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METHOD AND APPARATUS FOR AUTOMATIC ELECTRIC CORROSION-PROOFING

Filed March 28, 1966 3 Sheets-Sheet 1

FIG. 1

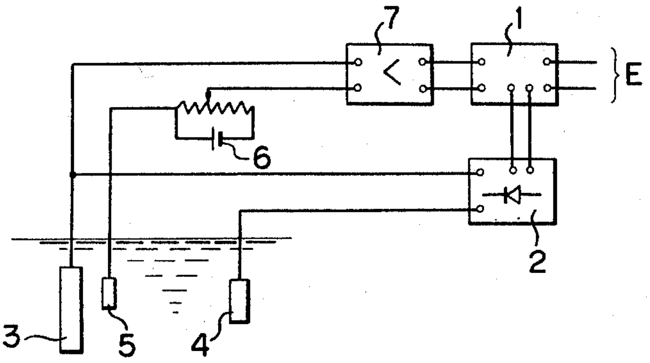

FIG. 2

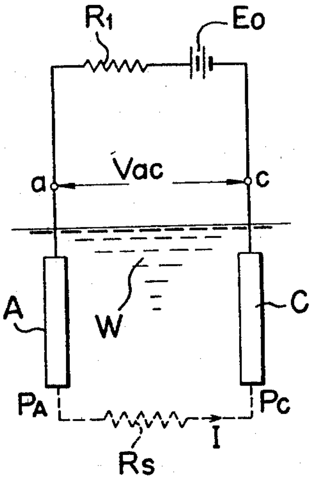

FIG. 8

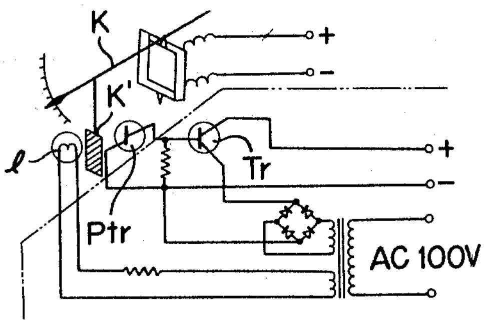

FIG. 3

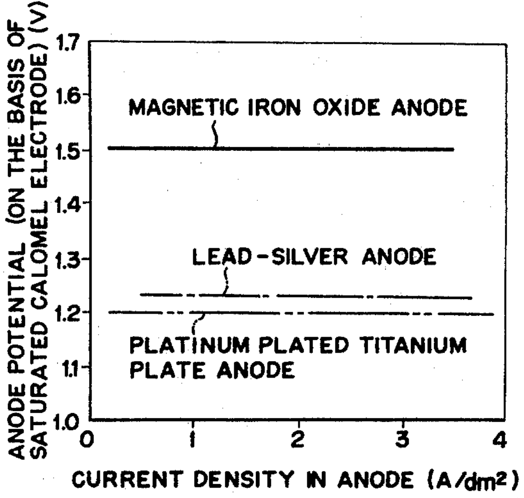

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FIG. 6

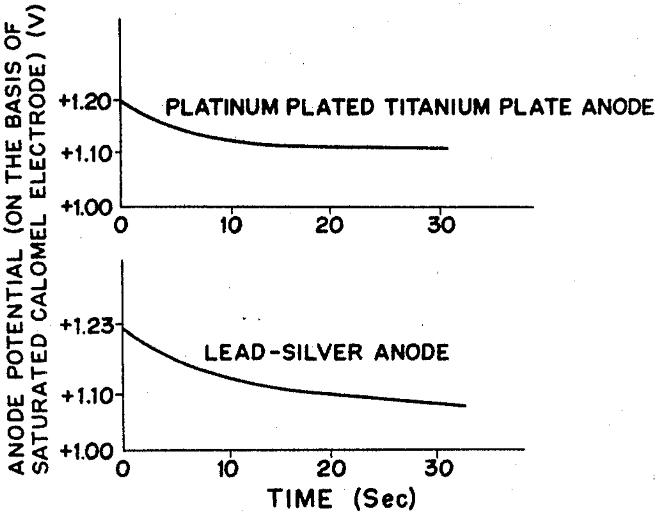

FIG. 7

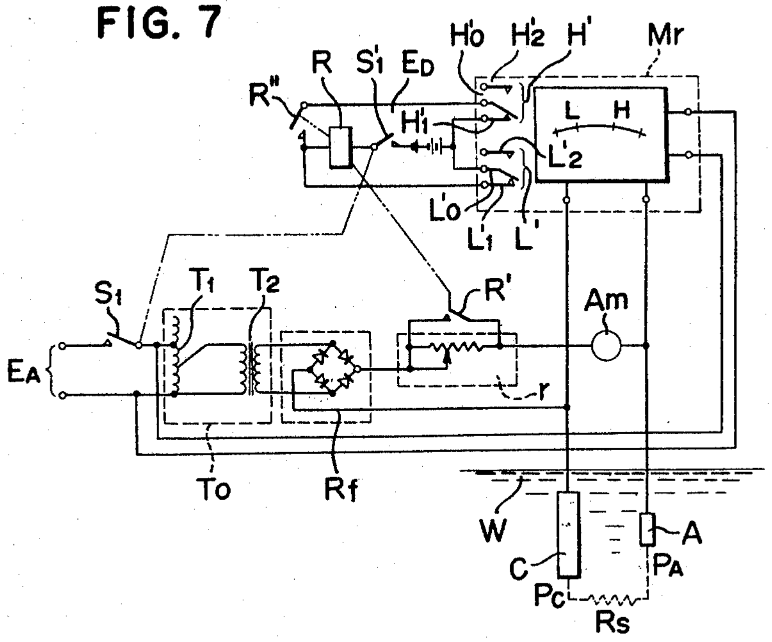

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FIG. 4

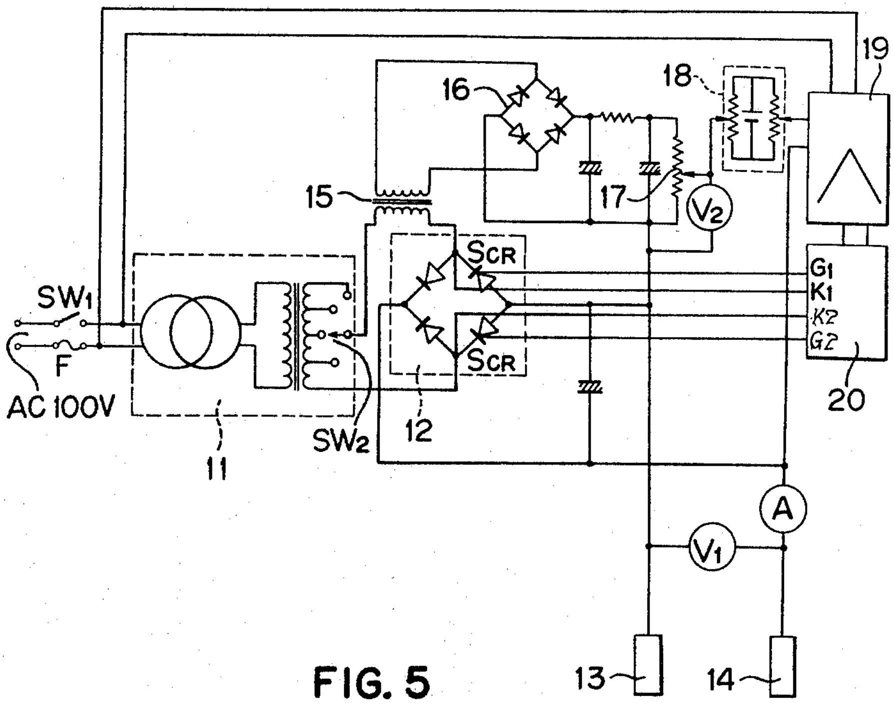


FIG. 5

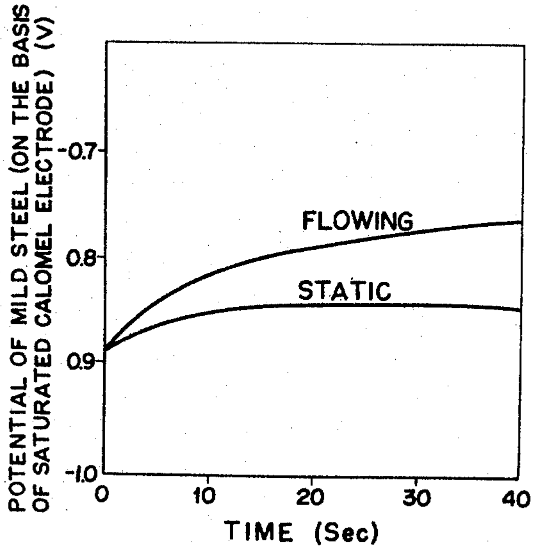
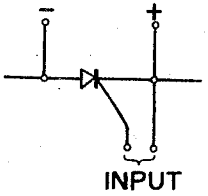


FIG. 9



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METHOD AND APPARATUS FOR AUTOMATIC ELECTRIC CORROSION-PROOFING

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U.S. Cl. 204—147 11 Claims

ABSTRACT OF THE DISCLOSURE

In a method and apparatus for corrosion proofing metallic structures immersed in an electrolyte, such as sea water, the metallic structure is used as a cathode and an anode is placed in spaced relation thereto, the usual third or "standard" electrode being omitted. A potential is applied between the anode and the metallic structure to cause a relatively small current to flow from the anode to the metallic structure, the latter acting as a cathode. The current is maintained at a value such that the potential of the metallic structure or cathode is maintained at a value at which the metallic structure is corrosion-proof. The potential drop between the metallic structure and the anode, and the resistance drop through the electrolyte or sea water, between the anode and the metallic structure, are continuously measured and the difference between the two measured values is maintained at a constant value equal to the work potential necessary to corrosion-proof the work. In a variation, the current flow may be maintained within relatively small values either side of the required potential value for the metallic structure.

This invention relates to the corrosion-proofing of metallic structures and, more particularly, to a novel method of and apparatus for automatically electrically corrosion-proofing metallic structures by detecting the potential difference between the work to be protected and a non-consumable anode and, responsive thereto, maintaining the corrosion-proofing electrolytic potential for the work at a predetermined value.

For the electrochemical corrosion-proofing of work pieces, which are usually metallic structures immersed in an electrolyte or electrolyte solution, the so-called corrosion-proofing process is employed. In this process, the work is a cathode having current flowing thereinto from an anode immersed in the solution in spaced relation to the cathode whose potential is thereby polarized to a corrosion-proofing potential. To effect perfect protection against corrosion of the work, it is essential to maintain the potential of the work at the corrosion-proofing value throughout the processing.

A known expedient designed to maintain the potential of the work at the proofing potential throughout the course of processing is to position a third electrode in relatively close opposition to the work. This third electrode may be a standard electrode of silver chloride, saturated calomel, or similar material. A potential is applied between the first-mentioned anode and the work, and a second potential is applied between the third or standard electrode and the work, and has a polarity

reversed with respect to the polarity of the first mentioned potential. Suitable control means are provided where, if the potential of the work deviates from a predetermined potential due to a change of the proofing conditions, a control signal is provided which regulates the potential applied between the first mentioned anode and the work in a correcting direction so as to maintain the proofing potential at a constant value.

A conventional arrangement of this type has the disadvantage that the proofing potential of the work is controlled only in the vicinity of the standard electrode, and hence the current density on the surface of the work is not uniform. Because of the characteristic of the standard electrode, no current can pass therethrough, which necessitates that the control arrangement be constructed as an expensive high-input resistance type device. An additional disadvantage is that the standard electrode is consumed, to some extent, and has a relatively short life.

An object of the present invention is to provide a simplified electro-corrosion-proofing method whereby the work can be maintained accurately at the proofing potential without the use of a standard electrode.

Another object of the invention is to provide a simplified automatic apparatus for electro-corrosion-proofing and not requiring the use of a standard electrode to maintain the work at the proofing potential.

A further object of the invention is to provide a method of and apparatus for corrosion-proofing work whereby the work can be kept at a potential in excess of the proofing potential merely by supplying the work with a constant current but intermittently.

Yet another object of the invention is to provide a method of and apparatus for corrosion-proofing work whereby satisfactory corrosion-proofing can be obtained by supplying, in alternation, two constant currents having respectively different values.

Yet a further object of the invention is to provide an improved method of and apparatus for electro-corrosion-proofing to prevent corrosion of a metallic structure immersed in an electrolyte solution and in which the potential difference between the work to be treated and a non-consumable anode is detected and utilized to control the proofing potential of the work to a predetermined value.

For an understanding of the principles of the invention, reference is made to the following description of typical embodiments thereof as illustrated in the accompanying drawings.

In the drawings:

FIG. 1 is an explanatory schematic and circuit diagram illustrating a conventional arrangement for electro-corrosion-proofing;

FIG. 2 is a view similar to FIG. 1, illustrating an arrangement in accordance with the present invention;

FIG. 3 is a potential-current density diagram with respect to non-consumable metallic anodes, explanatory of the principles of the invention;

FIG. 4 is a schematic wiring diagram of one form of apparatus embodying the invention;

FIG. 5 is a set of curves illustrating the change of potential with time immediately after the interruption of the proofing current supplied to a bare mild steel plate immersed in an electrolyte solution;

FIG. 6 is a set of curves of potential changes with respect to time immediately following interruption of the proofing current supplied to the work, with respect to non-consumable anodes maintained at a predetermined potential in flowing sea water;

FIG. 7 is a schematic wiring diagram of another embodiment of apparatus for practicing the invention, and related to the curves of FIGS. 5 and 6;

FIG. 8 is a schematic and circuit diagram of a contactless meter relay for gating silicon controlled rectifiers used in practicing the invention; and

FIG. 9 is a schematic wiring diagram illustrating the operation of the relay of FIG. 8 in gating a silicon controlled rectifier.

In the conventional prior art arrangement illustrated in FIG. 1, a corrosion-proofing potential is applied between the work piece and an anode **4**. A standard electrode **5** of silver chloride, saturated calomel, or the like is disposed in close opposition to work **3**, with all three elements **3**, **4** and **5** being immersed in an electrolytic solution, such as, for example, sea water. The potential between work **3** and anode **4** is applied from a source voltage controller **1** through a rectifier **2**.

Between standard electrode **5** and work **3** there is interposed a standard power source **6** for setting the potential of work **3**, source **6** having a polarity reversed with respect to the polarity of the potential applied from rectifier **2**. Source **6** is supplied through a miniature amplifier **7** connected to source voltage controller **1**.

With the arrangement shown in FIG. 1, if the potential of work **3** is equal to the potential set by standard source **6**, the input to amplifier **7** is zero. However, if the potential of work **3** deviates from a predetermined potential, as due to a change in the proofing conditions, an input corresponding to such difference is applied to amplifier **7**. As a result, the amplified output from amplifier **7** controls the controller **1** to adjust the voltage from source E and thereby adjust the proofing current in a correcting direction, such as to maintain the proofing potential of work **3** at a constant value.

In the arrangement of the invention shown in FIG. 2, an anode A and a work piece C to be corrosion-proofed, and both of which are metals, are immersed in a uniform electrolyte solution W and a voltage E is applied between anode A and cathode or work C from a D.C. power source E_0 having an internal resistance R_1.

If the potentials of anode A and cathode C are, respectively, PA and PC, both of which represent the sum of the natural potential and the polarized potential, the current supplied is I, the voltage between terminals *a* and *c* is V_{ac} and the sum of the resistance of the conductors and the liquid in the circuit *a*–A–C–*c* is R_S, then the voltage V_{ac} between terminals *a* and *c* can be expressed by the equation:

$$Vac=E-IR_1=P_A-P_C+IR_S \qquad (1)$$

Hence, the potential (P_C) of the work (C) is

$$-P_C=Vac-P_A-IR_S \qquad (2)$$

In Equation 2, the resistance R_S is a constant which depends on the configurations, dimensions, and relative positions of anode A and cathode C, and also on the specific resistance of the electrolyte solution. This means, therefore, that the cathode potential P_C can be controlled through control of the voltage Vac between the anode and cathode, the anode potential P_A and the current supplied I or, in other words, through the control of the voltage drop IR_S between the anode and cathode.

It has been experimentally confirmed by the inventors that, when non-consumable electrodes of precious metals, such as platinum and platinum alloys, magnetic iron oxide, lead-silver alloy, platinum plated titanium plate, and the like are employed as the material of anode A, the anode potentials P_A can be kept at constant values, in each case, as shown in FIG. 3. To wit, with respect to a standard electrode of saturated calomel immersed in sea water, the potential of a magnetic iron oxide anode is 1.5 v., that of a platinum plated titanium plate anode is 1.20 v., and that of a lead-silver anode is 1.23 v. In consideration of the current range which is necessary for corrosion-proofing of the work C, a constant anode potential P_A can be obtained by choosing a suitable surface area for the non-consumable electrode, as mentioned above.

Thus, if control is achieved so that the difference between the voltage Vac between the anode and cathode and the voltage drop IR_S due to the resistance R_S between the electrodes, that is $(Vac-IR_S)$, can be kept constant, it is possible to keep the potential P_C of the cathode C or work to be corrosion-proofed, at a constant level, that is, at the proofing potential. To carry out such control in practice, it is necessary only to detect the potential difference between the anode and cathode and to regulate accordingly the current to be supplied to the work by the anode.

One form of apparatus for practicing the invention is illustrated in FIG. 4. Referring to FIG. 4, the apparatus includes a slide rheostat-type transformer **11** for regulating the source voltage, and a rectifying means **12** incorporating silicon controlled rectifiers, referred to as SCR's. The work to be corrosion-proofed, and which is immersed in an electrolyte solution such as sea water, is indicated at **13**, and a non-consumable anode **14** is positioned in opposition to work **13** to supply current to the work, and is also immersed in the electrolyte solution.

A relatively small transformer **15** is operatively connected with the proofing current circuit to generate a voltage IR_S proportional to the proofing current I, and is connected across a rectifying means **16** incorporating silicon controlled rectifiers. Also connected across the rectifier means **16** is a potentiometer **17** providing the voltage IR_S for compensating for the resistance R_S between work **13** and anode **14** with respect to the current supplied to the input of the rectifying means. A voltage setting means is illustrated at **18** as including a source of constant voltage and a variable resistor for providing a selected constant voltage. The apparatus shown in FIG. 4 further includes a miniature voltage amplifier **19** and gating pulse generator **20** which supplies gating pulses to the silicon controlled rectifiers SCR in accordance with the intensity of the D.C. voltage as amplified by the miniature voltage amplifier **19**.

The voltage between the anode and work is indicated by a volt meter V_1 which indicates a voltage V_{ac}, and the voltage generated to compensate for the voltage drop IR_S of the resistance R_S between the work and the anode is indicated by a volt meter V_2.

In the circuit construction shown, the voltage of the voltage setting means **18** is set to the difference between the potential of the anode (on the basis of a saturated calomel electrode) and the proofing potential of the work. For example, if mild steel is corrosion proofed with the use of a platinum plated titanium plate as the anode, it is clear from FIG. 3 that the anode potential P_A is 1.2 v. (on the basis of a saturated calomel electrode) and the proofing potential of the work is −0.8 v. (on the basis of a saturated calomel electrode), and hence the voltage set on means **18** is $1.2-(-0.8)=2.0$ v. Next, a switch SW_2 for generating a voltage IR_S which compensates for a voltage drop due to solution resistance R_S, between work **13** and anode **14**, is closed, and the proofing current I is measured by an ammeter A, the voltage between the work and anode by voltmeter V_1, and the voltage generated by the potential circuit by voltmeter V_2. Then the variable resistance of the potential circuit is adjusted so that the relation $V_{A.C.}-IR_S=2.0$ may hold within the expected proofing current range. The value $(V_{A.C.}-2.0)/I$ represents the resistants (R_S) between the work and anode.

By the foregoing procedure, the set positions of the potential circuit and the voltage setting means **18** are de-

determined. Thus, the input voltage to the voltage amplifier **19** is

$$\Delta\epsilon = V_{\text{A.C.}} - \{P_A - P_C) - IR_S\} = 0$$

This means that the proofing current I is adjusted so that $\Delta\epsilon$ can be kept at zero and, because the work is kept at a constant proofing potential, its corrosion can be prevented.

With the apparatus of FIG. 4, corrosion proofing tests were conducted in a laboratory with a small aluminum boat, as follows:

(1) A corrosion proofing test was carried out on a bare mild steel plate having a surface area of 0.6 m.^2 and immersed in 70 l. of a 3% aqueous solution of sodium chloride, with platinum as the anode. Regardless of whether the work was kept still or moving, the average potential of the mild steel was kept at −0.8 v., with respect to a standard electrode of sea water-silver chloride.

(2) A small aluminum boat with a total wetted surface area of 156 m.^2 was subjected to a corrosion proofing test with a platinum plated titanium plate having a surface area of 0.71 dm.^2 attached as an anode abaft. With respect to a standard electrode of seat water-silver chloride, the stern could be kept at −0.88 v., the midship at −0.84 v., and the stem at 0.83 v.

Although the above embodiment has been described as a case wherein silicon controlled rectifiers are applied, it is also possible to apply other means such as transistors, saturable reactors, electromagnetic relays, and the like which those skilled in the art can readily employ without departing from the spirit of the present invention.

The arrangement of FIG. 4 provides a highly practical corrosion proofing method and apparatus whereby standard electrodes, which are inconvenient with respect to maintenance and handling, can be omitted and corrosion of metals can be prevented by a simplified circuit arrangement. The arrangement shown in FIG. 4 is intended to keep the value $V_{ac} - IR_S$ constant, but the same objective can be obtained by simplified means such as will be described hereinafter with the embodiment of the invention shown in FIGS. 7, 8 and 9.

In this other embodiment of the invention, two limits are established for the current necessary to provide corrosion proofing of a work or structure.

First, the upper limit I_1 and lower limit I_2, for the range of proofing current for carrying out corrosion proofing of a work or structure C to be proofed in a stabilized manner, are set. The lower current limit I_1 represents a constant current value below the proofing current applicable to structure C while the latter is kept still in the solution. The upper limit I_2 represents a constant current value above the proofing current applicable to structure C when the latter is in the solution having a most vigorous flowing condition. The anode A is assumed to be a non-consumable metallic body capable of maintaining a constant anode potential P_A in the current range $I_1 - I_2$. If therefore the proofing potential of structure C is P'_C, then the proofing potential, at a certain moment when the current value I_1 is maintained, will show an upper limit $P'_C + \alpha$ of proofiing potential necessary for accomplishing stabilized corrosion proofing, and the terminal voltage value $V'ac$ between the anode and cathode at that time will be

$$V'ac = P_A - (P'_C + \alpha) + I_1 R_S \quad (3)$$

Also, the proofing potential at a certain movement when the current value I_2 is maintained will show a lower limit value $P'_C - \alpha$ of the proofing potential necessary for stabilized corrosion proofing. Assuming that the terminal voltage between the anode and cathode then will be ($V''ac$), then

$$V''ac = P_A - (P'_C - \alpha) + I_2 R_S \quad (4)$$

where α represents a value, $\alpha \geqq 0$.

Thus, the terminal voltage values $V'ac$ and $V''ac$ between the anode and cathode, at the upper and lower limit values of the proofing potential which are necessary for accomplishing corrosion proofing in a stabilized manner, can be obtained. Now, therefore, if the terminal voltage Vac between the anode and cathode drops below the lower limit of the terminal voltage $V'ac$ while a current of the constant value I_1 is being supplied from the anode A to the structure C to be corrosion proofed in an electrolyte solution W, a current of constant value at the upper limit I_2 is supplied from the anode A to the structure C to be proofed thereby to lower the proofing potential. When the terminal voltage Vac between the anode and cathode has been brought by the current value I_2 to the upper limit value $V''ac$, the current I_1 is again supplied to raise the proofing potential, and these steps are repeated. Consequently, the cathode potential P_C can be stabilized and kept within a range defined by the upper limit $P'_C + \alpha$ and the lower limit $P'_C - \alpha$ of the proofing potential.

In the procedure above described, the lower limit current value I_1 is supplied when the terminal voltage Vac, between the anode and cathode, reaches the upper limit $V''ac$. It is possible, in this case, to shut off the power source E instead of supplying the current value I_1, thereby to keep the current at $I=0$ for some time. The inventors thus de-energized a structure C of bare mild steel plate, to be corrosion proofed, kept at a constant proofing potential in a 3% aqueous solution of sodium chloride, and also deenergized a nonconsumable metallic anode A kept at a constant potential in an inching flow of natural sea water, and actually determined the changes of potential with time immediately after the de-energizing. The results obtained were as shown in FIGS. 5 and 6, respectively.

As can be seen from FIGS. 5 and 6, both the anode and cathode did not immediately attain the natural potentials but showed some time delay. Taking advantage of this phenomenon, therefore, the potential P_C of the work or structure to be proofed can be detected by the terminal voltage value $V^\circ ac$ between the anode and structure with a current $I=0$, so as to be maintained at the proofing potential, in the same way as above described. Letting the anode potential at a certain moment during the period in which the current $I=0$ be $P'_A - \beta$ and the potential of the structure C be $P'_C + \alpha$, the terminal voltage value $V^\circ ac$ between the anode and cathode is

$$V^\circ ac = (P'_A - \beta) - (P'_C + \alpha) \quad (5)$$

wherein P'_A is an anode potential at the current density necessary for keeping the anode potential constant, and β is a value $\beta > 0$. Now if a current of constant value I_2 flows from an anode A to a structure C to be corrosion proofed, in an electrolyte solution W, and if the terminal voltage (Vac) between the anode and cathode has reached the upper limit value $V''ac$, the anode and cathode are both de-energized to a current $I=0$. When the terminal voltage Vac has dropped below the value $V^\circ ac$, after some time with current $I=0$, the constant current value I_2 is again supplied from anode A to structure C. When the terminal voltage Vac has reached the value $V'ac$ on supply of the current (I_2), the anode and cathode are both de-energized again, and it is only necessary to repeat the above sequence.

In Equations 4 and 5 above, the anode potential P_A is a constant value P'_A and, if the rates of potential changes due to de-energizing of the potentials of anode A and structure C are the same, then $\alpha \doteqdot \beta$ and therefore Equation 5 can be rewritten as $V^\circ ac = P_A - P_C - 2\alpha$. Accordingly, the potential P_C of the structure C to be proofed likewise can be kept in the range of the proofing potential $(P'_C + \alpha) > P_C > (P'_C - \alpha)$.

The just mentioned embodiment of the invention will now be described in some detail with particular reference to the schematic wiring diagram of FIG. 7. In FIG. 7, a 100 volt A.C. power source E_A is in operative connection with an anode A of non-consumable metal and which is disposed in opposition to a structure C to be corrosion-proofed in an electrolyte solution W. Source E_A is connected, through a switch S_1, with a source voltage regulator T_0 composed of an autotransformer T_1 and a transformer T_2, and with a full wave rectifier R_f including selenium rectifiers, a D.C. voltage regulator *r* including a first normally open contact R' of an electromagnetic relay R, and an ammeter A_m. Anode A and structure C are connected to the input terminals of a meter relay M_r whose power input terminals are connected through switch S_1 to source E_A.

Meter relay M*r* is designed so that it indicates the voltage between the anode A and structure C to be proofed, and so that, when the pointer moves beyond the higher limit value H or the lower limit value L, the relaying is changed over to the highest limit relay H' or the lower limit relay L', respectively. Lower limit relay L' closes its lower contact L_1', as shown, when the meter indication drops below lower limit value L, and closes its upper contact $L'_{2'}$ when the indication rises above the lower limit value L. Similarly, the higher limit relay H' closes its lower contact $H'_{1'}$, as shown, when the meter indication drops below the higher limit value H, and closes its upper contact $H'_{2'}$ when the indication rises above the higher limit value H. The lower contact $H'_{1'}$ of higher limit relay H', and the change-over contact L'_0 of the lower limit relay L' are connected to the positive pole of a DC power source E_D, and the negative pole of the power source E_D is connected to the lower contact $L_{1'}$ of the lower limit relay L' through a switch $S'_{1'}$, coupled to the switch S_1, and electromagnetic relay R. Contact $L'_{1'}$, may be connected to change-over contact $H'_{0'}$ of higher limit relay H' through the second normally open contact R'' of relay R. In the device of the above construction, the lower limit value L of meter relay M*r* is set to

$$P'_A-P'_C+I_1R_S-\alpha$$

and the higher limit value H is set to $P'_A-P'_C+I_2R_S+\alpha$. Next, switches S_1 and $S'_{1'}$ are closed, relay R is energized, and the contacts R' and R'' are closed.

In this condition, a current value I_2, greater than that of a proofing current with the electrolyte in the most vigorous flow condition, is set by the power source voltage regulator T_0. Then contact R' is opened and a current value I_1, greater than the minimum current necessary for keeping the anode potential P_A at a constant value P'_A, is set by DC voltage regulator *r*.

The apparatus of FIG. 7 now functions as follows. First, switches S_1 and S'_1, close to start the corrosion proofing. At the start of proofing, the potential P_C of the work C is higher than the predetermined proofing potential P'_C, and therefore the voltage V*ac* between work C and anode A corresponds to the lower limit value L on meter relay M*r*. In other words, the meter relay reads a voltage value less than $P'_A-P'_C-I_1R_S-\alpha$. Accordingly, the change-over contact L'_0 of lower limit relay L' of meter relay M*r* closes the lower contact L'_1, as shown, whereby relay R is energized and contacts R' and R'' are closed. Upon closure of contact R'', the change-over contact H'_{01} of higher limit relay H' closes lower contact H'_1 so that relay R can hold. Upon closure of the contact R', a constant voltage is applied between anode A and work C. In this case the resistance (R_S) between the two electrodes A and C can be regarded as constant in the same electrolyte solution, and therefore a substantially constant current I_2 flows between the electrodes A and C.

Thus, the terminal voltage V*ac* between the electrodes A and C, at this time, is $Vac=P'_A-P_C+L_2R_S$. In this equation, the anode potential P'_A and the voltage drop I_2R_S between electrodes A and C are constant, whereas the cathode potential P_C decreases gradually, with the result that the terminal voltage increases steadily. When the increasing terminal voltage V*ac* exceeds the lower limit value L of relay M*r*, contact L'_0, of relay L' changes over from contact L'_1 to contact L'_2. However, because contact H'_1 of higher limit relay H' is closed in this state, relay R holds until the terminal voltage V*ac* further rises to the higher limit value H at which contact $H'_{0'}$ of relay H changes over from contact H'_1 to contact H'_2. Thus, relay R holds until the terminal voltage V*ac* reaches the higher limit value H, and the current I_2 flows during this period.

The supply of current I_2 is interrupted the moment the terminal voltage V*ac* reaches the higher limit value H. However, as the higher limit value H is

$$Vac=P'_A-P'_C+I_2R_S+\alpha$$

the potential P_C of work C, immediately after interruption of current I_2, corresponds to the lower limit value of the proofing potential, $P'_C-\alpha$. When the terminal voltage V*ac* reaches the higher limit value H, contact H'_0 of relay H' is changed over to contact H'_2 and relay R is de-energized. Thereby, contact R' transfers and the current supply is changed over from I_2 to I_1. At this time the terminal voltage is $Vac=P'_A-P'_C+I_1R_S+\alpha$. From then on, by the current I_1, the potential P_A of anode A is maintained at P'_A, whereas the potential P_C of work C increases gradually because the latter cannot be kept polarized. With current I_1 now being supplied, the terminal voltage V*ac* drops until its value reaches

$$P_A-P'_C+I_1R_S-\alpha$$

That is, the potential of work C rises to the higher limit value $P'_C+\alpha$ of the proofing potential. Thereupon, contact L'_0 of relay L' of meter relay M*r* closes its lower contact L'_1 and changes over the supply of current from I_1 to I_2. As the current I_2 flows, the potential of work C again drops as above described, and the terminal voltage V*ac* begins increasing. Above the lower limit value L, the self-sustaining circuit operates, and the current I_2 continues to flow until the higher limit value H is attained. By the repetition of the above operation, the potential P_C of work C can be kept within the range of proofing potential $(P'_C-\alpha)<P_C<(P'_C+\alpha)$.

While the above description has been directed to the case in which the electrolyte solution W is kept still, the same applies to the case where the electrolyte solution W is flowing. When the electrolyte solution W is kept still, the potential P_C of the work is kept at a proofing potential within a range of $P'_C\pm\alpha$, but when the solution is flowing, the rate at which the work C is depolarized is increased. Thus, the potential of the work, after the terminal voltage V*ac* attains the upper limit H resulting in the change-over of current supply to the current I_1, reaches the lower limit value L within a shorter period of time than when the electrolyte solution W is kept still. For this reason, in a flowing electrolyte, the time during which the current I_1 flows is shortened, while the percentage of the time during which the current I_2 flows is increased, and more current flows than when the solution is kept still, while the potential of the subject C being corrosion proofed is kept within the range of $P'_C\pm\alpha$.

Usually, corrosion proofing of metallic structures such as work C can be accomplished by maintaining the potential of the structure at a value 0.2 to 0.3 v. lower than the natural potential P_C^N of the same structure in an electrolyte solution W. If therefore the proofing potential P'_C for the structure C to be corrosion proofed by the apparatus of FIG. 7 is $P_C^N-0.25$ and α is less than 0.05, then the potential P_C of the structure C will be controlled within the range of $(P_C^N-0.3)<P_C>(P_C^N-0.2)$.

In Table I, there are shown the results of experiments conducted, with a device of the type just described, upon test pieces of bare mild steel plate, 0.6 m.² in size, dipped in 70 l. of an aqueous solution containing 3% of sodium chloride, with a view to finding out the effects of flow conditions on the current and on the potential in a point of the bare mild steel plate.

TABLE I

Flow condition	$I_1=0.10$ a. average working time (sec.)	$I_2=0.53$ a. average working time (sec.)	Potential in a point on mild steel plate (on the basis of saturated calomel electrode)	
			Min. pot. (v.)	Max. pot. (v.)
Static	16.0	2.7	0.845	0.865
Flowing	2.5	2.7	0.850	0.870

The potential of mild steel in the 3% aqueous solution of sodium chloride was about 0.6 v. (on the basis of saturated calomel electrode). The potential of "live" platinum anode was 1.2 v. (on the basis of saturated calomel electrode) and the working current was $I_1=0.10$ a. or $I_2=0.53$ a. In this experiment, the voltage V_{ac} between anode A and the work C was so set that the lower limit $V'_{ac}=2.60$ v., set upper limit V''_{ac} was 3.08 v. and resistance R_S between anode A and work C was 1.8 ohms. The point at which the potential was determined was the point on the mild steel plate which showed an average potential. The flowing condition was obtained by circulating the solution at a constant flow rate with a centrifugal pump. The measured values are the averages in the stabilized state after the test pieces, both in the static and flowing conditions, were kept as they were for about an hour.

As will be clear from Table I, the time required for polarization of the work C to be corrosion proofed (mild steel) was not affected by the flow condition but the rate at which it was depolarized in the flowing state was very high as compared with that in the static state. Under the experimental conditions, the current I_2 flowed for 14.4% of the unit time in the static state and for 51.9% in the flowing state. Potentials differed slightly with the state, whether static or flowing. This was because potential distribution on the mild steel varied with the flow condition, the potential being concentrated close to the anode in the flowing state. Thus, it was confirmed by the experimental results as given in Table I that the apparatus of FIG. 7 is fully capable of performing automatic electro-corrosion proofing.

While the apparatus of FIG. 7 is of a contact type which uses a small electromagnetic relay in the change-over mechanism of meter relay Mr and an electromagnetic relay R for switching the proofing current between values, it is also possible to employ a contactless device as shown, for example, in FIG. 8. FIG. 8 shows a contactless meter relay circuit which actuates silicon controlled rectifiers replacing the contact R′ in FIG. 7. This circuit includes a phototransistor P*tr*, and the rays of light from a light projector are interrupted by a sub-index or shutter K′ attached to a moving pointer K. Thereby, a minute current flows through the phototransistor circuit which is kept at equilibrium, and this current is amplified by a transistor amplifier T*r*. In this way, a sufficient current or voltage to turn the SCR on or off is obtained.

Thus, an automatic electro-corrosion proofing device of the contactless type can be provided by incorporating a contactless meter relay, having two set points, as above, in lieu of the meter relay M*r*, electromagnetic relay R, and DC power ED of the apparatus shown in FIG. 7, by replacing contact R′ of the relay R with the SCR shown in FIG. 9, and by connecting the output obtained as the pointer passes through the lower limit set point of the contactless meter relay to the input terminal of the SCR and connecting the output obtained as the pointer passes through the upper limit set point of the relay to the reset input terminal. The operation of this contactless corrosion proofing apparatus, and the effects thereby attainable, are exactly the same as those of the apparatus shown in FIG. 7. As a control means for the corrosion proofing apparatus, the meter relay is most suitable because it is inexpensive and is capable of giving indication simultaneously with control. However, it is not objectionable to use other control means if it functions as a relay at the two set voltage points.

The apparatus of FIG. 7 can be used also in the case where electrodes A and C are de-energized, and the working current reduced to zero, as the terminal voltage reaches the value V''_{ac} with a constant current I_2 flowing. However, in this case, the D.C. voltage regulator *r* is omitted and the connections are made in such a manner that the output current of rectifier R_f can be switched on and off directly by contact R′. Thus, the connections are made in such a manner that the current can be completely interrupted when contact R′ of relay R is open. If the apparatus shown in FIG. 7 is modified in this manner, it will function as follows:

First, the lower limit value L of meter relay M*r* is set to $P'_A-P'_C-2\alpha$ and the higher limit value H is set to $P'_A-P'_C+I_2R_S+\alpha$. Current I_2 is set to a constant value above the proofing current value in the most vigorous flowing condition of the electrolyte. As corrosion proofing is started by closing switches S_1 and S'_1, the voltage V_{ac} between work C and anode A is indicated at a point below the lower limit value L of meter relay M*r* because, in this state, the potential P_C of work C is higher than the predetermined proofing potential P'_C, and the potential P_A of the anode A is lower than the potential P'_A obtained on initiation of current flow. Accordingly, lower limit relay L′ of the meter relay closes contact L'_1 and energizes relay R the relay remains transferred and a constant voltage is impressed between the electrode A and work C. The terminal voltage V_{ac} between the electrodes A and C, at this time, is $V_{ac}=P'_A-P_C+I_2R_S$. As the terminal voltage V_{ac} reaches the value

$$P'_A-P'_C-I_2R_S+\alpha$$

contact H'_0 of higher limit relay H′ is changed over to the contact H'_2. This de-energizes relay R with the result that the circuit is opened and the current I_2 is reduced to zero. The potential P_C of work C immediately before reduction of the current I_2 to zero is $P'_C-\alpha$, and the terminal voltage V_{ac} immediately after the reduction of the current I_2 to zero is $V_{ac}=P_A-P'_C+\alpha$.

With no current flowing, the potential P_A of anode A drops while the potential P_C of work C increases, and the terminal voltage V_{ac} declines to $P_A-P'_C-2\alpha$. In other words, the potential of the work C increases until it attains substantially the value $P'_C+\alpha$. As the terminal voltage V_{ac} drops to $P_A-P'_C-2\alpha$, lower limit relay L′ of meter relay M*r*, set to the above voltage value, closes the contact L'_1 and energizes the relay R, thereby resuming the supply of current I_2. The potential P_C of work C now begins dropping and the terminal voltage V_{ac} begins rising. Upon arrival of the terminal voltage at the value $V_{ac}=P'_A-P'_C+I_2R_S+\alpha$, the current I_2 is again reduced to zero by the transfer of higher limit relay H′.

By the repetition of the above sequence of operations, the potential P_C of work C is maintained substantially within the range of $(P'_C+\alpha)>P_C>(P'_C-\alpha)$. When the electrolyte solution W is in a flowing state, the voltage drop of work C caused by the current I_2, takes more time than when electrolyte W is in a static state, and hence the time required for terminal voltage V_{ac} to increase to the higher limit value $P_A-P'_C+I_2R_S+\alpha$ is prolonged. When the terminal voltage V_{ac} has reached the upper limit and no more current flows, the polarization of anode A and work C is lost more quickly than when electrolyte W is in the stationary or still state, and the lower limit is attained in a shorter period of time. This means that the working time of current I_2 is increased and its "off" time is shortened as compared with the case where the solution is kept still. While more current is supplied in the flowing state of electrolyte W, the current flow is responsive to the higher and lower limits of the terminal voltage V_{ac} in the same manner as in the static state of electrolyte W. Thus, regardless of the changes in the electrolyte flow conditions, the potential P_C of work C is maintained substantially within the range of $(P'_c+\alpha)>P_C>(P'_C-\alpha)$.

Table II shows the results of corrosion proofing tests conducted on test pieces of bare mild steel plate, 0.6 m.^{2} in size, dipped in 70 l. of an aqueous solution containing 3% of sodium chloride, with the apparatus as just described, using a platinum anode. The results respresent the effects of flow conditions upon the current and the potential in a point of bare mild steel plate.

TABLE II

Flow condition	I=0.7 a working time (sec.)	I=0 time (sec.)	Potential in a point of bare mild steel plate (on the basis of saturated calomel electrode)	
			Min. pot. (v.)	Max. pot. (v.)
Static	30	180	0.815	0.895
Flowing	24	12	0.850	0.875

In the above experiment, the voltage V*ac* between anode A and work C had a lower limit value V'*ac* of 1.97 v. and an upper limit value V''*ac* of 3.35 v., and the current I_2 was 0.70 a. The resistance R_S between anode A and work C was 1.8 ohms. The measuring points for the voltages were the points where average potentials for the mild steel plate were obtained. In Table II, there is some discrepancy between the potentials in the two different states, flowing and static. This is because potential distribution differs with the flow condition, and the potential tends to be concentrated close to the anode A in the flowing state, and further because the respective rates at which the anode A and mild steel plate C lose their polarization are not the same.

The potential of "live" platinum anode A was 1.2 v. (on the basis of saturated calomel electrode). Since the corrosion proofing potential of the mild steel plate C is about 0.8 to 0.9 v. (on the basis of saturated calomel electrode), the potentials given in Table II are well within the above range. As will be also clear from the table, the time required for polarization is not affected by the flow condition but the rate at which the polarization is lost in the flowing state is materially affected. In the flowing state, the current supplied is about five times as much as that supplied in the stationary or still state. In the above experiment, the flowing state was realized by circulating the solution by means of a centrifugal pump, and was a state in which a constant flow rate was attained. The measured values represent the average values after the attainment of constant and stabilized states. From the results given in Table II it was ascertained that the modified apparatus also can serve adequately as an automatic electro-corrosion proofing device.

As described hereinbefore, the present invention provides a simplified automatic electro-corrosion proofing method which comprises determining the potential difference between a non-consumable metallic body, used as an anode, and a structure to be corrosion proofed which is disposed opposite to the anode in an electrolyte anode to the structure in such a way that the above potential difference reaches a predetermined value corresponding to a range of a proofing potential for the structure and that the proofing potential is kept within the predetermined range, whereby the potential of the structure being corrosion proofed can be positively maintained in the range of proofing potential throughout and thus the corrosion proofing can be accomplished perfectly without the use of a standard electrode or the like.

What is claimed is:

1. A method for preventing corrosion of metallic structures immersed in an electrolyte solution, comprising the steps of: immersing an anode of non-consumable material in the electrolyte solution in spaced relation to the structure acting as a cathode; effecting a unidirectional current flow from the anode through the electrolyte solution to the structure; and regulating the current flow to maintain the difference between the potential, applied between the anode and the structure, and the resistance voltage drop, including the solution resistance voltage drop between the anode and the structure, within a predetermined limited range corresponding to the potential of the structure having a value at which the structure is corrosion-proof.

2. A method as claimed in claim 1, in which the current flow is maintained at a constant value.

3. A method as in claim 2, including the step of determining the potential difference between the anode and the structure; and, responsive to any drop of said potential difference below a predetermined value, supplying said current at said constant value.

4. A method as claimed in claim 3, including the step of, responsive to any increase of said potential difference above a second predetermined value, supplying said current at a different and smaller constant value.

5. A method as claimed in claim 3, including the step of, responsive to any increase of said potential difference above a second predetermined value, interrupting the flow of current between the anode and the structure.

6. A method as claimed in claim 5, including the step of, responsive to any drop of said potential difference below a first predetermined value, initiating the flow of current at a first constant value; responsive to an increase of said potential difference to said first predetermined value, interrupting the supply of current at said first constant value; and, responsive to an increase of said potential difference above said first predetermined value and above a second and higher predetermined value, initiating a flow of current from said anode to the structure at a constant value less than said first constant value.

7. A method as claimed in claim 1, including the step of, responsive to a variation of said difference and varying the current in a direction to restore said difference to a preselected value.

8. A method as claimed in claim 1, including the step of determining the potential difference between said anode and the structure; and, when said potential difference varies from a determined potential value, varying the current flow in a direction to restore the potential difference to such determined value.

9. Apparatus for preventing corrosion of a metallic structure immersed in an electrolyte solution comprising, in combination, a source of unidirectional potential; means connecting the structure to the negative terminal of said source; an anode of non-consumable material immersed in the electrolyte solution in spaced relation to the structure and connected to the positive terminal of said source; measuring means operable to measure the potential applied, between said anode and the structure, and the resistance voltage drop, including the solution resistance voltage drop, between said anode and the structure; and means operable, responsive to the potential difference between said measured applied potential and the resistance voltage drop to control the flow of current from said anode to the structure to maintain the potential difference between said applied potential and said resistance voltage drop within a predetermined limited range corresponding to the potential of the structure having a value at which the structure is corrosion-proof.

10. Apparatus as claimed in claim 9, including means operable by said measuring means, responsive to any drop of said potential difference below a first predetermined value, to initiate said current flow at a first constant value and, when said potential difference attains said first predetermined value, to interrupt the flow of current of said first constant value.

11. Apparatus as claimed in claim 10, including means operable by said measuring means, responsive to said potential difference increasing above said first predetermined value and above a second and higher predetermined value, to initiate a current flow from said anode

to the structure at a second constant value less than said first constant value.

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