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ELECTROCHEMICAL CELL FOR THE STUDY OF CORROSION BY POLARIZATION METHODS IN NON-CONDUCTING SOLUTIONS

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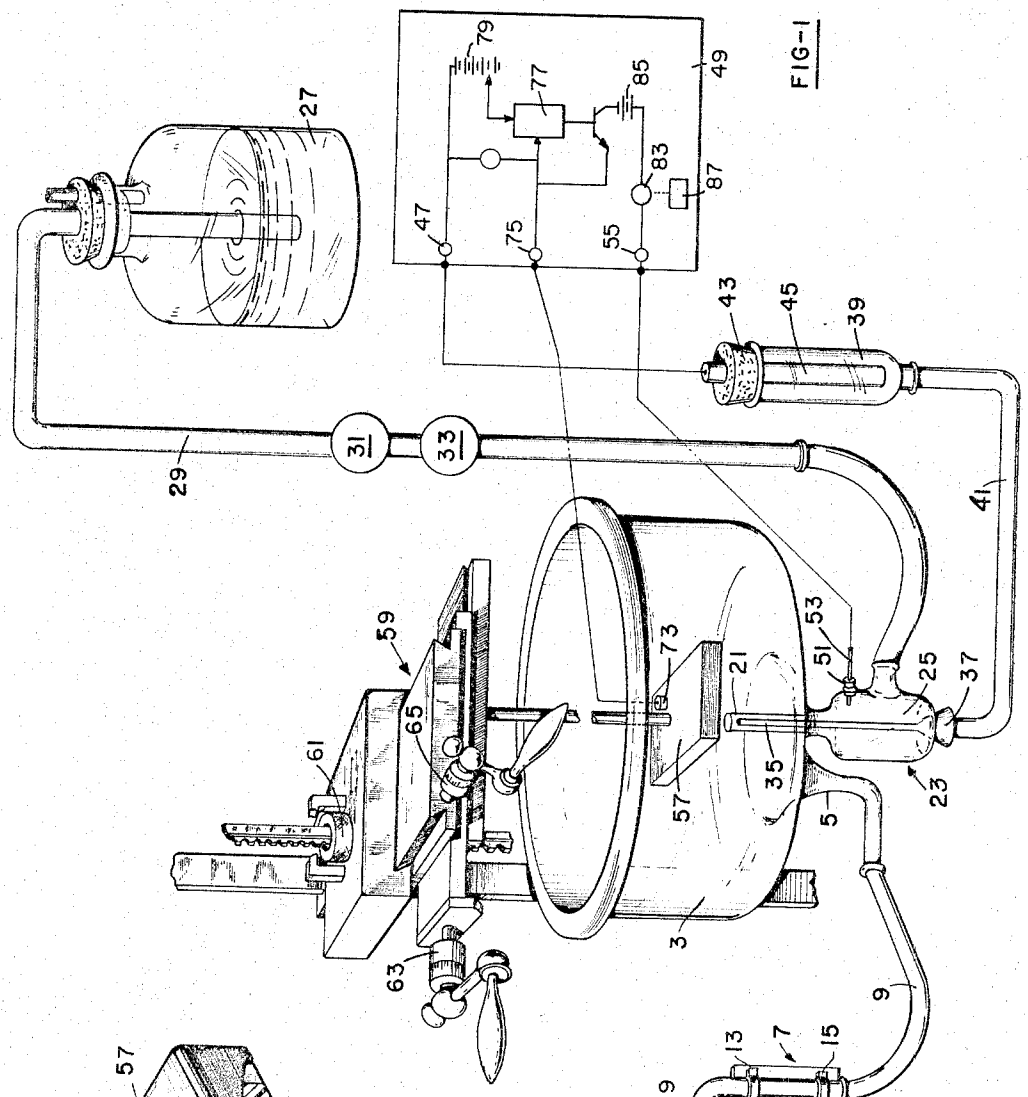


FIG-1

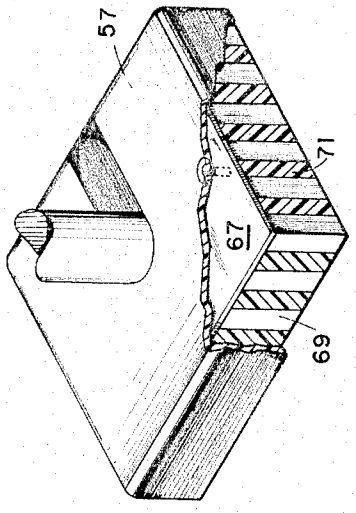


FIG-2

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ELECTROCHEMICAL CELL FOR THE STUDY OF CORROSION BY POLARIZATION METHODS IN NON-CONDUCTING SOLUTIONS

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ABSTRACT OF THE DISCLOSURE

The subject invention relates to apparatus for evaluating the rate of corrosion of a metallic electrode due to the presence of discontinuous droplets of a corrosive electrolyte in an electrically non-conductive fluid such as droplets of water in an aircraft fuel. The apparatus is designed so as to direct a flow of the corrosive electrolyte against the metallic surface which is to be evaluated and which is immersed in the non-conductive fluid. A potentiostat continuously monitors the potential of the metallic surface and records the changes in current required to maintain the said potential constant.

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

The present invention relates to novel and improved apparatus for investigating corrosion of metallic substances. More particularly, it relates to novel and improved electrochemical apparatus for investigating corrosion of metallic substances and/or the effectiveness of corrosive inhibitors in water insoluble non-conducting environments.

Intensive studies of the corrosion of metals in the presence of various types of electrolytes and corrosion inhibitors are often desirable in order to devise methods to control, minimize and/or arrest such corrosion. Various types of apparatus have been used in the past to investigate the corrosive character of electrolytics that are soluble or in continuous phase with the base liquid in which the specimen is immersed. It often becomes desirable, however, also to study the corrosive effect of an electrolyte which is dispersed in the form of discontinuous droplets or the like in a fuel, grease, or other non-soluble base liquid.

It is therefore a principal object of the present invention to provide novel and improved apparatus which may be employed to investigate the corrosive characteristics of metallic substances and/or the effectiveness of corrosion inhibitors in water insoluble non-conducting environments.

It is a further object of the present invention to provide novel and improved corrosion investigation apparatus in which the use of a new metallic specimen and/or a fresh solution in which it is immersed for each study at a unique potential is minimized or eliminated.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawing wherein:

FIG. 1 is a diagrammatic showing of a preferred embodiment of the present invention.

FIG. 2 is a detailed view of the specimen electrode shown in FIG. 1.

Referring now to FIGS. 1 and 2 of the drawing, it will be noted that the electrically non-conductive fluid, in which the corrosion inhibitor that is to be evaluated has been deposited, is disposed in the glass vessel or receptacle 3. The open end of the L-shaped fluid conduit or tube 5 which is fused or otherwise suitably disposed in the bottom of the receptacle 3 is connected to the tubular glass fluid level control device 7 through the flexible tubular conduit or the like 9. The fluid level control device 7 is slidably adjustable on its support 11 in the conventional clamp members 13 and 15 in any suitable manner. The beaker or receptacle 17 is preferably provided to accommodate overflow fluid from the tube 19 with adjustments of the fluid level in the receptacle. The elongated open tube 21 of the corrosive electrolytic injection device 23 is fused in the bottom of receptacle 3 and extends upwardly as shown into the interior of the receptacle. The corrosive electrolyte is supplied to the enlarged bulb portion 25 of the electrolytic injection device 23 from a suitable reservoir 27 through the flexible tube 29, needle valve 31 and stop cock 33. The capillary tube 35 is fused in the bottom of the bulb portion 25 of the electrolytic injection device and extends upwardly into the neck or upper tubular extension 21 of the injection device as shown. The enlarged tapered lower extremity of the capillary tube 35 accommodates an oppositely tapered plug or glass joint 37 through which as will be more apparent hereinafter another electrolytic solution is supplied from the enlarged test-tube-like container 39 and flexible tube 41. The tapered plug or glass joint 43 vacuum seals the oppositely tapered open end of container 39. The reference electrode 45 is preferably integrally attached to the plug 43 and extends through the plug downwardly into the electrolyte in container 39. Reference electrode 45 is electrically connected to terminal 47 of the electrostat 49. The tapered plug or glass joint 51 which engages the oppositely tapered tubular projection of bulb 25 similarly supports the inert platinum electrode 53 on its axis such that the electrode 53 extends through the plug into the interior of bulb 25. Electrode 53 is electrically connected to terminal 55 of the potentiostat 49. The specimen electrode 57 upon which the extent of corrosion is to be studied extends downwardly into receptacle 3 from its adjustable supporting and positioning mechanism or the like 59. Inasmuch as the specific structure of the electrode adjustment mechanism forms no part of the present invention, a full description of the same herein is omitted for the sake of simplicity. For a complete understanding of the invention, it need only be understood that adjustment of the vernier control devices 61, 63 and 65 respectively control movement of the electrode 57 in three mutually perpendicular directions above the electrolytic injection device 23 in receptacle 3. The electrode 57 itself preferably includes the metallic electrically conductive plate 67 and a plurality of regularly arranged poles 69 which extend downwardly from the plate. The plate and pole electrode structure is preferably encased in a suitable electrically non-conductive plastic material or substance 71. The electrical connector or jack 73 extends upwardly from the plate 67 and provides electrical contact between the electrode 57 and terminal 75 of the potentiostat 49.

Terminal 47 of the potentiostat 49, which is conventional in design, is connected to the differential amplifier 77 through the variable potential source 79. Terminal 75 of the potentiostat is also connected to amplifier 77. The output control signal of amplifier 77 is coupled to the base of transistor 81. The collector-emitter circuit of transistor 81 extends from terminal 55 of the potentiostat successively through the ammeter 83, the potential source 85, and the transistor to terminal 75 of the potentiostat. Recorder 87 is coupled to ammeter 83 in any suitable conventional manner.

In operation, the fuel or other electrically non-conductive fluid containing a predetermined concentration of

the corrosive inhibitor to be evaluated is first deposited in the receptacle 3. The device 7 is then adjusted so as to establish and maintain the desired level of the non-conductive fluid in receptacle 3. The vernier controls 61, 63 and 65 of the adjustment mechanism 59 are then set so that one of the poles of electrode 57 is positioned a predetermined distance immediately above the tubular extremity 21 of the corrosive electrolyte injection device 23. Stop cock 31 and needle valve 33 are then opened and adjusted such that a predetermined flow of a suitable corrosive electrolyte is established from the reservoir 27 through the injection device 23 to the juxtaposed pole of electrode 57. A predetermined electrolytic solution is then sealed in the container 39 and the container is positioned such that the solution rises in the capillary tube 35 to a point where electrical contact is established with the corrosive electrolyte in the tubular extension of the injection device 23. The variable potential source 79 of the potentiostat 49 is then set at the potential at which the study of the inhibitor is to be conducted. The potential developed by the reference cell at 75 between electrodes 45 and 57 and the potential of the variable source 79 are then compared to provide an error signal which is amplified in amplifier 77 and used to determine the bias at the base of transistor 81. When the potential at terminal 75 exceeds the preset potential of source 79, the bias at the base of transistor 81 decreases, the flow of current through the transistor control circuit decreases, and the potential of the specimen electrode at terminal 75 decreases. When the reference cell potential is less than the preset potential of source 79, the bias at the base of transistor 81 increases, the flow of current through the transistor control circuit increases, and the potential at terminal 75 increases. Ultimately, in any case, the effect of the potential developed by the reference cell supplemented by the potential at 75 developed by the flow of current through the control circuit between electrodes 53 and 57 provide a potential equal and opposite in polarity to the potential developed by the variable source 79. When this occurs, no error signal is fed into amplifier 77, no change in the flow of current through the transistor control circuit is produced, and a temporary state of equilibrium is established. As the corrosive electrolyte in time penetrates the protective film of the inhibitor on the surface of the specimen electrode 57, the potential developed by the reference cell tends to decrease. When this occurs, the error signal developed in amplifier 77 increases the bias at the base of transistor 81 and the flow of current through the control cell increases. This increase in the flow of current through the control cell increases the potential of the specimen electrode at terminal 75, nulls the error signal fed to amplifier 77 and maintains the potential across the reference cell constant. The change of current flow through ammeter 83 with time as recorded in recorder 85 then provides the desired electrochemical measure of the effectiveness of the inhibitor in retarding and/or arresting corrosion on the surface of electrode 57. In order to study the effect of the inhibitor at other preset potentials, the vernier controls 61, 63 and 65 are adjusted so that other poles of the electrode 57 are positioned above the injection device 23, the variable potential source 79 is reset to other desired study potentials, and change in the flow of current through ammeter 83 with time are similarly recorded. From the resulting curves, various comprehensive studies of the corrosion characteristics of non-conductive fluids as well as the effectiveness of corrosion inhibitors can be readily conducted.

It is to be understood that, although the improved apparatus of the present invention is described hereinabove in connection with an improved technique for the study of the effectiveness of various types of inhibitors, the apparatus may also be used in connection with the study of many other aspects of corrosion such as the physical and chemical adsorption bands of inhibitors, the adsorption and desorption rates of inhibitors, and temperature, concentration and fluid velocity effects on corrosion without departing from the spirit or scope of the invention.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. Electrochemical apparatus for studying corrosion of a metallic electrode in an electrically non-conductive fluid, said apparatus comprising:
   (a) means for suspending the electrode in the fluid, said electrode having a plurality of poles extending downwardly into the fluid;
   (b) means for exposing any pole of the electrode to a corrosive electrolyte;
   (c) a first electrolytic circuit which includes the electrode;
   (d) a second electrolytic circuit which includes the electrode; and
   (e) means including the said first electrolytic circuit for controlling the flow of current through the second electrolytic circuit so as to maintain the potential at the electrode constant.

2. Electrochemical apparatus for studying corrosion of a metallic electrode in an electrically non-conductive fluid, said apparatus comprising:
   (a) means for suspending the electrode in the fluid, said electrode having a plurality of poles extending downwardly into the fluid;
   (b) means for exposing any pole of the electrode to a corrosive electrolyte;
   (c) a first electrolytic circuit which includes the electrode;
   (d) a second electrolytic circuit which includes the electrode;
   (e) means including the said first electrolytic circuit for controlling the flow of current through the second electrolytic circuit so as to maintain the potential at the electrode constant; and
   (f) means for recording changes of current with time in the second electrolytic circuit.

3. Electrochemical apparatus for studying corrosion of a specimen electrode in an electrically non-conductive fluid, said apparatus comprising:
   (a) a receptacle in which the fluid is deposited;
   (b) a corrosive electrolytic injection device having a tubular extremity which extends into the interior of the receptacle;
   (c) means for suspending the specimen electrode in the fluid above the tubular extremity of the injection device;
   (d) means for directing a predetermined flow of a corrosive electrolyte through the tubular extremity of the injection device against the peripheral surface of the specimen electrode;
   (e) a control electrode immersed in the corrosive electrolyte;
   (f) a reference electrode immersed in a second electrolyte;
   (g) means for establishing electrolytic contact between the reference electrode and the specimen electrode; and
   (h) a potentiostat coupled to the specimen, control and reference electrodes.

4. Electrochemical apparatus for studying corrosion of a specimen electrode in an electrically non-conductive fluid, said apparatus comprising:
   (a) a receptacle in which the fluid is deposited;
   (b) means for suspending the specimen electrode in the fluid, said electrode having a plurality of poles extending downwardly into the fluid;

(c) a corrosive electrolytic injection device having a tubular extremity which extends into the interior of the receptacle;

(d) means for positioning any of the poles of the specimen electrode immediately above the tubular extremity of the injection device;

(e) means for directing a predetermined flow of a corrosive electrolyte through the tubular extremity of the injection device against the peripheral surface of the pole of the electrode positioned thereabove;

(f) a control electrode immersed in the corrosive electrolyte;

(g) a reference electrode immersed in a second electrolyte;

(h) means for establishing electrolytic contact between the reference electrode and the specimen electrode; and

(i) a potentiostat coupled to the specimen, control and reference electrodes.

5. Electrochemical apparatus for studying corrosion of a specimen electrode in an electrically non-conductive fluid, said apparatus comprising:

(a) a receptacle in which the fluid is deposited;

(b) a corrosive electrolytic injection device having a tubular extremity which extends into the interior of the receptacle;

(c) means for suspending the specimen electrode in the fluid above the tubular extremity of the injection device;

(d) means for directing a predetermined flow of a corrosive electrolyte through the tubular extremity of the injection device against the peripheral surface of the specimen electrode;

(e) a control electrode immersed in the corrosive electrolyte;

(f) a capillary tube that extends through the injection device and into its tubular extremity;

(g) a second electrolyte which is supplied to the capillary tube and establishes electrolytic contact with the corrosive electrolyte;

(h) a reference electrode immersed in a second electrolyte; and

(i) a potentiostat coupled to the specimen, control and reference electrodes.

6. Electrochemical apparatus for studying corrosion of a specimen electrode in an electrically non-conductive fluid, said apparatus comprising:

(a) a receptacle in which the fluid is deposited;

(b) means for suspending the specimen electrode in the fluid, said electrode having a plurality of poles extending downwardly into the fluid;

(c) a corrosive electrolytic injection device having a tubular extremity which extends into the interior of the receptacle;

(d) means for positioning any of the poles of the specimen electrode immediately above the tubular extremity of the injection device;

(e) means for directing a predetermined flow of a corrosive electrolyte through the tubular extremity of the injection device against the peripheral surface of the pole of the electrode positioned thereabove;

(f) a control electrode immersed in the corrosive electrolyte;

(g) a capillary tube that extends through the injection device and into its tubular extremity;

(h) a second electrolyte which is supplied to the capillary tube and establishes electrolytic contact with the corrosive electrolyte;

(i) a reference electrode immersed in a second electrolyte;

(j) a potentiostat coupled to the specimen, control and reference electrodes.

References Cited

UNITED STATES PATENTS

2,584,816	2/1952	Sands	204—195
2,585,060	2/1952	Wallace	204—195
3,162,585	12/1964	De Ford et al.	204—195

OTHER REFERENCES

Brennert, "J. of Iron Steel Inst.," vol. 135 (1937), pp. 101P–111P.

Lingane, "Electroanalytical Chemistry," 2nd ed., 1958, pp. 309, 310, 325–327, 329–331 and 339–341.

Posey et al., "J. of the Electrochemical Soc.," December, 1963, pp. 1183–1190.

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