corrosive solution, said metallic vessel and corrosive solution system having an anodic polarization curve wherein the metallic vessel and corrosive solution shows a minimum current region comprising imposing a uniform direct current potential between the vessel and an inert cathode in the solution in a direction to pass current from the vessel to the cathode until the potential difference between the vessel and a standard electrode electrochemically communicating with the solution reaches a level corresponding to a maximum positive potential within said region indicative of a predetermined maximum nobility of the vessel, then discontinuing said uniform direct current potential until the potential difference between the vessel and the standard electrode reaches a level corresponding to a minimum potential within said minimum current region which is indicative of a predetermined minimum nobility of the vessel, then again imposing said uniform direct current potential until the potential difference between the vessel and the standard electrode again reaches the first-mentioned predetermined level.

3. A method of anodically minimizing corrosion of a metallic vessel containing a corrosive solution, said metallic vessel and corrosive solution system having an anodic polarization curve having a passive range corresponding to a minimum current region comprising the steps of imposing a direct current voltage between the vessel as the anode and an inert electrode as the cathode in the said solution, and controlling said voltage so as to maintain the potential, between the vessel and a standard electrode connected to said solution, within the passive range.

4. The method of claim 3 wherein the metallic vessel is constructed of mild steel.

5. The method of claim 4 wherein the corrosive solution is a caustic solution.

6. The method of claim 4 wherein the corrosive solution is a sulfuric acid solution.

7. The method of claim 4 wherein the corrosive solution is a phosphoric acid solution.

8. The method of claim 4 wherein the corrosive solution is nitric acid solution.

9. The method of claim 4 wherein the corrosive solution is a liquid fertilizer.

10. The method of claim 3 wherein the metallic vessel is constructed of stainless steel.

11. The method of claim 10 wherein the corrosive solution is a caustic solution.

12. The method of claim 10 wherein the corrosive solution is a phosphoric acid solution.

13. The method of claim 10 wherein the corrosive solution is a sulfuric acid solution.

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14. The method of claim 10 wherein the corrosive solution is a nitric acid solution.

15. The method of claim 10 wherein the corrosive solution is a liquid fertilizer.

16. The method of claim 3 wherein the metallic vessel is constructed of titanium.

17. The method of claim 16 wherein the corrosive solution is a caustic solution.

18. The method of claim 16 wherein the corrosive solution is a sulfuric acid solution.

19. The method of claim 16 wherein the corrosive solution is a phosphoric acid solution.

20. The method of claim 16 wherein the corrosive solution is a nitric acid solution.

21. The method of claim 3 wherein the metallic vessel is constructed of an alloy of a metal selected from the group consisting of titanium, hafnium, and zirconium.

22. The method of claim 21 wherein the corrosive solution is a caustic solution.

23. The method of claim 21 wherein the corrosive solution is a sulfuric acid solution.

24. The method of claim 21 wherein the corrosive solution is a phosphoric acid solution.

25. The method of claim 21 wherein the corrosive solution is a nitric acid solution.

26. The method defined in claim 1 wherein the vessel is stainless steel and said inert electrode is platinum.

27. The method defined in claim 1 wherein the vessel is stainless steel and said standard electrode is a calomel cell.

28. The method defined in claim 1 characterized further in placing the standard electrode in communication with the solution by an electrolytic bridge.

References Cited by the Examiner

UNITED STATES PATENTS

2,221,997	11/40	Polin	204—196
2,483,397	10/49	Bonner	204—196
2,576,680	11/51	Guitton	204—147
2,584,816	2/52	Sands	204—231
2,759,887	8/56	Miles	204—196
2,764,543	9/56	Comstock et al.	204—231
2,803,797	8/57	Cowles	204—196
2,848,658	8/58	Mitchell	317—148.5
2,903,405	9/59	Sabins	204—196
2,918,420	12/59	Sabins	204—231
2,982,714	5/61	Sabins	204—196
2,998,371	8/61	Sabins	204—196
3,009,865	11/61	Mueller et al.	204—147

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