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CONTROL SYSTEM AND METHOD FOR ANODIC PROTECTION

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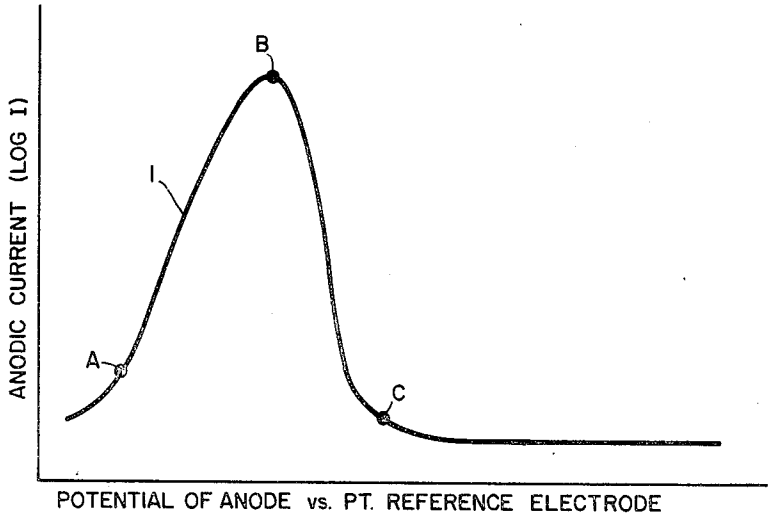
FIG. 1



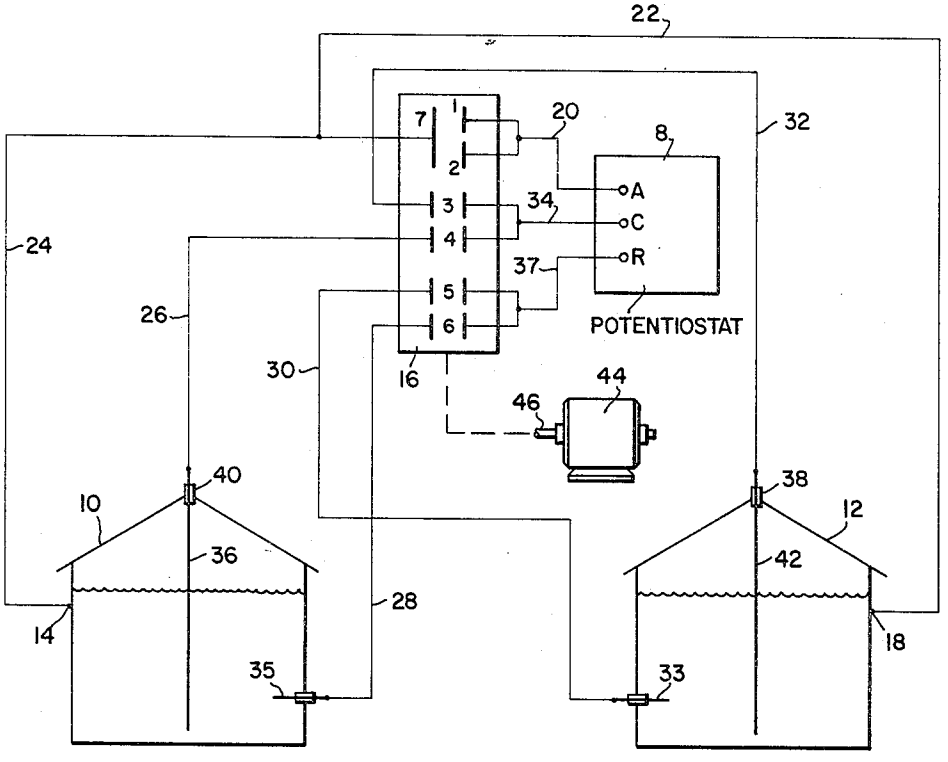


FIG. 2

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CONTROL SYSTEM AND METHOD FOR ANODIC PROTECTION

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ABSTRACT OF THE DISCLOSURE

A control system and method for automatically providing anodic protection for various types of structures, vessels and the like which normally contain or are in contact with highly corrosive solutions, which system makes use of a switching circuit which permits the simultaneous anodic protection of two or more structures while using only one potentiostat or control instrument.

This invention relates generally to a control system and method for avoiding corrosion. More particularly, the invention relates to a control system and method for automatically providing anodic protection for various types of structures, vessels and the like which normally contain or are in contact with highly corrosive solutions. Most specifically, the invention relates to the use of a switching system which permits the simultaneous anodic protection of two or more structures while using only one potentiostat or control instrument.

In its simplest terms, anodic protection is the process of passivating an active-passive metal by impressing an external anodic current on the metal. Three electrodes are necessary for anodic protection. The structure to be protected is made the anode, an inert metal is usually used for the cathode and an electrochemical half-cell is used as a reference electrode. A potentiostat regulates the current from the cathode to the anode in such a manner that the potential difference between the reference electrode and the anode is maintained independent of the total cell current. The cathode, anode and reference electrode are so positioned that they are in contact with the conductive corrosive fluid.

Anodic protection or in the alternative passivity, is achieved by the formation and maintenance of a protective film on the normally corrodible surface of the structure to be protected. While certain characteristics of this protective film are known there is still a considerable divergency of opinion as to the exact nature of the passive layer. The theories advanced in explaining the nature of this film have been put in three broad categories. First, the oxide film theory, which proposes that the metal to be protected (iron, for example) first dissolves and then reacts with oxygen to form a protective barrier of iron oxide. The second theory is the so-called adsorption theory which proposes that a monomolecular layer of adsorbed oxygen causes passivity. The third theory advanced is one which calls for an initial adsorption of oxygen followed by the development of an amorphous iron oxide structure. In regard to the above, reference may be had to the article by Sudbury et al, "Corrosion," vol 16, No. 2, February 1960 pp. 47T to 48T.

For the purposes of the instant invention, it will suffice to say in addition to the above, that the protective film formed will in fact, inhibit corrosion and that it possesses a certain amount of inherent stability. It has been found that this protective film is capable of sustaining itself over periods of several minutes without the application of an external current. It is this finding which allows applicant to depart from the prior art teachings

which call for the use of a supply of current to the anode during the entire period for which it is protected. The prior art teachings result in the necessity of using an individual potentiostat for each independent protection circuit. In contrast, applicant's invention allows the use of a single potentiostat or control instrument in the protection of two or more independent structures with no loss in the efficiency of protection. Applicant's invention thus results in markedly reduced costs for anodic protection systems.

It is therefore the principal object of this invention to provide an efficient and economical anodic protection system suitable for use in the control of corrosion of industrial structures formed from active-passive metals.

Another object of the invention is to provide a method of anodically protecting two or more independent structures using a single potentiostat or control instrument.

A further object is to provide apparatus for the simultaneous anodic protection of two or more independent structures normally subject to corrosion, wherein a single power source or potentiostat is employed.

Further objects and advantages of the instant invention will be apparent from the following description, reference being had to the accompanying drawings wherein:

FIG. 1 is a schematic drawing illustrating a typical anodic passivation curve.

FIG. 2 is a diagrammatic representation illustrating one method of applying the teachings of the instant invention.

The anodic protection apparatus and method, as contemplated by the instant invention, is applicable for use in a wide variety of situations where metallic surfaces are subject to corrosion due to chemical attack. Process reactors, storage equipment, boilers, and acids concentrators are examples of equipment whose service life may be materially extended by applying anodic protection techniques utilizing the system of the instant invention.

Referring to the drawings in detail and more particularly to FIG. 1, the curve illustrates a typical anodic passivation curve wherein the relationship between the total anodic current and the potential of the active-passive metal connected as anode with respect to the reference electrode is shown.

The operation of the instant invention can be conveniently discussed in the light of FIG. 1. Point A designates the normal active state of the active-passive metal in the conductive corrosive fluid. The critical passivating current of the metal, designated by Point B must be overcome to reach the anodic passivation range, the beginning of which is designated by Point C.

The hump, i.e. ABC, of the curve corresponds to the formation and stabilization of the protective film barrier hereinbefore discussed. As previously mentioned, once formed this film is capable of sustaining itself over a finite period of time without the application of an external current. Since it is this film which is directly responsible for the inhibition of corrosion it follows that the metal sought to be protected will remain free from corrosive attack while this film is intact. This remains true even where there is a temporary cessation in the flow of current to the anode. It has been found for example that this protective film will be stable for periods of up to several minutes in the system herein subsequently described.

By way of example, and not by way of limitation, FIG. 2 illustrates the use of the present invention for the simultaneous protection for two independent sulfuric acid storage tanks **10** and **12**. The single potentiostat **8** has its positive or anodic terminal A, connected to the input terminals of switches **1** and **2** of a cam timing switch **16** by means of electrical conductor **20**. Electrical conductors **22** and **24** are connected to the output terminal **7**, of

switches 1 and 2 and serve to conduct the current to the walls of tanks 12 and 10 respectively. Conductor 22 makes electrical contact with tank 12 at 18 and conductor 24 makes contact with tank 10 at 14.

The cathodic terminal C of potentiostat 8 is connected via electrical conductor 34 to the input terminals of switches 3 and 4 of cam timing switch 16. Conductor 32 having one end connected to the output terminal of switch 3 carries current to cathode 42 located in electrical contact with the fluid of tank 12. Cathode 42 is electrically insulated from the walls of tank 12 by insulation means 38. Electrical conductor 26 having one end connected to the output terminal of switch 4 carries current to the cathode 36 located in electrical contact with the fluid in tank 10. Cathode 36 is insulated from tank 10 by insulation means 40.

The reference electrode terminal R of potentiostat 8 is connected to the input terminals of switches 5 and 6 of cam timing switch 16 by electrical conductor 37. The output terminal of switch 5 is connected via electrical conductor 30 to reference electrode 33 located in electrical contact with the fluid in tank 12 while the output terminal of switch 6 is connected by means of conductor 28 to the reference electrode 35 located in electrical contact with the fluid in tank 10.

In the actual operation of the system described in FIGURE 2 sufficient current is applied to the walls of both tanks 10 and 12 (the anodes) to achieve the formation and stabilization of the protective film herein previously mentioned. Thereafter the protection of each tank is achieved by using the action of cam timing switch 16 in conjunction with potentiostat 8. The cam timing switch 16 is continuously cycled by means of motor 44 and drive shaft 46 so that when switches 1, 3 and 5 are closed, switches 2, 4 and 6 are open and when switches 2, 4 and 6 are closed, 1, 3 and 5 are open. The time between successive "open" periods for each set of switches may be on the order of several minutes since as previously discussed the protective film on the tank wall has some inherent stability and does not require current for its maintenance over such a time period.

It may be seen from FIG. 2 that when switches 1, 3 and 5 are closed (i.e. current passing through them) current is supplied to the anode (tank wall) and cathode 42 of tank 12. In addition, reference electrode 33 which may preferably be of the platinum type is connected via conductor 30 and switch 5 to the reference electrode terminal R of potentiostat 8.

In operation potentiostat 8 is preset at a potential value E_s, within the passive range of the anode being protected. This assigned potential value E_s is compared in comparator circuits present in potentiostat 8 with the existing potential E_I as measured between the reference electrode 33 and the anode (tank wall). The difference dE, between E_s and E_I is amplified in a voltage amplifier also present in potentiostat 8.

This amplified potential difference controls a power amplifier, also present with potentiostat 8, and it is this amplifier which furnishes the current which flows from the cathode to the tank walls (anodes) which is necessary to make the actual potential value E_I equal to the assigned value E_s. The potentiostat 8 may be of any suitable type such as that manufactured by Analytical Instruments Inc.

Again from FIG. 2 it is seen that when switches 2, 4 and 6 are closed the current flows to tank 10 through conductors 24 and 26 and it then is on its "on" cycle.

Thus, it is seen that each of the tanks being protected goes through a "on-off" cycle of receiving and not receiving current. The time periods of current "on" and current "off" are determined by the design of the cam (not shown) of cam timing switch 16, such design being readily accomplished by those skilled in the art. A preferred cycle for the system given is current "on" for 1 to 10 minutes and current off for the same period. It is to be

appreciated however that the period of current "on" need not necessarily be equal to the period of current "off." Furthermore, while the invention has been discussed in terms of affording protection to two vessels it is to be understood that it may be employed equally as well in systems having a plurality of vessels.

Laboratory tests on the system described above were conducted using carbon steel tanks containing 90% sulfuric acid and a platinum reference electrode. The anodic protection efficiency of this system using a cam timing switch to protect two tanks was compared to the anodic protection efficiency of a system where the current was continuously supplied to a single tank. The results of these tests are summarized in Table I. It will be understood that these experiments are illustrative only and that the invention is to be taken as limited only by the scope of the appended claims.

Table I

System:	Anodic protection percent efficiency
Trial 1—continuous current to single tank	25
Trial 2—continuous current to single tank	50
Trial 1—cam timing system—2 tanks	33
Trial 2—cam timing system—2 tanks	33

As may be seen from the above the overall anodic protection of the single tank having current supplied continuously is approximately 38% while the cam timing system exhibited an overall efficiency of 33%. Taking into account experimental error which was estimated at between ± 10, both systems are receiving approximately the same amount of protection.

Thus, the system taught by the instant invention affords approximately the same amount of protection even though each tank does not have current flowing to it for one half of the entire period during which it is being protected. It is readily apparent that this system offers advantages and economies heretofore unavailable in the prior art of anodic protection.

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

What is claimed is:

1. An improved anodic protection system for at least two independent structures comprising in combination, a potentiostatic device, said device having an anode terminal, a cathode terminal and a reference electrode terminal, electrical conduction means to connect said anode terminal of said potentiostatic device to each of said structures, said structures each having at least one cathode and at least one reference electrode, means to electrically connect said cathode terminal of said potentiostatic device to said cathodes, means to electrically connect said reference electrode to said reference electrode terminal of said potentiostatic device, and a cam timing switch interposed between the terminals of said potentiostatic device and said structures, and the cathodes and reference electrodes thereof, whereby current from said potentiostatic device is applied in cycles to each of said structures as anode, said current maintaining said structures as anodes within a predetermined potential range with respect to said reference electrodes.

2. The apparatus of claim 1 wherein said structures are carbon steel, sulfuric acid storage tanks.

3. A method for inhibiting the corrosion of at least two independent active-passive metal structures under the action of corrosive liquid comprising the following steps in combination:

(a) supplying a D.C. electric current between the first of said active-passive metal structures and at least one cathode electrically insulated from said metal

structure, said cathode being in contact with said corrosive liquid, said D.C. electric current being supplied from a potentiostatic device, said current also being of a magnitude sufficient to passivate said metal structure connected as anode and maintain the average potential of said metal structure connected as anode within a predetermined passive potential range with respect to a reference electrode in electrochemcial contact with the corrosive liquid;

(b) automatically switching said electrical current from said first active-passive metal structure to the second active-passive metal structure;

(c) repeating the switching cycle at such a frequency whereby both of said active-passive metal structures are anodically protected from corrosion.

4. The method of claim 3 wherein the frequency of said switching cycle is in the range of 1 to 10 minutes.

5. In a method for anodically protecting at least one active-passive metal structure the improvement comprising the step of supplying the current for a period of about 1 to 10 minutes and then switched off for a similar period before the cycle is repeated, to the structure being anodically protected.

6. In an anodic passivating system for the inhibition of corrosion of at least two independent structures the improvement comprising a cam timing switch, said switch being automatically operated whereby the passivation current is alternatingly supplied on a periodic basis first to one of said structures and then to the other said structure.

7. An improved anodic protection system for two independent active-passive metal storage structures for corrosive fluids comprising in combination:

(a) a potentiostatic device having at least one anode terminal, one cathode terminal and one reference electrode terminal;

(b) electrical conducting means to provide an electrical path from said anode terminal to each of said storage structures as anodes;

(c) at least one cathode deposed in said corrosive liquid of each of said structures;

(d) at least one reference electrode so deposed as to be in electrochemical contact with said corrosive fluid in each of said structures;

(e) said cathode being electrically insulated from said storage structures;

(f) electrical conductor means to provide an electrical path from said cathode terminal of said potentiostatic device to each of said cathodes;

(g) electrical conductor means to provide an electrical path from said reference electrode terminal of said potentiostatic devices to each of said reference electrodes;

(h) a cam timing switch, said switch forming a part of said electrical paths whereby current from said potentiostatic device is automatically supplied in cycles first to one of said structures connected as anodes and then to the other said structure connected as anode;

(i) said current being of sufficient magnitude to maintain each of said structures connected as anodes within a predetermined potential range with respect to said reference electrodes.

References Cited

UNITED STATES PATENTS

3,162,585	12/1964	De Ford et al.	204—195
3,208,925	9/1965	Hutchison et al.	204—147

FOREIGN PATENTS

979,109	1/1965	Great Britain.

OTHER REFERENCES

Riggs et al. "Corrosion," vol. 16, February 1960, pp. 58t–62t.

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U.S. Cl. X.R.

204—196, 228, 231