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3,409,526

METHOD AND APPARATUS FOR CORROSION PROTECTION

Filed Aug. 13, 1965

5 Sheets-Sheet 1

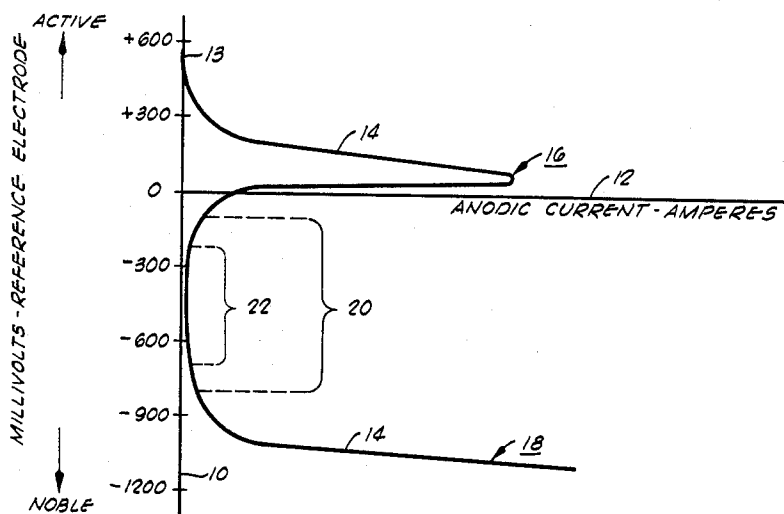


FIG. 1

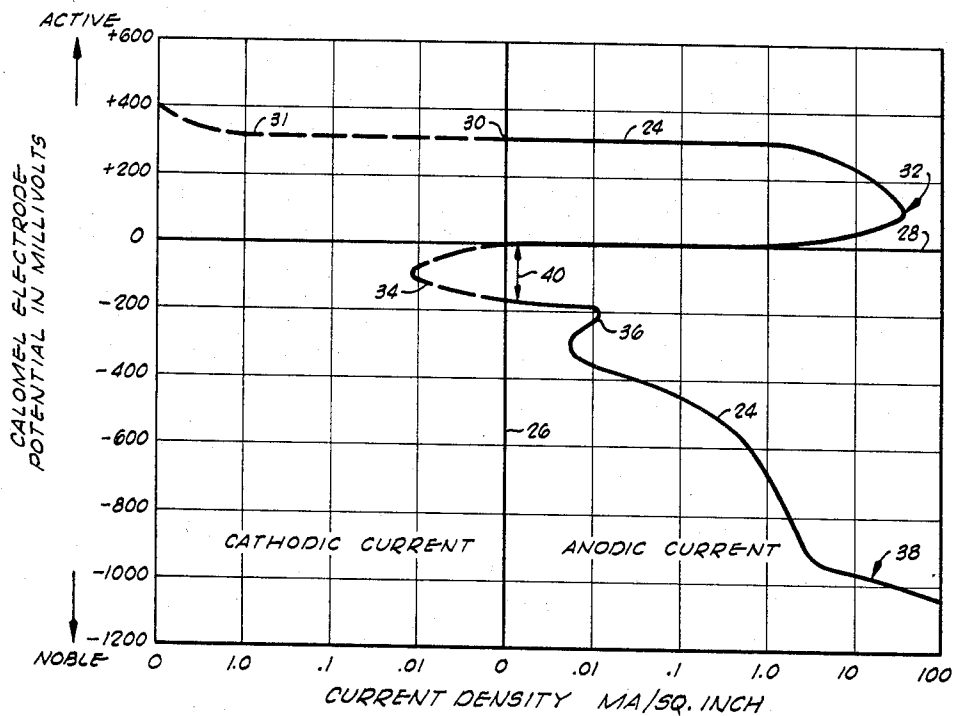


FIG. 2

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5 Sheets-Sheet 2

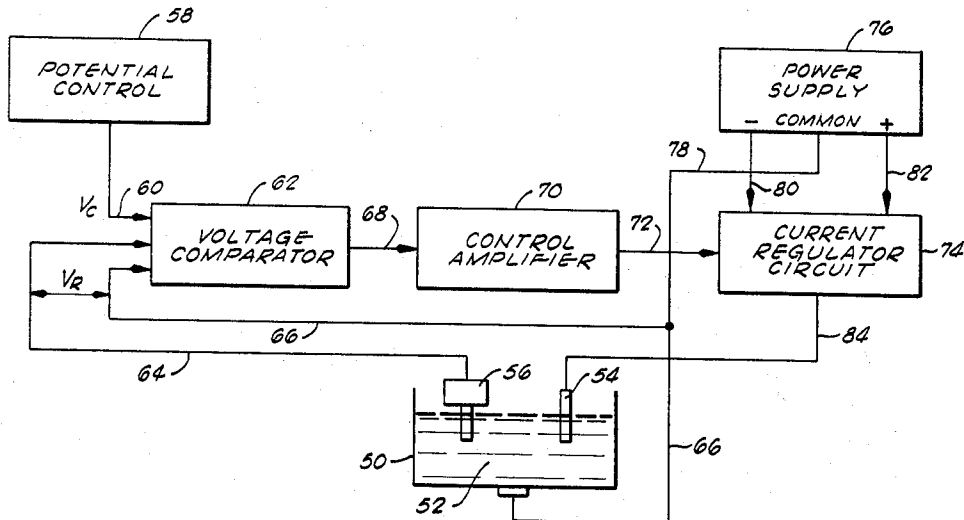


FIG. 3

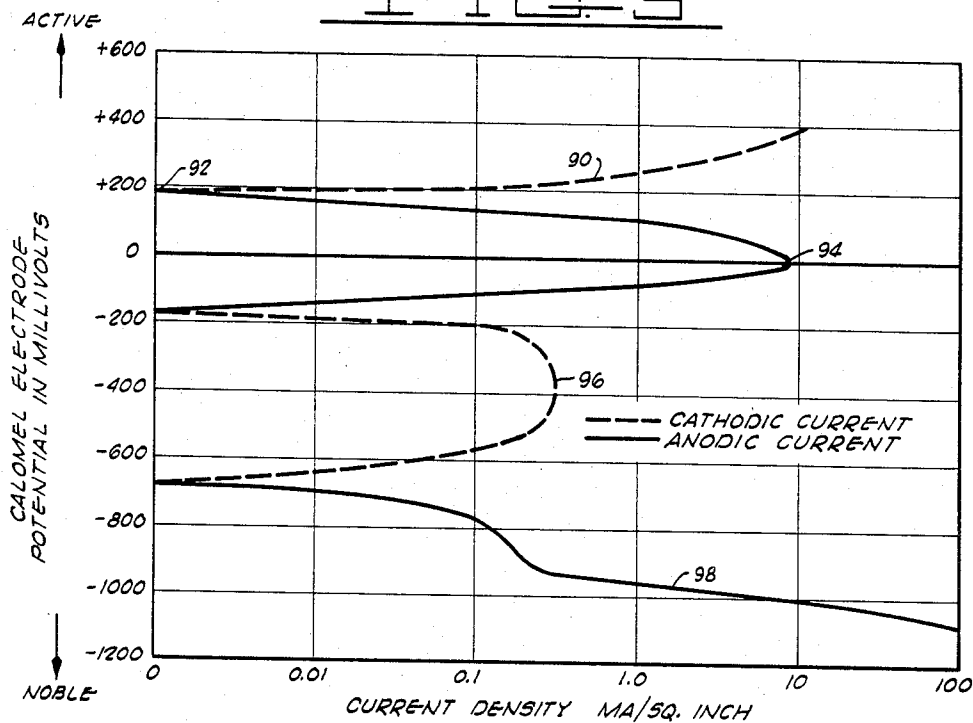


FIG. 4

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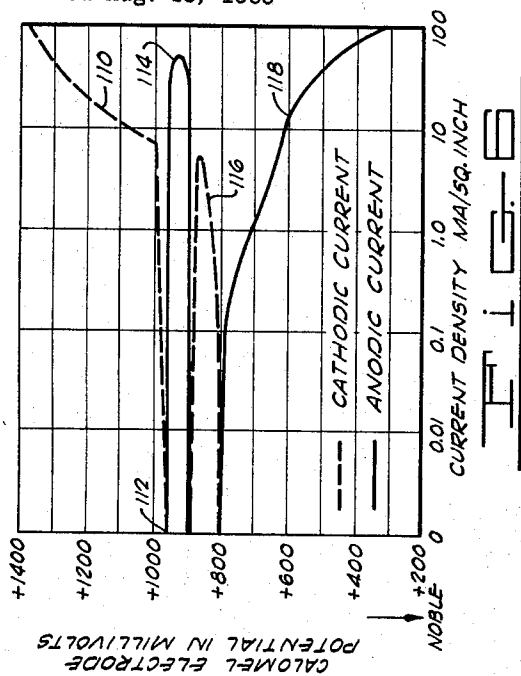
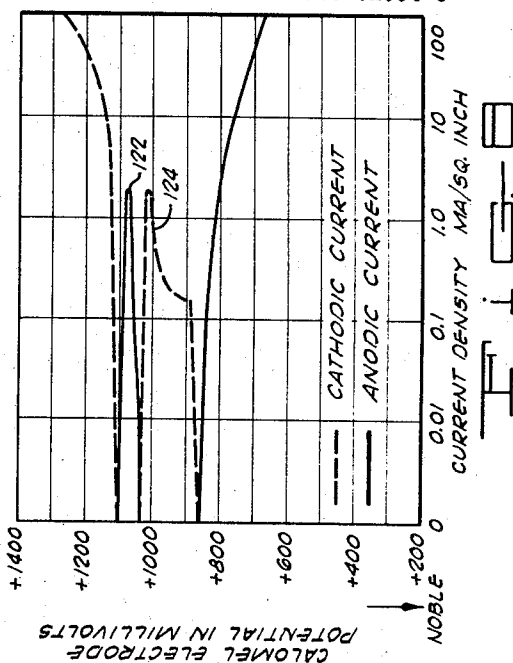
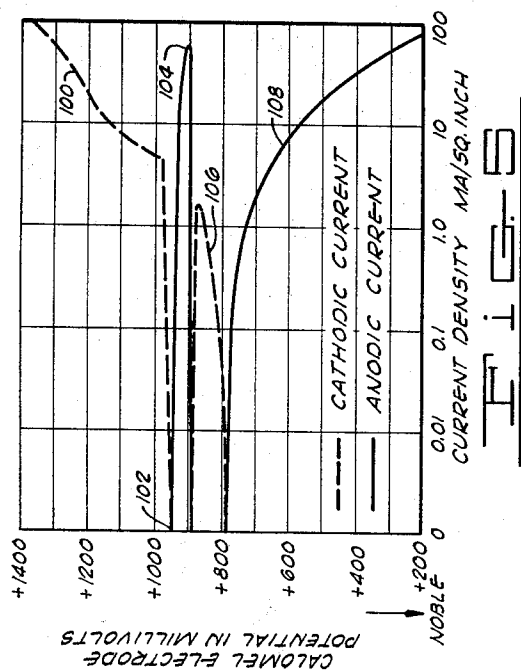
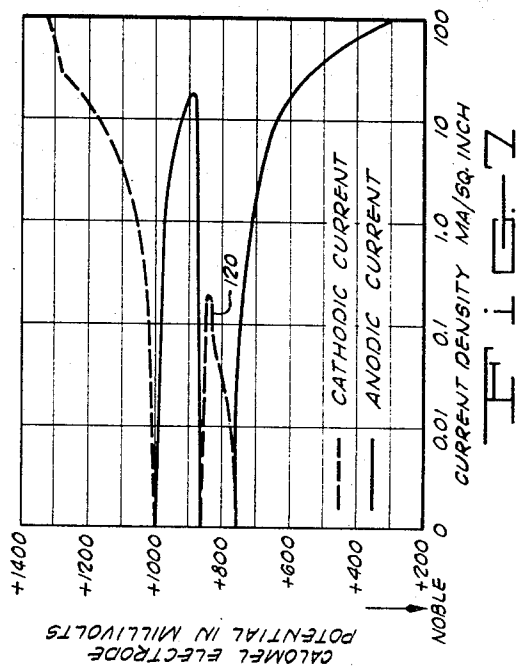
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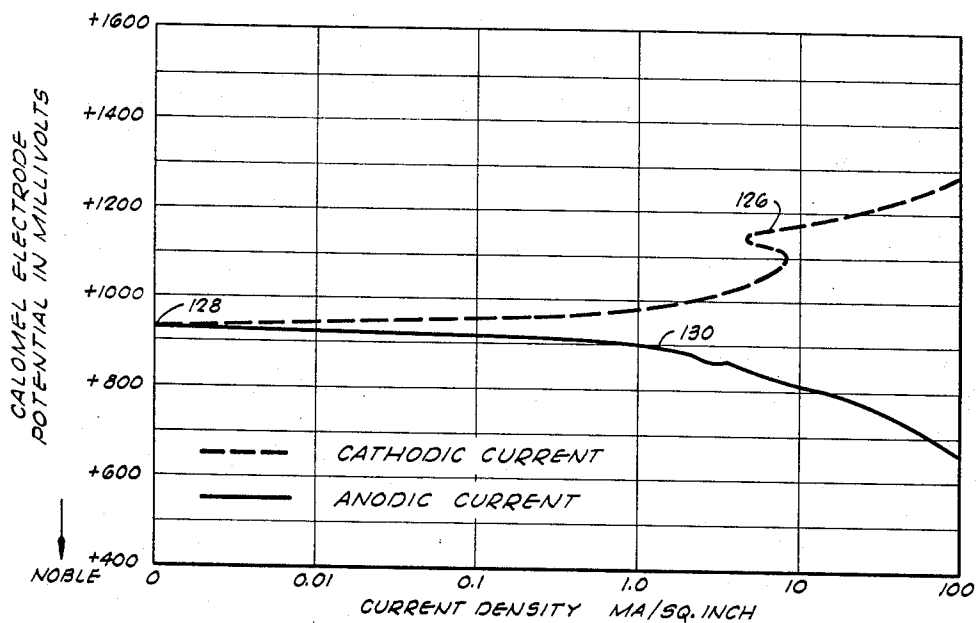


FIG. 9

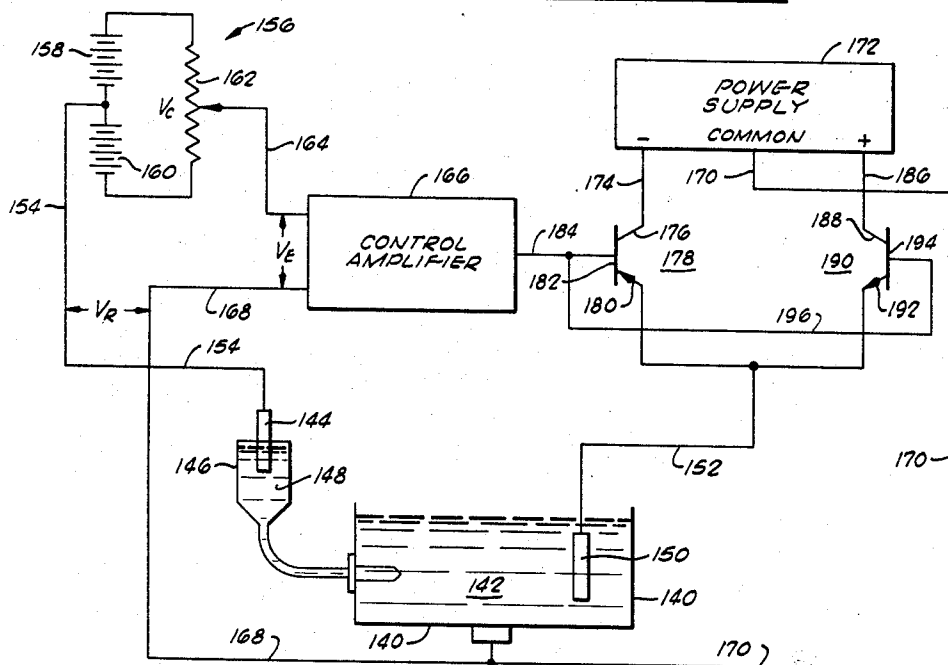


FIG. 10

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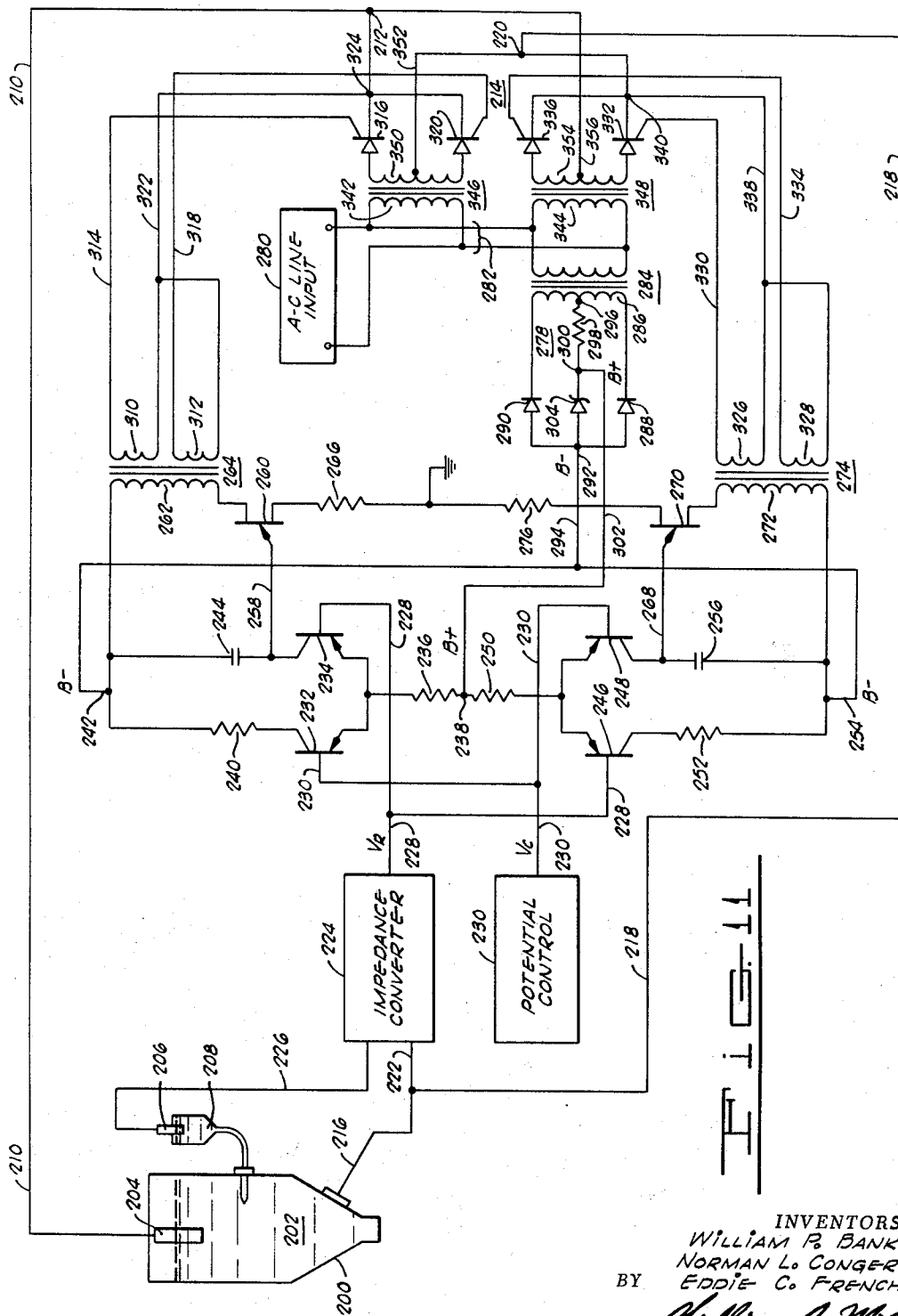
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METHOD AND APPARATUS FOR CORROSION PROTECTION

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3,409,526

METHOD AND APPARATUS FOR CORROSION PROTECTION

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Filed Aug. 13, 1965, Ser. No. 479,578
27 Claims. (Cl. 204-147)

The present invention relates to an improved method and apparatus for controlled potential corrosion protection of metallic bodies, and more particularly, but not by way of limitation, the invention is concerned with controlling the corrosion rate of certain types of special corrosion reaction wherein both anodic and cathodic currents are encountered at the interface of a metallic vessel and its corrosive solution.

As it is well known in the art of corrosion control, the corrosion of many metals may be prevented or largely reduced by inducing passivity in the metal by anodic polarization techniques. Recently, a method and apparatus for corrosion prevention by means of anodic polarization has been developed wherein a metallic specimen, such as a vessel to be protected against corrosion by a chemical contained therein, is anodically polarized with respect to an inert electrode suspended in the corrosive electrolyte in the vessel. An electrical current is passed between the metallic vessel and the inert cathode in a manner such as to maintain the electrical potential of the vessel in a so-called passive region, that is, a potential range in which the rate of corrosion of the vessel is minimized. The magnitude of the current which is applied between the vessel and the inert cathode is at all times determined by the potential of the metallic vessel, with the current being varied as necessary in order to maintain the potential of the vessel in the region of passivity.

In the commercial systems which have been developed for protecting a metallic member through anodic polarization, a reference electrode of constant potential is placed in electrical communication with the corrosive electrolyte contacting the metallic member, and the potential difference between such reference electrode and the metallic member is constantly monitored. This potential difference, which may be termed the reference potential, is constantly compared electrically with a second potential which is derived as a control potential. The control potential is the potential difference which, according to predetermined polarization curve data, must exist between the metallic member and the reference electrode if the vessel is to be maintained in a passive state. The continuous electrical comparison of the reference potential with the control potential results in the continuous generation of an error voltage which provides a signal usable to increase or decrease the amount of current passed between the metallic member and the inert cathode suspended in the electrolyte. In other words, the potential of the metallic member is constantly monitored, and the anodic corrosion control system functions to develop an error signal in the manner described to constantly maintain the metallic member at a passive potential.

The above types of anodic passivation system have been developed in a variety of equipments for specific corrosion control applications. Generally speaking, anodic passivation systems are employed in metal-electrolyte

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combinations that include highly conductive solutions which exhibit the property of establishing a passive range with the metal in question. Hence, anodic passivation is particularly adaptable to usage in iron or stainless steel storage or processing vessels which contain a corrosive, electrolyte solution, such as, sulphuric acid, phosphoric acid, sodium hydroxide, lithium hydroxide, aluminum sulphate, nitric acid and many other corrosive liquids which find extensive commercial employ.

It has now been discovered that there is another class of corrosion reactions which exhibit a somewhat different behavior at the metal-electrolyte interface during corrosion. That is, when the metal-electrolyte system is in its passive range, both anodic and cathodic currents are generated within the passive potential range of the metal. This special polarization behavior was noted in systems of Carpenter 20 Steel containing a solution of sulphuric acid and zinc. Other additional metal-electrolyte systems have also been found to exhibit the special polarization behavior; for example, systems of stainless steel containing hot, concentrated alum solutions, and a pulp digester system consisting of a carbon steel vessel containing alkaline sulphide cooking liquor. Still other metal-electrolyte systems will exhibit the special polarization behavior and would thus be suitable subjects for the employ of the present invention.

The present invention contemplates a method and apparatus for controlled potential corrosion protection in metal-electrolyte systems which exhibit special polarization behavior wherein a region of cathodic current activity as well as a region of anodic current activity is present at the more noble, non-corroding metal potentials. The method requires that polarization current of either polarity be available for application to the metal vessel, depending upon the potential of the vessel and its corresponding anodic or cathodic current requirements as determined from the characteristic E versus I curve for the particular metal-electrolyte system. The apparatus of the invention provides electrical connections so that current may be passed from a suitable bi-polar power source through the anode, the electrolyte and an auxiliary electrode immersed in the electrolyte. The control equipment is such that the polarity of the current applied from the external power source can be reversed in accordance with the current density requirement as dictated by the instantaneous polarization current at the metal-electrolyte interface, that is, whether anodic or cathodic current flow. A reference electrode is also immersed in the corrosive solution such that it may continually monitor the potential of the vessel for comparison with a preset control point voltage to provide an indication whereby the power supply can be continually controlled as to the polarity of its application between the vessel and auxiliary electrode.

It is an object of the present invention to provide a method of corrosion protection for metal-electrolyte systems which exhibit a special polarization current behavior.

It is another object of the present invention to provide a corrosion protection method for a class of metal-electrolyte systems which include Carpenter 20 Steel-sulphuric acid systems, steel-alum systems, and digesters, particularly of the carbon steel-alkaline sulphide liquor type.

It is further an object of the present invention to provide a method of corrosion protection for metal-electro-

lyte systems which exhibit both anodic and cathodic current density regions within the more noble, non-corroding range of vessel potentials.

It is still another object of the present invention to provide apparatus for monitoring vessel potential and controlling the polarity of voltage output from a power supply to the vessel system in accordance with the potential indication.

It is yet another object of the invention to provide apparatus for generating control signals in response to predetermined vessel potential values for the purpose of controlling the polarity of application of a direct current power supply between a metallic vessel and an auxiliary electrode.

Finally, it is an object of the present invention to provide corrosion protection for a class of metal-electrolyte systems exhibiting special polarization current behavior wherein the potential of the vessel can be continually monitored with respect to a reference control voltage to provide a further voltage indication which controls a power source to apply either positive or negative polarity of current to the vessel, depending upon whether there is anodic or cathodic current activity at that particular potential of the vessel.

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

In the drawings:

FIG. 1 illustrates an exemplary polarization curve of the usual type which is characterized by the presence of anodic current density within the entire passive range;

FIG. 2 illustrates a polarization curve which shows special polarization characteristics;

FIG. 3 is a block diagram of an equipment suitable for carrying out the present method;

FIG. 4 is a polarization curve for a Carpenter 20 Steel-Sulphuric acid/zinc system which exhibits special polarization behavior;

FIGS. 5, 6, 7, 8 and 9 show a family of polarization curves for a 1020 mild steel-alkaline sulphide liquor system at the respective temperatures of 150°, 207°, 250°, 300° and 350° Fahrenheit;

FIG. 10 is one form of apparatus suitable for carrying out the present method; and

FIG. 11 is an alternative form of apparatus for carrying out the method.

FIG. 1 illustrates a typical anodic polarization curve depicting the anodic current behavior of a stainless steel vessel containing sulphuric acid. This is the usual form of E vs. I characteristic curve of the type suitable for anodic polarization techniques as previously ascribed to the prior art. It should be noted that the current is anodic through the entire range of vessel potentials, that is, from the active potentials through the more noble potentials. The ordinate 10 is graduated in millivolts and indicates the metal potential as derived from a saturated calomel electrode in contact with the corrosive solution. The abscissa is graduated in amperes and indicates the relative anodic current flow between the vessel (anode) and a cathode immersed in the electrolytic solution.

The value of about +600 millivolts found at point 13 (zero amperes current) of the current density curve 14 is defined as the natural corrosion potential. This potential may be shifted toward the noble end of the electromotive series by applying current through the electrolyte between the stainless steel vessel (anode) and the inert cathode electrode. The amount of current required to shift the potential in the more noble direction increases along the curve 14 until a point 16, the Flade arrest potential, is reached. At the Flade arrest potential, the amount of current required to shift the potential decreases rapidly and remains at a very low value until the transpassive region 18 is reached.

The potential range above the Flade point 16, from

about 100 millivolts up to 600 millivolts, the natural corrosion potential, is termed the active region. Corrosion is greatly accelerated in this portion of the curve. Below the Flade potential 16 and within the bracketed portion 20, there is what is termed the passive region of the curve wherein corrosion is practically halted, as shown by the very small relative value of anodic current. When the vessel potential (to the reference electrode) shows still further decrease, the condition passes into the transpassive region wherein high current flow is again present and corrosion protection is lost. The bracketed portion 22 denotes a desired range of passivity at which effective corrosion protection can be carried out. An anodic protection system would function to maintain the potential of the containing vessel (with respect to a calomel reference electrode) within the potential limits of the region 22; however, the potential limits as set by the larger bracket 20 could also be used to give reasonably good corrosion protection.

The method and apparatus of the present invention is concerned with a special polarization behavior as exhibited by certain metal-electrolyte systems, an example of which is shown by way of FIG. 2. FIG. 2 shows a semilog E vs. I plot, polarization curve 24, which was derived for 304 stainless steel in contact with hot, concentrated alum solution containing 14 percent aluminum oxide (Al_2O_3) at 220° F. The potential measurements were taken by means of a saturated calomel electrode in electrode in electrochemical contact with the hot alum solution at 80° F. The ordinate 26 is calibrated in millivolts to show the potential difference between the calomel standard electrode and the metallic vessel and the abscissa 28 is calibrated logarithmically to show the current density of the metal-electrolyte system in milliamperes per square inch of the metallic vessel of the system. Further, although 304 stainless steel is specified here, it should be understood that similar behavior is evident with other stainless steels or alloys having a high nickel or chromium content.

At the potentials more active than the natural corrosion point 30 there is a primary cathodic current region 31 wherein the metal is actively corroding. As current is applied to the system to reduce the potential to a more noble or more stable value, a very high initial anodic current is required to move the vessel potential from the natural corrosion point 30 (about +300 millivolts) through the Flade arrest point 32. With further potential decrease the anodic current density drops abruptly and becomes cathodic in character as shown by the secondary cathodic current region 34. With still further decrease in the vessel potential, the polarization curve indicates that anodic current density is once again present (below about -200 millivolts) which traverses a short peak 36, of no particular consequence, and finally goes to the transpassive condition, indicated by region 38 of the polarization curve 24.

It should be understood that the potential of the reference voltage in FIGS. 2, 4 and 5 through 9 are opposite in polarity to values which would be shown under the standard convention as adopted by the International Union of Chemistry and Applied Physics. This convention maintains that potentials moving from active to noble should progress from negative to more positive potentials. The potentials under the convention are measured by a reference electrode which is connected to the common side of the measuring circuit. However, the potentials as shown and described herein are measured with respect to the common side of the measuring circuit, an integral part of the system, as will be described.

The method disclosed herein enables corrosion protection of metal-electrolyte systems which exhibit such special polarization behavior by first applying anodic current to take the system through the Flade potential 32 and thereafter utilizing a reference potential as sensed by a reference electrode for controlling the amount and polar-

ity of current application to the system. Thus, the requirements for corrosion protection may require either cathodic or anodic current flow within the corrosion protection range of more noble metal potentials. That is, the range of metal potentials more noble than the Flade arrest potential at which the current density between the metal and electrolyte is at a low value and the metal-electrolyte system is maintained stable and non-corroding.

In applying the method to a metallic vessel-corrosive solution system, it is necessary to control the vessel potential continuously by application of the proper polarity of current through the solution. The required manner of current application will be apparent from a polarization curve which is established for the particular metal and solution. A high value of anodic current is first applied to shift the vessel potential to a value slightly below the Flade arrest potential and, in cases of special polarization behavior, this will be a non-corrosive cathodic current region. The vessel-solution system can then be maintained within that region by controlled application of reversed or cathodic current through the solution.

In a certain few metal-electrolyte systems which exhibit the special polarization behavior, it has been found that existing anodic passivation equipment can be used to prevent corrosion to some extent. For example, equipment such as that disclosed in U.S. Patent No. 3,127,337, entitled "Anodic Passivation System"; issued to Conger et al. and assigned to the present assignee.

This equipment can be applied in its usual manner to lower the potential of a metallic vessel through the Flade arrest point and into the secondary cathodic current region whereupon anodic current application can be ceased. In these few metal-electrolyte systems the vessel potential will remain in the secondary cathodic current region for appreciable periods of time due to the inherent nature of the system to seek a stable, non-corroding potential. However, this type of protection is limited to a few applications and does not have the versatility required for reliable controlled potential corrosion protection of the large majority of the metal-electrolyte systems which exhibit special polarization behavior.

FIG. 3 shows a block diagram of a corrosion protection equipment which has the required versatility to carry out the method set forth herein. The vessel 50, a control electrode in the metal-electrolyte system, contains a corrosive solution 52, and an auxiliary electrode 54 and a reference electrode 56 are immersed in contact with the corrosive solution 52. The auxiliary electrode 54 is formed of a material which is non-reactive with the corrosive solution, preferably platinum or another of the inert metals. The reference electrode 56 consists of a standard half-cell, many types of which are employed in the corrosion control art, which may be placed in electrochemical contact with the solution 52 through an agar or potassium chloride (KCl) salt bridge juncture.

A potential control circuit 58 supplies a predetermined control voltage V_c on the lead 60 to the voltage comparator or differential amplifier 62. Similarly, the reference electrode 56 supplies its voltage indication on lead 64 to voltage comparator 62 while the vessel electrode connection 66 supplies the common vessel potential to the voltage comparator 62. The voltage comparator 62 senses the potential difference between the voltage on lead 64 and the common vessel voltage on lead 66 to derive a relative vessel potential, the reference voltage V_r . This relative vessel potential is then compared with the control potential V_c on lead 60 which is preset at a value derived from the polarization curve of the particular metal-electrolyte system in conjunction with the particular half-cell 56 which is employed. Thus, the voltage comparator 62 derives an output signal on lead 68 which is indicative of the amount and polarity of potential difference between the vessel 50 and the preset potential control 58. There are various forms of voltage comparator 62 which could be

employed in the system and these will be further described in connection with specific apparatus.

The difference or error control voltage V_e on lead 68 is then amplified in a control amplifier 70 and applied on lead 72 to a current regulator circuit 74. A high current power supply 76, providing both negative and positive output current sources, has its common terminal connected via a lead 78 to lead 66 and to the metallic vessel 50. A negative current output lead 80 and a positive current output lead 82 are then connected through the current regulator circuit 74 which has a single output lead 84 connected to the auxiliary electrode 54. The current regulator circuit 74 is responsive to the control signal on lead 72 from control amplifier 70 to switch either the negative current (lead 80) or the positive current (lead 82) for connection to the auxiliary electrode lead 84. The current regulator circuit 74 also responds proportionally to the control signal on lead 72 to vary the amount of current passing through the switch connection to the auxiliary electrode lead 84. A complete description of suitable current regulator circuitry is to be further described in connection with specific apparatus.

There are various other metal-electrolyte systems which show such special polarization characteristics that the present method of controlled potential corrosion protection is required. Polarization curves for each of the metal-electrolyte systems exhibits the expected swing from the primary cathodic current region through the natural corrosion point to the Flade arrest point and then through a sharp decrease of anodic current. With further increase towards the more noble vessel potential, the systems pass through a region of secondary cathodic current density and then back to the anodic current condition and finally into the transpassive region of anodic current density. The following curves of FIGS. 4 through 9 are shown in a different form from FIG. 2 with both the anodic and cathodic current density patterns being shown on the same side of the ordinate. It should be understood however that the curves are the same type as shown in FIG. 2 and the variation is merely a space-saving measure.

FIG. 4 shows the graph or polarization curve for another metal-electrolyte system which finds extensive commercial employ and which exhibits special polarization behavior. The curve indicates the current density versus the vessel potential for Carpenter 20 steel in 200 grams per liter sulphuric acid and 65 grams per liter zinc at 65° C. The vessel potential indicated on the ordinate is indicated with respect to a saturated calomel half-cell as the reference electrode and the reference electrode was maintained at 80° Fahrenheit in electrochemical contact with the sulphuric acid/zinc solution. The system exhibits the expected primary cathodic current region 90 at the most active potentials with a rapid transition through the natural corrosive point 92 at about 200 millivolts vessel potential. Further decrease of the vessel potential indicates that the current density increases rapidly to the Flade arrest point 94, at about 0 millivolts vessel potential; and then falls rapidly to the secondary cathodic current region 96. At a vessel potential of about -700 millivolts the current density once again becomes anodic and thereafter it passes into the transpassive region 98.

Inspection of the curve indicates that a secondary cathodic current region 96, from about -200 millivolts to -700 millivolts, constitutes a range of potential values more noble than the Flade arrest point 94 wherein the vessel is in a stable, non-corrosive condition. Thus, it would be desirable to employ the controlled potential protection system to maintain the vessel potential between -200 and -700 millivolts and to prevent corrosion of the Carpenter 20 steel vessel.

The 500 millivolt range of the cathodic current region 96 is more than adequate since the protection system at most only requires about 50 to 100 millivolts of correc-

tion range about a control point. Thus, the operator may choose an optimum value at which to set the control point within the secondary cathodic current range. This will depend upon the shape and amount of current density in the secondary cathodic current loop of each particular metal-electrolyte system. Similar behavior of special nature is exhibited by many metal-electrolyte systems which include zinc ions in solution and thus the present method of corrosion protection is particularly applicable.

FIGS. 5 through 9 illustrate a family of polarization curves for a metal-electrolyte system which finds extensive industrial usage. The curves indicate the current density and therefore the corrosion effects of alkaline sulphide liquors in pulp digesters. Corrosion has been a great problem with all pulp digesters having practical utility and the equipment cost and replacement expenses necessitate the application of an effective controlled potential protection method. In the operation of a pulp digester, the metallic digester vessel is charged with the pulp and alkaline sulphide liquor, and the batch process is then carried on for a number of hours at a high temperature of about 350° F. Once the digester and its contents is up to operating temperature, at about 350° F., there is little or no danger of corrosion, at least not such as would definitely require corrosion protection. However, corrosion is extremely high during the heating period and this is where the problem arises. The following family of curves will illustrate the variations of behavior of the pulp digester metal-electrolyte system at the various temperatures of operation and this consideration accentuates the need for a flexible and accurate controlled potential protection system.

FIG. 5 shows a first polarization curve for a pulp digester system at 150° F. which is somewhat below the starting temperature of a typical pulp digester process. Since the usual or average liquid charge to an alkaline sulphide pulp digester can consist of volumes of white (active) and black (spent) liquors as dilute as 50/50 volume percent, the polarization curves were determined for a 50/50 volume percent mixture of white and black liquors. The active or charging liquor is approximately 4.7 weight percent sodium hydroxide (NaOH) and 1.6 weight percent sodium sulphide (Na₂S). The metal of the system is 1020 mild steel, one of the carbon steel materials commonly used in pulp digester vessels. Also, in each of the curves of FIGS. 5 through 9, the vessel or metal potential is indicated with respect to a saturated calomel half-cell at 80° F. (thus it is in heat insulative, electrochemical contact with the charged solution).

As shown in FIG. 5, the primary cathodic current region **100** is evident at the more active or highly corrosive vessel potentials. Then the curve drops to zero current density at about +950 millivolts, the natural corrosion potential **102**. The current density then becomes anodic and rises rapidly to the Flade arrest point **104** and at a vessel potential slightly below 900 millivolts the anodic current density ceases and the exchange reverses to a cathodic current density as outlined by the secondary cathodic current region **106**. Thus, there is a cathodic current between vessel potentials from about +875 millivolts in the noble direction to about +800 millivolts and this would constitute a desirable range in which to set a control point of the controlled potential protection apparatus. As the digester vessel is made more noble, that is, the vessel potential becomes more negative than the +800 millivolts, the current density becomes anodic and traverses into the transpassive region **108**.

FIG. 6 shows the 1020 mild steel-alkaline sulphide polarization curve at 207° F. as it would exist shortly after a digestion process was begun. This curve shows the similar current density characteristics, that is, a primary cathodic current region **110** through a natural corrosion point **112** and then through the anodic current region and Flade arrest point **114** to the secondary cathodic current region **116**, the desired stable control

point. The secondary current region **116** still shows a vessel potential range between about 800 and 900 millivolts wherein very effective control can be maintained and then at more noble potentials the current density would become anodic into the transpassive region **118** of the curve. This curve is highly similar to the 150° F. curve (FIG. 5) but it should be noted that the Flade arrest point **114** is at a slightly higher vessel potential as is the natural corrosion point **112**.

FIG. 7 illustrates the curve with the same digester materials after the operating temperature has reached 250° F. The general form of the curve is still the same although the various sectors of cathodic and anodic current are changed somewhat in shape. The secondary cathodic current region **120** still provides a reasonably wide potential range between the digester potential vessels of about 750 to 850 millivolts. This is more than ample control voltage range and the controlled potential protection system can be set to maintain the digester in a non-corroding condition. FIG. 8 shows the same curve after the reaction temperature has reached 300° F. Again the overall shape of the curve is changed, however, the general form is similar as there still remains a Flade arrest point **122** as well as a region of secondary cathodic current **124**. At 300° F. the secondary cathodic current region **124** shows the presence of cathodic current over an increased potential range of the metallic vessel. The vessel would be maintained in a stable, non-corrosive condition as long as its potential was in the range from about +875 millivolts to about 1050 millivolts. The potential control point of a protection system could be set anywhere within this 175 millivolt spread to effect corrosion protection.

FIG. 9 shows the polarization curve for the digester system after it has reached 350° F., its cooking or processing temperature. It should be noted here that there is no typical anodic Flade arrest point, merely a primary cathodic current region **126**, a natural metal-electrolyte potential **128** at about 925 millivolts which is largely non-corroding, and an anodic current region **130** which extends into the transpassive condition of the metal polarization. In this the cooking condition, the pulp digester system exhibits little or no corrosion; hence, corrosion protection is not necessary once the pulp digester vessel has attained its processing heat of 350° F. As previously stated however, the great and excessive amount of corrosion takes place during the time between the initial charge of the cooking liquor into the digester vessel at much lower temperatures and up to the time when the processing temperature of 350° F. is reached. Thus, the controlled potential corrosion protection system is employed during this time of heat-up to combat the excessive corrosion taking place in that period. It is important also to note that a corrosion protection system for such pulp digestion processes must exhibit certain flexibility since the vessel potential ranges of secondary cathodic current are continually varying as the temperature climbs to the final processing level.

The following table lists the corrosion rates and other pertinent data for 1020 mild steel in alkaline sulphide liquor. Comparison of the various results will indicate the severe corrosion which takes place during the heat-up period of the process. Observation of the results obtained at 350° F. or the cooking temperature will reveal the contrast in data and the relative corrosive stability of the metal-electrolyte system at the highest temperature.

The test data of the table (below) was compiled with laboratory equipment using 1020 mild steel coupons immersed in a 50/50 volume percent mixture of white and black alkaline sulphide liquors at the various temperatures as listed. The reference potentials, taken with respect to the 1020 mild steel coupons, are the potentials for a saturated calomel half-cell; hence, they are relative potential values for the mild steel coupons in each instance. The unprotected coupons were periodically

activated by passing a few milliamperes of cathodic current through the coupon at the beginning of the test, and then at intervals throughout the test, if necessary, to keep the coupon potential at a stable corroding value.

rosive solution 142. The power application lead 152 is connected to the auxiliary electrode 150 from a power source to be described. The reference electrode 144 is connected via a lead 154 to a potential control circuit or

Temperature, ° Fahrenheit	Pressure, p.s.i.g.	Liquid Phase Corrosion Rate, Milli-inches per year		Number of Acti- vations	Unpro- tected Coupon Potential, Millivolts	Polarization Potential, Millivolts	Current Density, Milliamperes/ sq. inch
		Unpro- tected	Polarized				
147	-----	557	0.0	3	950	840	0.015 Cathodic.
208	-----	86	0.0	1	980	850	0.083 Cathodic.
250	15	31	0.0	2	1,085	875	0.05 Cathodic.
300	50	161	0.0	9	1,145	975	0.22 Cathodic.
350	100	423	0.0	15	1,145	875	0.07 Anodic.
350	100	0	0.0	0	885	845	0.18 Anodic.

The activated, unprotected coupons corroded at a high rate, ranging from 31 to 557 milli-inches per year in the temperature interval between 147° and 350° F. The tendency of the unprotected coupons to spontaneously shift to the stable non-corroding potential value increases markedly at the higher temperatures. This tendency is consistent with conclusions which can be drawn from the respective curves of FIGS. 5 through 9.

The coupon corrosion rates for the polarized or protected phase of the tests were zero throughout the entire temperature range from 147° to 350° F. At the temperature below 350° F., the coupons were polarized at potentials corresponding to the secondary cathodic current region of the polarization curve. At 350° Fahrenheit, the secondary cathodic region is absent from the polarization curve, and the coupons were maintained at a potential corresponding to a low anodic current density. These results prove the value of the present method of controlled potential corrosion protection for metal-electrolyte systems exhibiting special polarization behavior.

APPARATUS

There are several forms of apparatus which have been constructed for use in controlled potential corrosion protection. Some alternative forms which are suitable for performing the present method are set forth hereinafter. As will become apparent, the different equipments exhibit certain advantages and disadvantages for particular corrosion protection applications due to their inherent circuit characteristics and power handling capabilities.

One embodiment of the controlled potential corrosion protection apparatus is illustrated in FIG. 10. The apparatus might be employed with any of the metal-electrolyte systems exhibiting the special polarization behavior as previously discussed. For example, the metal-electrolyte system may comprise the materials as set forth with regard to FIG. 4. That is, the metallic vessel 140 would be formed from Carpenter 20 steel and the corrosive solution 142 contained therein would be 200 grams per liter sulphuric acid and 65 grams per liter zinc. Also, in keeping with the polarization curve of FIG. 4, the reference electrode 144 would be a saturated calomel half-cell. As previously stated, the standard electrode could be one of several other suitable types such as a silver-silver chloride cell, copper-copper sulfate cell, molybdenum-molybdenum oxide, and so forth; however, the polarization curve (FIG. 4) requires the use of calomel since it was compiled from such reference.

The reference electrode 144 is shown communicating electrochemically with the corrosive solution 142 through a suitable electrolytic bridge 146 to prevent the reference voltage cell from coming into direct contact with the solution 142. While an electrolytic bridge 146 is shown communicating with the solution 142, it should be understood by those skilled in the art that various well-known equivalents may be used to ionically couple the reference electrode 144 to the corrosive solution 142.

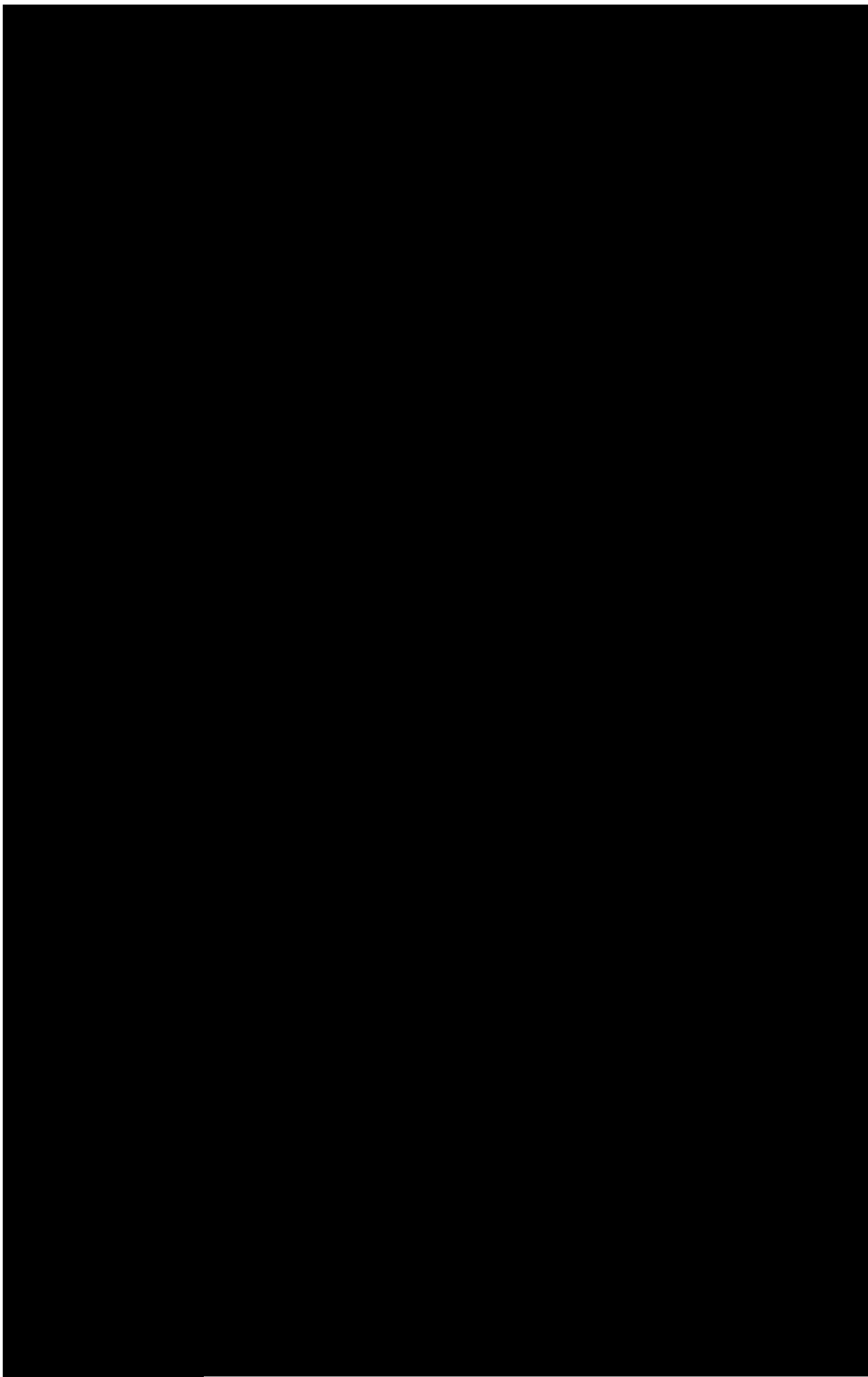
An auxiliary electrode 150, formed from an inert material, is suitably maintained in direct contact with the cor-

differential amplifier shown generally as 156 and consisting of series connected D-C sources 158 and 160 having a potentiometer 162 connected across their output. The reference voltage lead 154 is then connected to the mid point between the series connected D-C sources 158 and 160 and the variable output from potentiometer 162, the error voltage lead 164, is applied as an input to a control amplifier 166.

A power lead 168 is applied from the metallic vessel 140 to the input of control amplifier 166 and a parallel power lead 170 is applied to the common or mid-potential point of a power supply 172. The control amplifier 166 may be any of several well-known types of error amplifier which are used in the corrosion art. The only requirements being that the amplifier have high input impedance, that it be reasonably stable and free from drift due to temperature, and that it should have high sensitivity since the total range of control signals must be effected from relatively small input signal strength. The power supply 172 may be one of the conventional types of power supply which rectifies A-C input power and provides both a negative and a positive output D-C voltage with respect to a common or mid-potential. Such power supply equipment is a matter of choice and the proper selection would require only normal skill in the art.

A negative output 174 from power supply 172 is connected to the collector 176 of a PNP-type transistor 178. The emitter 180 is connected via the power lead 152 to the auxiliary electrode 150 and the base 182, the control element of transistor 178, is connected to receive the output from control amplifier 166 via lead 184. The positive output terminal of power supply 172 is connected via lead 186 to the collector 188 of an NPN-type transistor 190. The negative emitter 192 is also connected through the power lead 152 to the auxiliary electrode 150 and the base 194 also receives control voltage on lead 196 from the output of control amplifier 166.

The transistors 178 and 190 being connected in parallel, but for opposite conduction, serve as a proportional current regulation circuit to apply varying amounts of either cathodic or anodic current flow through the load circuit; consisting of the electrochemical cell formed by the metallic vessel 140, the corrosive solution 142, and the auxiliary electrode 150. When the output control voltage on lead 184 from control amplifier 166 is more negative than a pre-determined mid value, the transistor 178 will conduct such that the negative terminal of power supply 172 is in the circuit with the auxiliary electrode 150. In this condition, the common lead 170 carries a more positive potential and the current flow through the corrosive solution 142 is anodic, that is, the metallic vessel 140 is positive with respect to the auxiliary electrode 150. When the output control signal from control amplifier 166 shifts to a more positive value, the transistor 178 will be cut off and the transistor 190, being of opposite conduction type, completes a circuit for conduction from the positive output lead 186 of power supply 172 through the emitter 192 and the power lead 152 to the auxiliary electrode 150. In this situation, the polarity of current flow



lead 216 to the impedance converter 224. The half-cell reference electrode 206 is also connected on lead 226 to the input of impedance converter 224. The impedance converter 224 is a well-known type of amplifier stage which provides an output voltage indicative of the reference potential on lead 226 as taken with respect to the metallic vessel 200. Further, the impedance converter stages 224 are preferably employed with adequate feedback to maintain unity gain at the output.

Thus, the actual potential V_r of the metallic vessel 200 is indicated on the output present on lead 228 from the impedance converter 224. A potential control circuit 230, similar to the potential control 156 of FIG. 10, provides a control point or set point voltage on lead 232 for application to the power control circuitry as will be described. The potential control 230 may take any of various forms of variable direct current source and the elaboration of this circuit will depend upon the accuracy required in the particular corrosion protection application.

The circuitry which is employed for detecting difference between the reference voltage V_r on lead 228 and the control point voltage V_c on leads 230 consists of oppositely oriented, balanced pairs of PNP-type transistors. A first balanced pair, transistors 232 and 234 are connected in parallel through a suitable dropping resistor 236 to the positive power supply terminal 238. The collector of transistor 232 is connected through a resistance 240 to the negative power supply terminal 242 and the collector of transistor 234 is connected through a capacitor 244 to the negative power supply terminal 242. The capacitor 244 is a timing capacitor for a relaxation oscillator circuit which operates to charge in conjunction with the transistor 234 conduction as will be described. A second balanced pair, transistors 246 and 248 are connected in identical configuration. That is, the respective emitters are connected together and lead through a resistance 250 to the positive terminal 238 and input transistor 246 has its collector tied through resistance 252 to the negative terminal 254 while the collector of output transistor 248 is connected through another timing capacitor 256 to the negative terminal 254.

The type of control which this circuitry exercises over the power supply 214 is what may be termed phase control. That is, the circuitry develops a pulse type control signal having a phase variation proportional to the difference between the potential of metallic vessel 200 and the control point potential V_c . The metallic vessel potential or reference voltage V_r present on leads 228 is applied to the base of output transistor 234 of one balanced pair while it is also applied to the base of input transistor 246 of the other balanced pair. In the same manner, the control point voltage V_c present on leads 230 is applied to the base of the output transistor 248 of the second balanced pair while being applied to the base of input transistor 232 of the first balanced pair. Thus, any difference voltage between the reference voltage V_r and the control point voltage V_c will cause opposite conduction as between the two balanced pairs of transistors, transistors 232 and 234 and transistors 246 and 248. Therefore, the outputs from the balanced pairs of transistors will always have an opposite relationship.

A first output taken from the collector of transistor 234 on a lead 258 is applied to the emitter of a unijunction transistor 260, a relaxation oscillator element. The base number one of the unijunction transistor 260 is conducted through the primary 262 of transformer 264 to the negative power supply terminal 242. The base number two of unijunction transistor 260 is connected through a suitable resistance 266 to the system ground. Similarly, the output from the second balanced pair of transistors 246 and 248 is taken from the collector of transistor 248 via lead 268 to the emitter of a unijunction transistor 270, also a relaxation oscillator element. The base number one of transistor 270 is connected through the primary 272 of a transformer 274 to the negative power supply

terminal 254. The base number two of transistor 270 is connected through a resistance 276 to the system ground; thus providing a unijunction transistor circuit which is identical to the previously described unijunction transistor 260 circuit. However, the respective emitters will be alternately controlled as will be described in connection with the operation of the apparatus.

The system is energized by a full wave, unfiltered power supply 278. An A-C line input source 280 supplies line voltage on leads 282 to the transformer 284 and secondary 286. Transformer 284 would be any of the well-known types which provide an output voltage value suitable for energizing transistorized equipment. The ends of the secondary winding 286 are connected to the respective cathodes of suitable rectifiers 288 and 290 and their respective anodes are tied together at a terminal point 292 and negative supply lead 294. The center tap 296 is connected to a properly chosen dropping resistor 298 and then to terminal 300 which constitutes the positive output as present on the lead 302. A Zener diode 304 is connected between the negative terminal 292 and the positive terminal 300 for the purpose of output amplitude regulation. The breakdown voltage of this Zener diode would be a matter of design choice but to cite an example, one form of the apparatus in present use employs a 25 volt regulation.

It should be restated that the power supply 278 provides a full-wave rectified output and that it is unfiltered. Hence, the output voltage is a series of plateaus and the output voltage value drops completely to zero at each half cycle. This intermittent D-C potential source is important to the proper operation of the circuitry as the periodic zero voltage values serve to synchronize the conduction of unijunction transistors 260 and 270 to provide a highly accurate phase indication.

In the circuit of unijunction transistor 260, the base number one circuit is connected through the primary 262 of transformer 364 and the secondary windings 310 and 312 provide output voltages suitable for gating "on" the SCR components (Silicon Controlled Rectifiers) in the high current supply 214. The winding 310 is connected via lead 314 to the gate electrode of SCR 316 and the winding 312 is connected via lead 318 to the gate electrode of SCR 320. The opposite sides of each of secondary windings 310 and 312 are tied together to a lead 322 which is connected to a point 324, shorted to the output power supply terminal 212.

Similarly, the unijunction transistor 270 energizes the primary 272 of transformer 274 such that SCR control voltages are induced in the secondary windings 326 and 328. Secondary winding 326 is connected by lead 330 to the gate electrode of an SCR 332 and the secondary winding 328 connects by lead 334 to the gate electrode of an SCR 336. In this connection of transformer 274 the remaining leads of secondary windings 326 and 328 are tied together and connected on a lead 338 to a terminal 340 which is shorted to the power supply output terminal 220. Thus, the alternate energization of transformers 264 or 274 by the respective unijunction transistor 260 or 270 will result in one or the other direction of current flow from the high current power supply 214 as will be described.

The polarization power source, high current power supply 214, is energized by the A-C line input 280 on the leads 282 to the parallel primary windings 342 and 344 of respective transformers 346 and 348. The center tapped secondary 350 has its end leads connected to the anodes of the SCR elements 316 and 320 and the respective cathodes of SCR's 316 and 320 are connected to the terminal point 324, a negative potential terminal which is common to the power supply output terminal 212. The center tap of secondary winding 350 is connected by means of lead 352 to the other power supply output terminal 220.

The connection for the transformer 348 is opposite to that of transformer 346. Thus, the end leads of the center tapped secondary winding 354 are each connected to the anodes of the SCR's 336 and 332, however, the cathode connections of SCR's 332 and 336 are connected together and to the terminal 340 which, in turn, is common to the power supply output terminal 220 of the high current power supply 214. The center tap of secondary winding 354 is connected by lead 356 to the other output terminal 212.

In operation of the apparatus, a polarization curve is first derived for the particular materials of metallic vessel 200 and the corrosive solution 202 so that corrosion protection apparatus can be properly preset. For example, for a 1020 mild steel-alkaline sulphide pulp digester system such as that in FIGS. 5 through 9, the initial set point or control point voltage should be set within the cathodic current density range 106 of FIG. 5. The potential control 230 would then be set to provide some control point voltage V_c in the range between +800 millivolts and +880 millivolts. Thus, corrosion protection is effected when the metal-electrolyte system is brought within this range. However, it should be remembered that the pulp digestion process takes place over a wide range of temperatures from about 150° F. (FIG. 5) to about 350° F. (FIG. 9). Thus, it may be necessary to shift the control point during the pulp digestion process in order to maintain continuous protective polarization. Probably one potential shift would be all that is required and that would fall near the end of the heating up portion of the digestion process. FIG. 8 shows the cathodic current region at about 300° F. and a shift in the potential range of the secondary cathodic current region is apparent. Thus, it would probably be desirable to shift the setting of potential control 230 upward about 100 millivolts during passage of the process through a temperature range including 300° F.

Once the initial set point is set into potential control 230 the metallic vessel 200 can be charged with the alkaline sulphide digestion liquor or corrosive solution 202. This initial condition would exhibit behavior coincident to the polarization curve of FIG. 5, taken at the lower 150° F. temperature. It should be understood however that some digestion processes are charged or started at 212° F. and, in this event, the polarization curve of FIG. 6 would provide a similar starting reference.

When solution 202 is first charged into the vessel 200, the metal-electrolyte system assumes its natural corrosion potential. In FIG. 5, this would pertain to the point 102 at about 950 millivolts vessel potential whereat the vessel-solution is actively corroding. This vessel potential of 950 millivolts is sensed then by the calomel half-cell 206 and conducted as the reference voltage V_r on lead 226 to the input of the impedance converter 224. The impedance converter 224 provides a reference voltage output V_r on lead 228 for application to the voltage differential detection circuitry. Also, the potential control circuit 230 provides the preset control point voltage V_c on lead 230 for simultaneous application to the detection circuitry.

It should then be noted that the reference voltage V_r on leads 228 and the control point voltage V_c on leads 230 are oppositely applied as between the input and output transistors of the two balanced pairs of transistors. That is, the reference voltage V_r on leads 228 is applied to the output transistor 234 of one balanced pair while being applied to the input transistor 246 of the other balanced pair, and the control voltage V_c on leads 230 is applied to the input transistor 232 on the one balanced pair while being applied to the output transistor 248 of the other balanced pair. Thus, since the transistors 232, 234, 246 and 248 are of the type PNP, a more negative base signal applied to the output side of one or the other of the balanced pairs will cause differential conduction. When the reference voltage V_r on the base of transistor

234 is more negative than the control point voltage V_c on the base of transistor 232, conduction is increased through transistor 234 to fire the relaxation oscillator circuit of unijunction transistor 260 as will be described below. Similarly, in the other balanced pair the opposite reaction is induced by applying the reference voltage V_r to the base of the input transistor 246 while applying the control point voltage V_c to the base of transistor 248. In this instance, a more negative control point voltage V_c will cause conduction sufficient to energize the relaxation oscillator circuit comprising the unijunction transistor 270.

In the initially charged vessel-solution system, the reference voltage V_r of the metallic vessel is higher than the control point voltage V_c . Therefore, the balanced pair of transistors 246 and 248 first come into play since the control point voltage V_c is more negative than the reference voltage V_r . Transistor 248 conducts an amount determined by the difference of the reference voltage V_r and control point voltage V_c to energize the relaxation oscillator. The oscillation is effected by periodic conduction of the unijunction transistor 270 as controlled by the resistance-capacitance time of the capacitor 256 in series with the emitter-collector effective resistance of the transistor 248. Hence, as the transistor 248 increases in conduction, the emitter-collector resistance decreases thereby shortening the resistance-capacitance time such that the unijunction transistor 270 fires at a faster rate. That is, it fires sooner in each half cycle of the applied power supply voltage (from power supply 278) to cause a pulse of current conduction through the primary 272 of transformer 274. This pulse voltage is apparent in the secondary windings 326 and 328 and is conducted on respective leads 330 and 334 to the gate electrode of the respective SCR's 336 and 332 to gate them into conduction. Thus, with the SCR's 336 and 332 conducting, the current flow is such that output terminal 220 is a positive terminal and output terminal 212 is negative. Therefore there is anodic current flowing through metal-electrolyte system and the vessel 200 is the anode while the auxiliary electrode 204, which is connected to the output terminal 212 of the power supply 214, is a cathode.

At first, the anodic current will be caused to flow heavily since the comparison of the reference voltage V_r and the control point voltage V_c are the greatest. This, in turn, will cause highest differential conduction in transistor 248 and thus earlier firing of the unijunction transistor 270 in each half cycle of the energizing voltage from power supply 278. Then as the anodic current flows and the vessel potential moves through the Flade arrest point 104 (FIG. 5) the potential of the vessel 200 is reduced thereby decreasing the error voltage or difference between the reference voltage V_r and the control point voltage V_c . This, of course, allows the unijunction transistor 270 to be fired progressively later in each half cycle of the power application to thereby fire the SCR members 332 and 336 later in each half cycle, thus applying less average power to the vessel-solution system. It should be noted that the power supply 278, mentioned previously as being unfiltered, plays an important part in the synchronization of the system. It provides positive and negative supply voltages which drop to zero on each half cycle thereby synchronizing or providing a regular and reliable starting point for the R-C combination, transistor 248 and the capacitor 256 of the relaxation oscillator (unijunction transistor 270).

As the vessel potential decreases through the primary anodic current region containing the Flade arrest 104 (FIG. 5) and passes into the cathodic current density region 106 (FIG. 5), the vessel potential will arrive at the preset control point voltage V_c . In this condition, the reference voltage V_r and the control voltage V_c will be equal and no corrosion protection power application is effected. Since this cathodic current density region is a stable vessel potential more noble than the Flade arrest potential, it is

desirable to maintain the potential within this region of secondary cathodic current.

When the vessel potential, as detected by the reference voltage V_r , drifts toward a more noble or less positive voltage than that of the control point voltage V_c , the other balanced pair of transistors 232 and 234 and the respective relaxation oscillator, unijunction transistor 260, will be energized to effect control. The reference voltage V_r , being more negative than the control point voltage V_c , reduces the emitter-collector resistance of transistor 234 thereby causing conduction and energization of the other relaxation oscillator, unijunction transistor 260. As before, the timing capacitor 244 and the transistor 234 act to time the firing point of the unijunction transistor 260 such that increasing conduction advances the firing point in each half cycle of operation as controlled by the unfiltered power supply 278. Upon firing of the unijunction transistor 260, the transformer 264 provides induced firing pulses in secondary windings 310 and 312 which are applied on leads 314 and 322 to the respective gate electrodes of SCR's 316 and 320. When these SCR's 316 and 320 are gated on the current flow is opposite to that produced previously by gating on the SCR's 332 and 336. That is, current flow is from the SCR's 316 and 320 to the intermediate terminal 324 and output terminal 212 and then on lead 210 to the auxiliary electrode 204. The return being from the metallic vessel 200 through the lead 218 and back to the output terminal 220 of the high current power supply 214. In this application the applied current is cathodic in character, that is, with respect to the metal-electrolyte system, the auxiliary electrode 204 now acts as an anode while the vessel 200 is the cathode.

The apparatus can thus provide either anodic or cathodic current to the vessel-corrosive solution system and in amounts proportional to the vessel potential and a predetermined control point voltage V_c . The special polarization behavior of particular metal-electrolyte systems must first be determined and then the range of potential which is suitable for corrosion protection can be set into the potential control 230. In the operation described, that for a pulp digestion process, the potential control 230 would require several settings during the heat up and cooking process. It should be understood, however, that each metal-electrolyte system will have its own specialized behavior characteristics and that the flexibility of control afforded by the present apparatus is a very desirable feature.

It has been found that some systems can be brought through the Flade potential to a more noble, non-corrosive vessel potential and that they will remain in that condition for a long period of time with no further potential variation. In the event that there should be a vessel potential change, however, the control apparatus will apply either the anodic current or cathodic current to counteract the potential change and bring it back to the set point or pre-determined potential control voltage. In most systems there will be a drift of the vessel potential in one direction or the other after it has been initially brought to the stable, non-corrosive potential. This then requires periodic current application to the vessel-solution system, either anodic or cathodic, and the apparatus of FIGS. 10 and 11 serve to provide the current flow of proper polarity and amounts in response to an error voltage as detected with respect to the actual vessel potential.

It should be understood that there are other equivalents which could be substituted for the specific components of the apparatus disclosed herein. It is contemplated that a high current power supply may be constructed using rectifier elements of the "gate turn-off" type such that either anodic or cathodic current could be applied through the vessel-solution system with highly accurate regulation.

While only a few particular metal-electrolyte systems have been disclosed with respect to the present method and apparatus, it is foreseen that there will be a great many metal-corrosive solution combinations which will exhibit the special polarization behavior. The method and

apparatus of the present invention will be applicable to all of such systems and, due to its inherent versatility, the method and apparatus can be employed in conventional corrosion protection applications as well. That is, the apparatus may be used with all metal-electrolyte systems exhibiting behavior which includes the presence in the polarization curve of stable current densities, either anodic or cathodic, at potentials lying between the Flade arrest and the transpassive potential region.

Changes may be made in the combination and arrangement of elements and steps as heretofore set forth in this 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.

What is claimed is:

1. A method of corrosion protection for a metallic vessel containing a corrosive solution, said metallic vessel and corrosive solution system having a polarization curve wherein increasing noble vessel potentials are characterized by anodic current density through the Flade arrest potential and then cathodic current density, comprising the steps of:

applying direct current energy between the metallic vessel and an electrode immersed in said corrosive solution; and
controlling the polarity of said applied direct current energy in accordance with the potential of the metallic vessel.

2. A method of corrosion protection for a metal-corrosive solution system, said system having both anodic and cathodic current regions in the polarization curve, comprising the steps of:

monitoring the potential of the metal;
passing direct current energy between the metal and the corrosive solution; and
controlling the polarity of said direct current energy in accordance with said potential of the metal.

3. A method of corrosion protection for a metallic vessel containing a corrosive solution comprising the steps of:

monitoring the potential of the metallic vessel;
passing direct current between the metallic vessel and an electrode immersed in said corrosive solution; and
controlling the polarity of the direct current with said monitored potential such that anodic current flows at initial, actively corroding vessel potentials and cathodic current flows at a more noble, non-corrosive vessel potential.

4. A method of corrosion protection for a metallic vessel containing a corrosive solution, said metallic vessel and corrosive solution system having a polarization curve wherein the system shows a minimum current region of cathodic current density at vessel potentials more noble than the Flade arrest potential, comprising the steps of:

applying direct current energy between the metallic vessel and an electrode immersed in said corrosive solution; and
controlling the polarity and amount of applied direct current energy in accordance with the polarity and amount of potential difference detected between said metallic vessel and a reference electrode immersed in said solution.

5. A method as set forth in claim 4 wherein:

positive direct current energy is applied to the vessel upon detection of first predetermined indications by said reference electrode; and
negative direct current energy is applied to the vessel upon detection of second predetermined indications by said reference electrode.

6. A method of controlled potential corrosion protection in metallic vessel-corrosive solution systems which exhibit special polarization behavior comprising the steps of:

applying anodic current between the metallic vessel

and an electrode immersed in said solution at vessel potentials which are more active than a predetermined voltage; and
 applying cathodic current between said vessel and electrode immersed in said solution when the vessel potential is more noble than a predetermined voltage. 5
 7. A method as set forth in claim 6 wherein said metallic vessel-corrosive solution comprises:
 metal-electrolyte systems which exhibit a vessel potential range of cathodic current density at vessel potentials more noble than the Flade arrest potential. 10
 8. A method as set forth in claim 7 wherein said metallic vessel-corrosive solution system comprises:
 stainless steel and a hot, concentrated alum solution. 15
 9. A method as set forth in claim 7 wherein said metallic vessel-corrosive solution system comprises:
 Carpenter 20 steel and a sulphuric acid/zinc solution. 20
 10. A method as set forth in claim 7 wherein said metallic vessel-corrosive solution system comprises:
 carbon steel and an alkaline sulphide liquor. 25
 11. A method as set forth in claim 6 wherein said metallic vessel-corrosive solution comprises:
 metal-electrolyte systems which exhibit a vessel potential range of cathodic current density at vessel potentials more noble than the Flade arrest potential; and 30
 said systems exhibit a range of anodic current density at vessel potentials still more noble than said cathodic current vessel potential range. 35
 12. Apparatus for corrosion protection of a metallic vessel containing a corrosive solution, said metallic vessel and corrosive solution system having a polarization curve wherein the vessel and solution shows a minimum cathodic current region at vessel potentials more noble than the Flade arrest potential, comprising:
 electrode means in contact with said solution; 40
 direct current means connected between said electrode means and said metallic vessel; and
 automatic means for applying positive direct current to said vessel to control the current density when it is anodic and for applying negative direct current to 45
 control the current density when it is cathodic. 50
 13. Apparatus for controlled potential corrosion protection of a metal-corrosive solution system comprising:
 a source of direct current energy;
 means for applying said direct current energy between 55
 the metal and an electrode immersed in said corrosive solution;
 means for sensing the potential of the metal; and
 automatic means for controlling the amount and polarity of said direct current energy in accordance with 60
 said sensed potential. 65
 14. Apparatus for corrosion protection of a metallic vessel containing a corrosive solution, said vessel-solution system having a polarization curve wherein a low cathodic current density exists at vessel potentials more noble 70
 than the Flade arrest potential, comprising:
 electrode means in contact with said solution;
 direct current means connected between said electrode means and said metallic vessel;
 reference electrode means in contact with said solution and electrically connected to said metallic vessel; and
 automatic means controlling said direct current means to apply negative current to said vessel in response to a first predetermined range of voltages as detected 75
 between said vessel and said reference electrode means and to apply positive direct current to said vessel in response to a second predetermined range of voltages as detected between said vessel and said reference electrode means.

electrode means immersed in said solution;
 a direct current source connected between said electrode and said vessel;
 reference electrode means in electrolytic contact with said solution, and electrically connected to said vessel to detect its potential;
 automatic means for comparing the potential detected by said reference electrode with a reference potential to develop a control voltage; and
 automatic means connected to receive the control voltage and regulate the polarity and amount of direct current which is applied from said direct current source.
 16. Apparatus for controlled potential corrosion protection of a metallic vessel-corrosive solution which exhibits special polarization behavior, comprising:
 a direct current source;
 an electrode adapted to contact the solution;
 means for applying direct current between the metallic vessel and said electrode;
 means for sensing the potential of the metallic vessel; and
 automatic means responsive to said sensed potential for controlling said means for applying so that anodic current flows at vessel potentials more active than the Flade arrest potential and cathodic current flows at potentials more noble than the Flade arrest potential.
 17. Apparatus for controlled potential corrosion protection of metallic vessel-corrosive solution systems which exhibit special polarization behavior, comprising:
 a source of direct current energy;
 an auxiliary electrode immersed in said solution;
 a reference electrode in contact with said solution and electrically connected to said metallic vessel for sensing a reference potential;
 means for providing a predetermined control point voltage; and
 automatic means for applying anodic direct current between said metallic vessel and auxiliary electrode when said reference potential is more active than said control point voltage, and for applying cathodic direct current when said reference potential is more noble than said control point voltage.
 18. Apparatus for corrosion protection of a metallic vessel containing a corrosive solution, comprising:
 electrode means immersed in said solution;
 a direct current source having its output connected between said electrode and said metallic vessel;
 a reference electrode immersed in said solution and electrically connected to said metallic vessel;
 automatic means for comparing the voltage between said metallic vessel and said reference electrode with a reference voltage to develop a first control voltage when said reference voltage differs in a first polarity and a second control voltage when said reference voltage differs in the opposite polarity; and
 automatic means responsive to said first and second control voltage for respectively applying positive and negative polarities of direct current from said source to the vessel.
 19. Apparatus for controlled potential corrosion protection of a metallic vessel containing a corrosive solution comprising:
 an auxiliary electrode immersed in said corrosive solution;
 a direct current power source connected between said metallic vessel and said auxiliary electrode;
 means for sensing the potential of the metallic-vessel;
 automatic means for comparing the sensed vessel potential with a predetermined control point potential to derive a control voltage; and
 automatic means controlled by said control voltage for varying the amount and polarity of the output of said direct current source.

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20. Apparatus for controlled potential corrosion protection of metallic vessel-corrosive solution systems which exhibit special polarization behavior, comprising:

- a direct current source;
- an auxiliary electrode immersed in said solution;
- a reference electrode immersed in said solution and electrically connected to said metallic vessel for sensing the potential of the vessel;
- means for providing a predetermined control point voltage;
- automatic means for comparing said vessel potential and control point voltage to derive an error voltage; and
- automatic means conductive in response to said error voltage to regulate the amount and polarity of direct current from said source through said metallic vessel, corrosive solution and auxiliary electrode.

21. Apparatus as set forth in claim 20 wherein said means conductive in response to said error voltage comprises:

- a PNP transistor having the collector connected to the negative terminal of said direct current source, the emitter connected to said auxiliary electrode, and the base connected to receive said error voltage;
- an NPN transistor having the collector connected to the positive terminal of said direct current source, the emitter connected to said auxiliary electrode, and the base connected to receive said error voltage; and
- a common, mid-potential of said direct current source being connected to said metallic vessel.

22. Apparatus as set forth in claim 20 wherein said means for comparing comprises:

- a first differential amplifier receiving the reference potential and the more noble control point voltage at respective inputs to derive an error voltage at the output; and
- a second differential amplifier receiving the control point voltage and the more noble reference potential at respective inputs to derive an error voltage at the output.

23. Apparatus as set forth in claim 22 wherein said means conductive in response to said error voltage comprises:

- a first relaxation oscillator conductive in response to an error output voltage from said first differential amplifier to cause a first polarity of output from said direct current source; and
- a second relaxation oscillator conductive in response to an error output voltage from said second differential amplifier to cause a second polarity of output from said direct current source.

24. Apparatus as set forth in claim 23 wherein said direct current source comprises:

- an A-C voltage source;
- a first pair of semi-conductor controlled rectifiers connected to said A-C source for full-wave rectification;
- a second pair of semi-conductor controlled rectifiers connected in parallel to said A-C source for full-wave rectification and in reversed polarity to said first pair of said rectifiers;
- means for gating said first pair of rectifiers into conduction during the conduction of said first relaxation oscillator; and
- means for gating said second pair of rectifiers into conduction during the conduction of said second relaxation oscillator.

25. Apparatus for controlled potential corrosion protection of a metallic vessel containing a corrosive solu-

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tion, wherein the vessel-solution system exhibits special polarization behavior, comprising:

- an auxiliary electrode immersed in said corrosive solution;
- a reference electrode in electrolytic contact with said corrosive solution and electrically connected to said metallic vessel for deriving a reference potential;
- potential control means for providing a predetermined control point potential;
- a direct current power supply having negative, positive and common output terminals, said common terminal being connected to said metallic vessel;
- a PNP transistor having the collector connected to said negative power supply terminal and the emitter connected to said auxiliary electrode;
- an NPN transistor having the collector connected to said positive power supply terminal and the emitter connected to said auxiliary electrode; and
- a voltage comparator receiving said reference potential and control point potential to derive an error voltage the output of which is connected in parallel to the bases of the PNP and NPN transistors.

26. Apparatus for controlled potential corrosion protection of a metallic vessel-corrosive solution system which exhibits special polarization behavior, comprising:

- an auxiliary electrode immersed in said corrosive solution;
- a reference electrode in electrolytic contact with said corrosive solution for deriving a reference potential;
- potential control means for providing a predetermined control point potential;
- differential amplifier means for providing a first error voltage when said reference potential exceeds said control point potential and a second error voltage when said reference potential is more negative than said control point potential;
- an alternating-current voltage source;
- a first pair of semi-conductor controlled rectifiers connected to said alternating-current voltage source as a full-wave rectifier with the positive output terminal connected to the metallic vessel and the negative output terminal connected to said auxiliary electrode;
- a second pair of semi-conductor controlled rectifiers connected in parallel with said first pair and connected to said alternating-current voltage source as a full-wave rectifier with the negative output terminal connected to the metallic vessel and the positive output terminal connected to said auxiliary electrode;
- a first relaxation oscillator intermittently conductive for a duration determined by said first error voltage to gate-on said first pair of semi-conductor controlled rectifiers to apply anodic current through said metallic vessel and corrosive solution; and
- a second relaxation oscillator intermittently conductive for a duration determined by said second error voltage to gate-on said second pair of semi-conductor controlled rectifiers to apply cathodic current through said metallic vessel and corrosive solution.

27. Apparatus as set forth in claim 26 which is further characterized to include:

- a low voltage, unfiltered power supply which drops to zero in each half cycle for synchronously energizing said first and second relaxation oscillators.

No references cited.

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