



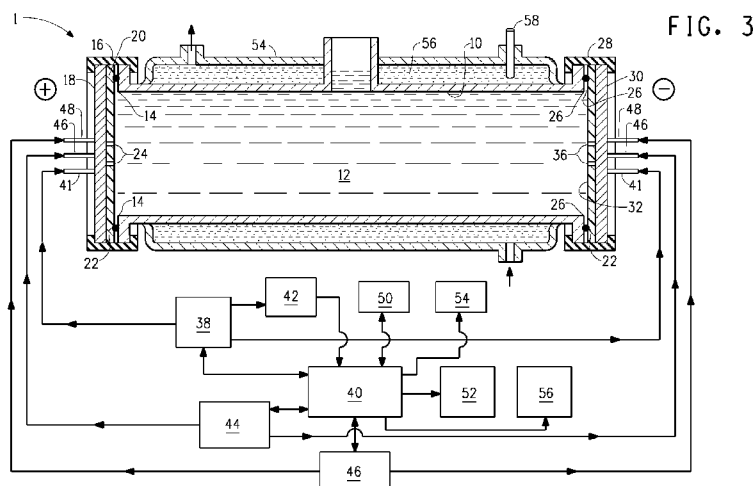
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(54) **Title:** PROCESS FOR EVALUATING CORROSION RESISTANCE OF COATING



(57) **Abstract:** The present invention is directed to a process for corrosion resistance evaluation of coated metals substrates, such as autobodies. An anode and cathode coated with protective coating being tested are exposed to an electrolyte in a chamber of a corrosion resistance evaluator. These coatings are provided with predetermined and standardized defects, such as micro-holes to accelerate the corrosion of the underlying metal substrate in a predictable and repeatable manner. The coated cathode/anode pair is subject to a start-up period followed by series preset DC voltages for preset durations that are interspaced with recovery periods. The impedance data collected are then used to arrive at the corrosion performance resistance of the coating applied over the cathode/anode pair. The foregoing evaluator substantially reduces the time required to test corrosion from several days (40 plus days) to few days (about two days).

WO 2010/078547 A1

Title

**Process for Evaluating Corrosion Resistance of Coating****Field of Invention**

5 [01] This application claims priority from US Provisional Serial Number 61/204159 filed on January 2, 2009 and US Provisional Serial Number 61/289484 filed December 23, 2009, both of which are hereby incorporated herein by reference.

[02] The present invention is directed to a corrosion resistance evaluator suitable for evaluating the corrosion resistance of multi-coated and single coated metal substrates and more particularly directed to a corrosion resistance evaluator and to a  
10 process used therein for evaluating the corrosion resistance of multi-coated and single coated metal substrates at an accelerated rate.

**Background of Invention**

[03] Currently, no short term (less than 2 days) test method exists to evaluate the long-term corrosion protection afforded by a protective coating from a coating  
15 composition, such as automotive OEM or automotive refinish coating compositions, applied over a metal substrate, such as automotive body. The current standard test methods rely primarily on environmental chamber exposure, followed by visual and mechanical testing of the metal with its protective coating. This kind of testing is long (up to 40 days or more exposure time), subjective, highly dependent on the exposure  
20 geometry, and on the person doing the evaluation. Consequently, these methods are not very reproducible. The corrosion resistance data is qualitative, and therefore the relative performance of an acceptable coating cannot be easily determined. Any new test method must correlate well with the traditional, the accepted, standard environmental chamber test methods, must be reproducible, and must supply a  
25 qualitative and quantitative ranking of the unknown direct-to-metal (DTM) corrosion resistant coating.

[04] The experimental corrosion test methods have been reported for reducing the test duration. These methods primarily utilize electrochemical impedance spectroscopy (EIS) or AC impedance technology. Since these AC impedance based  
30 methods typically only offer a more sensitive tool for detecting corrosion at an early stage of exposure time, the corrosion process itself is not accelerated by these methods. Therefore, these methods still require relatively long exposure times before the meaningful data can be obtained. The length of time needed to get meaningful corrosion data approaches that of the standard methods. More  
35 importantly, the corrosion resistance data obtained by these methods, particularly during the initial exposure time, are primarily dictated by the intrinsic defects of the coatings. These intrinsic defects generally produced during the preparation of coated

samples are not necessarily related to the actual performance of the coatings. Misleading information could be obtained if the data are not analyzed correctly. Consequently, the standard convention methods are still favored. Therefore, a need still exists for a device and a process that not only accelerates the corrosion of  
5 protectively coated metal substrates but also mimics the corrosion typically seen in working environments, such as those experienced by bodies of automobiles during use.

### Statement of Invention

The present invention is directed to a process for evaluating corrosion  
10 resistance of an anode coating applied over a surface of an anode and corrosion resistance of a cathode coating applied over a surface of a cathode comprising:

(i) sealably positioning said anode in an anode holder located on a chamber of a corrosion resistance evaluator, said chamber containing an electrolyte therein such that a portion of said anode coating is exposed to said electrolyte, said portion  
15 of said anode coating having an anode defect thereon;

(ii) sealably positioning said cathode in a cathode holder located on said chamber such that a portion of said cathode coating is exposed to said electrolyte, said portion of said cathode coating having a cathode defect thereon;

(iii) directing a computer of said evaluator through computer readable  
20 program code means residing on a usable storage medium located in said computer and configured to cause said computer to perform following steps comprising:

- a) subjecting said portions of said anode coating and said cathode coating to a start-up period;
- b) directing an impedance measurement device in communication with said  
25 computer and is connected to said cathode and said anode to measure n1 set of impedances A during said start-up period at preset intervals, wherein each said set of ac impedances A are measured at preset frequencies ranging from 100000 to  $10^{-6}$  Hz of AC power at desired AC voltages with an amplitude ranging from 10 to 50 mV supplied by an  
30 alternating current variable power generator in communication with said computer, said alternating current variable power generator having AC output leads that connect to said cathode and anode;
- c) determining start-up solution resistances ( $^{Sta}R_{sol,n1}$ ) by selecting a real part of said impedance A at a start-up solution frequency selected from 500 to  
35 100000 Hz from each said set of said impedances A;

- d) determining start-up resistances ( $^{Sta}R_{Sta.n1}$ ) by selecting a real part of impedance A at a start-up frequency selected from  $10^{-1}$  to  $10^{-6}$  Hz from each said set of said impedances A;
- 5 e) directing a direct current variable power generator to apply n2 preset DC voltages in a stepwise manner for n2 preset durations, wherein said direct current variable power generator is in communication with said computer and is connected to said cathode and said anode; and wherein said direct current measurement device in communication with said computer and connected to said cathode and said anode is used to measure said preset
- 10 DC voltages;
- f) directing said impedance measurement device to measure a set of impedances B at the end of each of said preset duration at said preset frequencies of AC power with said amplitude supplied by said alternating current variable power generator to produce n2 said sets of said
- 15 impedances B;
- g) determining stepped-up solution resistances ( $^{Stp}R_{sol.n2}$ ) by selecting a real part of said impedance B at stepped-up solution frequency selected from 500 to 100000 Hz from each said set of said impedances B;
- h) determining stepped-up resistances ( $^{Stp}R_{Stp.n2}$ ) by selecting a real part of
- 20 impedance B at a stepped-up frequency selected from  $10^{-1}$  to  $10^{-6}$  Hz from each said set of said impedances B;
- i) subjecting said portions of said anode coating and said cathode coating to n3 preset recovery periods in between each of said preset durations;
- j) directing said impedance measurement device to measure a set of
- 25 impedances C at the end of each of said preset recovery periods at said preset frequencies of AC power with said amplitude supplied by said alternating current variable power generator to produce n3 said sets of said impedances C;
- k) determining recovery solution resistances ( $^{Rec}R_{sol.n3}$ ) by selecting a real
- 30 part of impedance C at a recovery frequency selected from 500 to 100000 Hz from each said set of said impedances C;
- l) determining recovery resistances ( $^{Rec}R_{Rec.n3}$ ) by selecting a real part of impedance C at recovery frequency selected from  $10^{-1}$  to  $10^{-6}$  Hz from each said set of said impedances C;
- 35 m) calculating corrosion performance resistance ( $R_{perf}$ ) of said anode and said cathode pair by using the following equation:

$R_{\text{perf}} = [\sum \text{Sta}_{f_{n1}} (\text{Sta}R_{\text{Sta.n1}} - \text{Sta}R_{\text{Sol.n1}})]/n1 + [\sum \text{Stp}_{f_{n2}} (\text{Stp}R_{\text{Stp.n2}} - \text{Stp}R_{\text{Sol.n2}})]/n2 + [\sum \text{Rec}_{f_{n3}} (\text{Rec}R_{\text{Rec.n3}} - \text{Rec}R_{\text{Sol.n3}})]/n3$ , wherein  $n1$ ,  $n2$ ,  $n3$  and  $n3$  range from 1 to 100; and  $\text{Sta}_{f_{n1}}$ ,  $\text{Stp}_{f_{n2}}$ , and  $\text{Rec}_{f_{n3}}$  range from 0.0000001 to 1; and

n) causing computer 40 to direct a computer monitor 52 to:

- 5 (n1) display the corrosion performance resistance ( $R_{\text{perf}}$ ),  
 (n2) direct a printer 54 to print the corrosion performance resistance ( $R_{\text{perf}}$ ),  
 (n3) transfer the corrosion performance resistance ( $R_{\text{perf}}$ ) to a remote computer 56 or a remote database, or  
 10 (n4) a combination thereof.

### Brief Description of Drawing

[05] Figure 1 broadly illustrates the process of anodic metal dissolution that occurs at anode.

15 [06] Figure 2 broadly illustrates the process of delamination that occurs at cathode.

[07] Figure 3 illustrates a longitudinal cross-sectional view of one embodiment of the corrosion resistance evaluator of the present invention.

20 [08] Figure 4A, 4B, 4C and 4D represent a flowchart of means for configuring computer readable program code means used in the device of the present invention illustrated in Figure 3.

[09] Figure 5 illustrates one of the typical protocols used in the process of the present invention.

25 [10] Figures 6 and 7 illustrate the deliberately created artificial defects on anode and cathode coatings for exposing the underlying surface of metal anodes and cathodes.

[11] Figure 8 illustrates a plan view of yet another embodiment of the present invention that provides for multiple chambers.

30 [12] Figure 9 illustrates a cross-sectional view of the embodiment of Figure 8 taken along the cross-section 9-9, illustrating the expeditious means for permitting escape of gases generated during the corrosion testing process.

[13] Figure 10 illustrates the Nyquist plot of AC impedance data obtained on E-coat H during start up period.

[14] Figure 11 illustrates the expanded left part of the Nyquist plot of ac impedance data obtained on E-coat H during start up period.

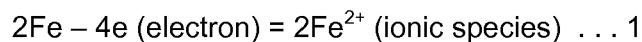
35 [15] Figure 12 illustrates the expanded right part of the Nyquist plot of ac impedance data obtained on E-coat H during start up period

[16] Figure 13 illustrates the correlation and comparison of the results obtained by using the corrosion evaluation process of current invention against those obtained by using a well known conventional cyclic corrosion evaluation test.

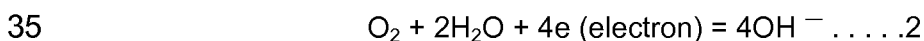
#### Detailed Description of Preferred the Embodiment

5 [17] The evaluation of corrosion resistance of single layer or multilayer protective coatings, such as those resulting from an automotive OEM paint, an automotive  
 10 refinish paint, a marine paint, an aircraft paint, an architectural paint, an industrial paint, a rubberized coating, a polytetrafluoroethylene coating, or a zinc-rich primer, typically applied over metal substrates, such as steel, aluminum and copper, is very important for determining the working life of a product, such as an automobile, a ship or a crane.

[18] When a metal substrate, such as an automobile body, is exposed to atmosphere, its surface is covered by a thin film of water produced by the  
 15 condensation of moisture in air, although it may not be visible due to the extremely low thickness of the film. Many micro electrochemical corrosion cells can develop on the surface of metal substrate underneath the water film due to the non-uniform properties of the metal substrate. Such non-uniformity can result from the differences in chemical composition of the metal, differences in metal microstructure, or due to the differences in mechanical stress of the surface of a metal. Such non-  
 20 uniformity can lead to the formation of electrode potential difference on the surface. It is believed that when the surface of metal is covered by the electrolyte, such as water formed by the condensation of moisture, the locations with a lower electrode potential turn into an anode while the locations with a higher electrode potential turn into a cathode. These anodes and cathodes, covered with the electrolyte, can form  
 25 many micro electrochemical corrosion cells across over the entire surface of metal, which in turn can produce corrosion. A workable corrosion cell is generally composed of three sub-processes – an anodic process, a cathodic process, and an electrolyte pathway to transfer ionic species. The anode process in the corrosion is the metal that loses electrons to form its ionic species and thus can be dissolved into  
 30 the electrolyte as illustrated in the following manner:



[19] When the condition is neutral, the cathode process in the corrosion is the reduction of oxygen which gains the electrons released from the anode in the following manner:



[20] This oxygen, required by the cathode process, generally comes from the oxygen dissolved in the water. In the electrolyte, such as water,  $\text{Fe}^{2+}$  released from

the anode transports towards cathode, and at the same time,  $\text{OH}^-$  produced on the cathode transports toward anode. Eventually, they neutralize each other to keep the electrolyte at a neutral condition. For a workable micro corrosion cell, the anode and cathode process have to occur at the same time. The corrosion stops whenever  
5 either of them is eliminated. For the corrosion of coated systems, a similar corrosion mechanism occurs, but with some special features described below.

**[21]** Due to the coverage of metal surface by coating, it takes a long time for the water to permeate through the coating thickness to approach the interface of coating/metal substrate. Corrosion occurs only when the water approaches the  
10 metal surface, or more specifically, the interface of coating/metal substrate. However, if the coating has defects, such as micro-cracks, corrosion can be initiated immediately inside these defects. As a result, the corrosion data obtained by a conventional AC impedance evaluation method, dictated or distorted by the intrinsic defects of the coating, may not represent the actual true performance of the coating.  
15 As noted by the cathode reaction (in Equation 2 above), the pH of the cathode area is increased significantly when corrosion occurs. For many coating formulations, such an increased pH promotes delamination of coating film from the metal substrate, which is one of the primary coating failure modes.

**[22]** Under working conditions, these micro-anodes and micro-cathodes are  
20 randomly distributed across the entire surface of metal substrate and they are not distinguishable. However, in the device and process of present invention, the anode and cathode are separated so that these anodic and cathodic processes can be controlled and accelerated individually.

**[23]** The preferred embodiment of this invention provide for:

25 **[24]** An AC impedance method suitable for sensitively detecting any change caused by the corrosion of metal substrate under the coating film;

**[25]** A cathode separated from an anode in the device and process allows one to respectively separately control and accelerate the corrosion process occurring on the cathode and anode;

30 **[26]** Artificial defects are provided on the anode and cathode so that the effect of the intrinsic defects can be eliminated.

**[27]** The present invention provides for a device and a process for  
comprehensively evaluating the performance of coatings under various controlled and accelerated conditions. In the start up period, the performance of the coatings is  
35 evaluated under a natural condition. In the stepped-up period, the performance of the coatings is evaluated at an accelerated condition. In this period, the anodic corrosion process at the anode site and the delamination process on the cathode site

are accelerated separately and gradually by means of sequentially stepped DC voltages applied across the cathode and anode. The inhibitive effect at the anode site, and the delamination resistance on the cathode site are evaluated at the same time. In the recovery period, the recovery performances of the coatings are  
5 evaluated after stopping the severe corrosion that occurs when stepped DC voltages are applied across the cathode and anode.

**[28]** Figures 1 and 2 illustrate the typical anodic dissolution process that occurs at an anode (Figure 1) and the delamination processes that occur at a cathode (Figure 2) of the present invention.

10 **[29]** Figure 1 illustrates the anodic end of the device of the present invention of a typical multi-coating system applied over a metal substrate 110, Figure 1 includes a dry conversion coating layer (phosphate layer) 112 typically ranging in thickness from 2 to 50 nanometers applied over a metal substrate 110, followed by a dry layer of an electro-coated primer 114 typically ranging in thickness from 25 to 250 micrometers,  
15 then followed by a dry layer of either a basecoating or a sealer-basecoating combination 116 typically ranging in thickness from 20 to 50 micrometers for the sealer, and 50 micrometers to 120 micrometers for the basecoating (color coating). Typically, basecoating 116 is protected with a dry layer of a clearcoating 118 ranging in thickness from 30 micrometers to 100 micrometers. A standardized defect is  
20 represented by a defect 120 that exposes metal substrate 110 to an electrolyte 122, such as 3% sodium chloride containing dissolved oxygen. If the metal substrate 110 is a cold rolled steel, ferrous ions are released in the electrolyte and over time, the surface of substrate 110 corrodes to form pits 124, rust scales etc. Then the size of defect 120 can increase over time by corrosion, which then separates the multi-  
25 coating from metal substrate 110 and corrodes and damages the underlying surface.

**[30]** Figure 2 illustrates the cathodic end of the device of the present invention. Figure 2 shows a typical multi-coating applied over an automobile metal body 210, which includes a dry layer of a conversion coating 212 applied over metal substrate 210, followed by a dry layer of an electro-coated primer 214 followed by a dry layer of  
30 a basecoating 216 followed by a dry layer of a clearcoating 218, all having thicknesses mentioned in the paragraph above. A standardized defect is represented by a defect 220 that exposes metal substrate 210 to an electrolyte 222, such as 3% sodium chloride containing dissolved oxygen. When cathodic reactions occur, driven by the DC voltages applied, it is believed the pH at the cathode site will  
35 be increased due to the reduction of oxygen, and a higher pH will promote the delamination of the multi-coating from metal substrate 210 thereby further exposing the underlying metal surface. In addition, hydrogen 224 can be produced if the DC

voltage applied is high enough, which can further promote a delamination process 226 (shown in Fig. 2) of the cathode by the mechanical action from evolved hydrogen burbles.

5 [31] Therefore, it is necessary to develop a testing device and process therefor to expeditiously evaluate the corrosion resistance of protective coatings. One embodiment of a corrosion evaluator 1 for the present invention is shown in Figure 3. Evaluator 1 includes a chamber 10, typically made of inert material, such as glass to retain an electrolyte 12 therein. Chamber 10 is preferably cylindrical in shape. Some of typical electrolytes can include an aqueous solution containing sodium chloride at 10 a concentration of 3 parts by weight based on 100 parts by weight of the aqueous solution, or an aqueous solution that simulates acid rain or corrosive chemical solutions, such as those to which typical manufacturing equipment may be exposed. The aqueous solution containing sodium chloride is preferably used.

15 [32] One end of chamber 10 is provided with a flanged opening 14 over which an anode holder 16 can be mounted to retain an anode 18 made from various types of steel, aluminum, and copper. Anode 18 is coated with an anode coating 20 made of a single layer or a multilayer protective coatings resulting from an automotive OEM paint, automotive refinish paint, marine paint, aircraft paint, architectural paint, industrial paint, rubberized coating, polytetrafluoroethylene coating, or zinc-rich 20 primer. One approach to prevent leaking of electrolyte 12 can be to provide an 'O' ring 22 retained in a circular groove on the flange of opening 14, whereby anode holder 16 retains anode 18 against 'O' ring 22. Anode holder 16 can be made of flexible material, such as rubber or it could be a clamp that grips anode 18. Anode coating 20 is provided with an anode defect 24 that exposes the surface of anode 18 25 to electrolyte 12.

[33] At the other end of chamber 10 is provided with a flanged opening 26 over which a cathode holder 28 can be mounted to retain a cathode 30 made from various types of steel, aluminum, and copper. Cathode 30 is coated with a cathode coating 32 made of a single layer or a multilayer protective coatings resulting from an 30 automotive OEM paint, automotive refinish paint, marine paint, aircraft paint, architectural paint, industrial paint, rubberized coating, polytetrafluoroethylene coating, or zinc-rich primer. One approach to prevent leaking of electrolyte 12 can be to provided an 'O' ring 22 retained in a circular groove on the flange of opening 26, whereby cathode holder 28 retains cathode 30 against 'O' ring 22. Cathode holder 35 28 can be made of flexible material, such as rubber or it could be a clamp that grips cathode 30. Cathode coating 32 is provided with a cathode defect 36 that exposes the surface of cathode 30 to electrolyte 12.



[39] It can be shown that the impedance of a resistor is independent of frequency, while the impedance of an inductor is increased as a function of frequency and the impedance of a capacitor is inversely proportional to the frequency. As mentioned above, in most cases, the impedance (Z) of a circuit is usually the combination of three ideal electrical elements and the actual impedance can be described by the following complex function:

$$Z(L, C, R) = Z(L) + Z(C) + Z(R) = R + j(2\pi fL - 1/(2\pi fC)) = \text{real part} + j \text{imaginary part} \dots (6)$$

[40] Evaluator 1 further includes a computer usable storage medium 50 located in computer 40, which is in communication with direct current variable power generator 38, direct current measurement device 42, alternating current variable power generator 44 and impedance measurement device 46, wherein computer readable program code means 400 (described in Figures 4A, 4B, 4C and 4D) reside in said computer usable storage medium 50.

[41] Computer readable program code means 400 include:

[42] means 410 for configuring computer readable program code devices to cause computer 40 to subject said portions of anode coating 20 and cathode coating 32 to a start-up period, which can range from half an hour to one thousand hours, preferably from 3 to 15 hours.

[43] means 412 for configuring computer readable program code devices to cause computer 40 to direct impedance measurement device 46 to measure n1 set of impedances A during the start-up period at preset intervals, wherein each said set of AC impedances A are measured at preset frequencies ranging from 100000 to  $10^{-6}$  Hz, preferably from 10000 to  $10^{-2}$  Hz, of AC power supplied by alternating current variable power generator 44.

[44] means 414 for configuring computer readable program code devices to cause computer 40 to determine start-up solution resistances ( $^{Sta}R_{Sol.n1}$ ) by selecting a real part of said impedance A at a start-up solution frequency selected from 500 to 100000 Hz, preferably from 5000 to 10000 Hz, from each said set of the impedances A.

[45] means 416 for configuring computer readable program code devices to cause computer 40 to determine start-up resistances ( $^{Sta}R_{Sta.n1}$ ) by selecting a real part of impedance A at a start-up frequency selected from  $10^{-1}$  to  $10^{-6}$  Hz, preferably from  $10^{-2}$  to  $10^{-3}$  Hz from each said set of the impedances A.

[46] means 418 for configuring computer readable program code devices to cause computer 40 to direct current variable power generator 38 to apply n2 preset DC voltages in a stepwise manner for n2 preset durations, wherein direct current

measurement device 42 in communication with computer 40 and connected to cathode 30 and anode 18 is used to measure the preset DC voltages; and wherein the foregoing preset duration ranges from half an hour to ten hours, preferably from half an hour to two hours. Typically DC voltages range from half a volt to four volts with half a volt increments.

5

**[47]** means 420 for configuring computer readable program code devices to cause computer 40 to direct impedance measurement device 46 to measure a set of impedances B at the end of each of the preset duration at the preset frequencies of AC power with said amplitude supplied by alternating current variable power

10

generator to produce  $n_2$  said sets of said impedances B.

**[48]** means 422 for configuring computer readable program code devices to cause computer 40 to determine stepped-up solution resistances ( $^{Stp}R_{sol.n2}$ ) by selecting a real part of said impedance B at stepped-up solution frequency selected from 500 to 100000 Hz, preferably from 5000 to 10000 Hz, from each said set of the impedances

15

B.

**[49]** means 424 for configuring computer readable program code devices to cause computer 40 to determine stepped-up resistances ( $^{Stp}R_{Stp.n2}$ ) by selecting a real part of impedance B at a stepped-up frequency selected from  $10^{-1}$  to  $10^{-6}$  Hz, preferably from  $10^{-2}$  to  $10^{-3}$  Hz, from each said set of the impedances B.

20

**[50]** means 426 for configuring computer readable program code devices to cause computer 40 to subject the portions of anode coating 20 and cathode coating 32 to  $n_3$  preset recovery periods in between each of said preset durations wherein said preset recovery periods range from half an hour to ten hours, preferably from 30 minutes to 3 hour.

25

**[51]** means 428 for configuring computer readable program code devices to cause computer 40 to direct impedance measurement device 46 to measure a set of impedances C at the end of each of the preset recovery periods at the preset frequencies of AC power with said amplitude supplied by alternating current variable power generator 44 to produce  $n_3$  said sets of said impedances C.

30

**[52]** means 430 for configuring computer readable program code devices to cause computer 40 to determine recovery solution resistances ( $^{Rec}R_{sol.n3}$ ) by selecting a real part of impedance C at a recovery frequency selected from 500 to 100000 Hz, preferably from 5000 to 10000 Hz, from each said set of the impedances C.

35

**[53]** means 432 for configuring computer readable program code devices to cause computer 40 to determine recovery resistances ( $^{Rec}R_{Rec.n3}$ ) by selecting a real part of impedance C at recovery frequency selected from  $10^{-1}$  to  $10^{-6}$  Hz (preferred ( $10^{-2}$  to  $10^{-3}$  Hz) from each said set of said impedances C.

**[54]** means 434 for configuring computer readable program code devices to cause computer 40 to calculate corrosion performance resistance ( $R_{\text{perf}}$ ) of anode 18 and cathode 30 pair by using the following equation:

$$R_{\text{perf}} = [\sum^{\text{Sta}}_{f_{n1}} (\text{Sta}R_{\text{Sta}.n1} - \text{Sta}R_{\text{Sol}.n1})]/n1 + [\sum^{\text{Stp}}_{f_{n2}} (\text{Stp}R_{\text{Stp}.n2} - \text{Stp}R_{\text{Sol}.n2})]/n2 + [\sum^{\text{Recf}}_{f_{n3}} (\text{Recf}R_{\text{Recf}.n3} - \text{Recf}R_{\text{Sol}.n3})]/n3, \text{ wherein } n1, n2, n3 \text{ and } n3$$

5 range from 1 to 100, preferably  $n1$  ranges from 5 to 15,  $n2$  and  $n3$  range from 3 to 10; and  $\text{Sta}f_{n1}$ ,  $\text{Stp}f_{n2}$ , and  $\text{Recf}f_{n3}$  range from 0.0000001 to 1, preferably range from 0.1 to 1.

Generally,  $n2$  is equal to  $n3$ . By way of clarification, if  $n1$  is 5, then inside  
10 sigma,  $n1$  in the numerator would be 1, 2, 3, 4, and 5 and  $n1$  in the denominator would be 5.

**[55]** means for 436 configuring computer readable program code devices to cause computer 40 to direct a computer monitor 52 to display the corrosion performance resistance ( $R_{\text{perf}}$ ), direct a printer 54 to print the corrosion performance resistance  
15 ( $R_{\text{perf}}$ ), transfer the corrosion performance resistance ( $R_{\text{perf}}$ ) to a remote computer 56 or a remote database, or a combination thereof.

**[56]** Figure 5 illustrates one of the typical protocols used in the process of the present invention. Total time for performing the test can range from 2 hours to 350 hours, preferably 20 hours to 40 hours.

20 **[57]** Preferably, direct current variable power generator 38, direct current measurement device 42, alternating current variable power generator 44 and impedance measurement device 46 can all be positioned in a single stand-alone unit for convenience and ease of operation. Such a unit (Unit B1) was obtained from Solartron Analytical located at Farnborough, Hampshire, United Kingdom.

25 **[58]** In order to eliminate the effect of random intrinsic defects of coatings, applicants made a surprising discovery that by deliberately creating the standardized defects of known sizes and shapes on cathode and anode coatings and exposing the underlying anode/cathode surface to an electrolyte, the anodic dissolution of the underlying anodes and the delamination process of the underlying cathodes can be  
30 substantially accelerated in a predictable and reproducible manner when DC voltage are applied across the cathode and anode. Figure 6 illustrates such deliberately created defects 618, 620, and 622 on anode or cathode coating 612 applied over a cathode or anode 610 that is positioned against chamber 614 having an 'O' ring 616. The most desirable defect is defect 620, although Defect 618 is acceptable since it  
35 does expose the underlying surface of cathode or anode 610 to the electrolyte, whereas defect 622 is unacceptable as it does not expose the underlying surface of cathode or anode 610 to the electrolyte.

**[59]** Preferably, anode or cathode defect, as illustrated in Figure 7 include a plurality of circular openings 712 disposed on coating 710 that expose the underlying surface of the anode or cathode to the electrolyte. Circular openings 712 preferably have a diameter in the range of from 5 micrometers to 3 millimeters, each circular opening 712 being uniformly separated from one another by 10 to 2000 times the diameter of circular openings 712. As a result, corrosion effect illustrated by a zone 714 on one opening 712 does not spill over and affect the corrosion process on an adjacent opening 712A. Alternatively, anode or cathode coating 710 can be provided with 1 to 100 of circular openings 712 per square centimeter of said cathode or anode.

**[60]** Preferably, anode 18 and cathode 30 have identical shape (preferably circular) and thickness. Preferably, anode coating 20 is identical to cathode coating 32 and preferably, anode defect 24 is identical to cathode defect 36. As a result, any deviations between the set of cathode and anode can be eliminated.

**[61]** Evaluator 1 can be provided with a thermal jacket 54 to maintain the temperature of electrolyte 12 at a desired temperature. Typically, a heat transfer fluid 56, such as water can be used to maintain the temperature of electrolyte 12 in the range of 0.5°C to 99.5°C. A conventional temperature probe 58 in communication with computer 40 can be used to maintain the temperature of electrolyte 12 at a desired temperature.

**[62]** Evaluator 1 can be configured to provide two or more chambers whereby all such chambers can be maintained under similar conditions for comparing the corrosion resistance of one set of protective coatings against other, i.e., cathodes having different types of cathode coatings applied thereon can be compared for coating delamination performance (the lesser the delamination the better will be coating corrosion resistance properties). Similarly, anodes paired with corresponding cathodes having identical anode coatings applied thereon can be compared for corrosion resistance of one type of said anode coating to the other type of said anode coating. Preferably, each paired cathode and anode will have identical coating applied thereon. Figure 8 illustrates multi-chamber 800 construction whereby chambers 810 provided with thermometer wells 816 are enclosed within a thermal jacket 812 with outlet 818.

**[63]** Figure 9 shows a cross-section of the embodiment of the present invention of Figure 8 taken along the cross-section 9-9. Embodiment 900 includes anode assembly 910 and cathode assembly 912 forming a leg 914 of an inverted 'Y' ( $\lambda$ ) to permit any gas generated in electrolyte 916 during use or gas bubbles adhered on the surface of coated coupons during installation to escape readily from a cylindrical

chamber 918, which can be provided with a thermal jacket 920 containing heat transfer fluid 922 having an inlet 924 and an outlet 926. Chamber 918 can be further provided with a thermometer well 928 and a support 930.

5 [64] In the alternative, applicants also contemplate another embodiment of the present invention wherein a chamber in the form of inverted 'U' ( $\cap$ ) with the anode and cathode positioned at the bottom of each leg of the inverted 'U' shaped chamber having an opening at the apex of the inverted 'U' shaped chamber to permit any gas generated in the electrolyte during use to escape readily from the chamber.

10 [65] The present invention is also directed to a process that utilizes the evaluator 1 described in Figure 3. The process evaluates the corrosion resistance of anode coating 20 applied over a surface of anode 18 and corrosion resistance of cathode coating 32 applied over a surface of cathode 30 by utilizing the following steps:

15 (i) sealably positioning anode 18 in anode holder 16 located on chamber 10 of corrosion resistance evaluator 1, chamber 10 containing electrolyte 12 therein such that a portion of anode coating 20 is exposed to electrolyte 12, the portion of anode coating 20 having anode defect 24 thereon;

(ii) sealably positioning cathode 30 in cathode holder 28 located on chamber 10 such that a portion of cathode coating 32 is exposed to electrolyte 12, the portion of cathode coating 32 having cathode defect 36 thereon;

20 (iii) directing computer 40 of evaluator 1 through computer readable program code means 400 (shown in Figures 4A, 4B, 4C and 4D) residing on usable storage medium 50 located in computer 40 and configured to cause computer 40 to perform following steps comprising:

25 (a) subjecting the portions of anode coating 20 and cathode coating 30 to a start-up period;

30 (b) directing impedance measurement device 46 in communication with computer 40 and is connected to cathode 30 and said anode 18 to measure  $n_1$  set of impedances A during the start-up period at preset intervals, wherein each said set of impedances A are measured at preset frequencies ranging from 100000 to  $10^{-6}$  Hz of AC power with an amplitude ranging from 10 to 50 mV at desired AC voltages supplied by alternating current variable power generator 44 in communication with computer 40, alternating current variable power generator 44 having AC output leads 46 that connect to cathode 30 and anode 18;

35 (c) determining start-up solution resistances ( $^{Sta}R_{sol,n1}$ ) by selecting a real part of the impedance A at a start-up solution frequency selected from 500 to 100000 Hz from each said set of the impedances A;

- (d) determining start-up resistances ( $^{Sta}R_{Sta.n1}$ ) by selecting a real part of impedance A at a start-up frequency selected from  $10^{-1}$  to  $10^{-6}$  Hz from each said set of said impedances A;
- 5 (e) directing direct current variable power generator 38 to apply n2 preset DC voltages in a stepwise manner for n2 preset durations, wherein direct current variable power generator 38 is in communication with computer 40 and is connected to cathode 30 and anode 18; and wherein direct current measurement device 42 in communication with computer 40 and connected to cathode 30 and anode 18 is used to measure said preset
- 10 DC voltages;
- (f) directing impedance measurement device 46 to measure a set of impedances B at the end of each of said preset duration at said preset frequencies of AC power at said amplitude supplied by alternating current variable power generator 44 to produce n2 said sets of said impedances
- 15 B;
- (g) determining stepped-up solution resistances ( $^{Stp}R_{sol.n2}$ ) by selecting a real part of said impedance B at stepped-up solution frequency selected from 500 to 100000 Hz from each said set of said impedances B;
- (h) determining stepped-up resistances ( $^{Stp}R_{Stp.n2}$ ) by selecting a real part of
- 20 impedance B at a stepped-up frequency selected from  $10^{-1}$  to  $10^{-6}$  Hz from each said set of said impedances B;
- (i) subjecting said portions of anode coating 20 and cathode coating 32 to n3 preset recovery periods in between each of said preset durations;
- (j) directing impedance measurement device 46 to measure a set of
- 25 impedances C at the end of each of said preset recovery periods at said preset frequencies of AC power at said amplitude supplied by alternating current variable power generator 44 to produce n3 said sets of said impedances C;
- (k) determining recovery solution resistances ( $^{Rec}R_{sol.n3}$ ) by selecting a real
- 30 part of impedance C at a recovery frequency selected from 500 to 100000 Hz from each said set of said impedances C;
- (l) determining recovery resistances ( $^{Rec}R_{Rec.n3}$ ) by selecting a real part of impedance C at recovery frequency selected from  $10^{-1}$  to  $10^{-6}$  Hz from each said set of said impedances C;
- 35 (m) calculating corrosion performance resistance ( $R_{perf}$ ) of said anode and said cathode pair by using the following equation:

$$R_{\text{perf}} = \left[ \sum \text{Sta}_{f_{n1}} (\text{Sta}R_{\text{Sta}.n1} - \text{Sta}R_{\text{Sol}.n1}) \right] / n1 + \left[ \sum \text{Stp}_{f_{n2}} (\text{Stp}R_{\text{Stp}.n2} - \text{Stp}R_{\text{Sol}.n2}) \right] / n2 + \left[ \sum \text{Rec}_{f_{n3}} (\text{Rec}R_{\text{Rec}.n3} - \text{Rec}R_{\text{Sol}.n3}) \right] / n3$$
, wherein  $n1$ ,  $n2$ ,  $n3$  and  $n3$  range from 1 to 100; and  $\text{Sta}_{f_{n1}}$ ,  $\text{Stp}_{f_{n2}}$ , and  $\text{Rec}_{f_{n3}}$  range from 0.0000001 to 1; and  
 (n) causing computer 40 to direct a computer monitor 52 to:

- 5 (n1) display the corrosion performance resistance ( $R_{\text{perf}}$ ),  
 (n2) direct a printer 54 to print the corrosion performance resistance ( $R_{\text{perf}}$ ),  
 (n3) transfer the corrosion performance resistance ( $R_{\text{perf}}$ ) to a remote computer 56 or a remote database, or  
 10 (n4) a combination thereof.

**[66]** The process of the present invention can be used comparing the corrosion resistance of one type of coating against another type of coating by testing them under similar conditions and protocol by utilizing multiple chambers such as those shown in Figure 8. Cathodes having different types of cathode coatings applied thereon and said anodes having different types of anode coatings applied thereon can be compared to evaluate delamination resistance of one type of cathode coating to the other type of cathode coating. It should be understood that each set of paired cathode and anode would have identical coating applied thereon. Simultaneously, anodes having different types of anode coatings applied thereon can be compared to evaluate corrosion resistance of one type of anode coating to the other type of anode coating.

### Examples

#### Comparative corrosion data from conventional corrosion test method:

**[67]** The correlation between a conventional 40-day cyclic corrosion test and the corrosion test of the present invention was performed by using eight conventional E-coat systems. To vary the corrosion performance, eight E-coating systems designated as coating A, B, C, D, F, G, H and I comprising different phosphate pretreatments, different formulations, different baking temperatures and baking times were applied on test panels made of cold rolled steel. All the test panels were identical in size, shape and thickness. A coated test panel was defined as a coupon. After coating was applied and cured, each coupon was scribed with grid pattern. The conventional 40-day cyclic corrosion test used in the correlation verification utilized 40 cycles of the corrosion test. Each cycle lasting 24 hours included the first 8 hour of electrolyte spray exposure comprising repeated sequences consisting of half hour exposure to electrolyte spray followed by one and half hours of a rest period. The electrolyte used was a mixture of 0.9% NaCl, 0.1%  $\text{CaCl}_2$  and 0.25%  $\text{NaHCO}_3$ , all in weight percentage based on the total weight. The foregoing eight hour electrolyte

spray exposure was followed by 8.0 hour humidity exposure at 50°C and 100% RH and then 8.0 hour exposure at 60 °C in oven. Duplicate coupons for each of the E-coating systems were used in the test. Each coupon after the aforescribed conventional corrosion test was subjected to creep test using a conventional creep measurement device and the creep in millimeters was reported. The creep data were then transferred into the corrosion resistance by using the following equation:

$$\text{Equivalent corrosion resistance (ohm)} = B/\text{Creep} = 300000/\text{Creep}$$

wherein B is a transformation factor in ohm/mm, which can be affected by the kind of metal substrate used and the aggressiveness of the corrosion testing method. The data transformation was necessary for the purpose of comparison since the data obtained by the corrosion resistance evaluator of the present invention were in the form of corrosion resistance.

**Corrosion data from the corrosion test method of the present invention:**

[68] Eight E-coating systems designated as coating A, B, C, D, F, G, H and I were applied on coupons and cured. On the coated surfaces of such coupons, six holes with a diameter of 300 microns were drilled to provide standardized anode and cathode defect, respectively. Each of the holes penetrated through the thickness of the coating and stopped at the interface of metal/ coating. Standardized anode and cathode defects were identical.

[69] The corrosion test evaluator was based on a 26 hour test protocol that included 5 sets of AC impedance measurements during 12 hours of start-up period (DC Volts = 0), followed by four preset durations, each duration lasting two hours at stepped voltages starting from 0.5 Volts, followed by 1 Volt, 2 Volts, and 3 Volts. One set of AC impedance measurement was performed at the end of each preset duration. A 1.5 hour of recovery period was used in between each preset duration. One set of AC impedance measurement was made at the end of each recovery period. The corrosion performance resistance of the coating was calculated by using the following equation:

$$R_{\text{perf}} = \left[ \sum^{Staf_{n1}} (StaR_{Sta.n1} - StaR_{Sol.n1})/n1 + \left[ \sum^{Stpf_{n2}} (StpR_{Stp.n2} - StpR_{Sol.n2})/n2 + \left[ \sum^{Recf_{n3}} (RecR_{Rec.n3} - RecR_{Sol.n3})/n3 \right] \right] \right]$$

wherein n1 is 5, n2 is 4, and n3 is 4 and  $Sta_{f_{n1}}$ ,  $Stp_{f_{n2}}$ , and  $Rec_{f_{n3}}$  are all equal to 1.

[70] The foregoing  $StaR_{Sta.n1}$ ,  $StpR_{Stp.n2}$ , and  $RecR_{Rec.n3}$  were determined by the real part of the ac impedance at  $10^{-2}$  Hz from each of the respective ac impedance measurements obtained in the respective periods.  $StaR_{Sol.n1}$ ,  $StpR_{Sol.n2}$ , and  $RecR_{Sol.n3}$  were determined by the real part of the ac impedance at 100000 Hz from each of the respective ac impedance measurements obtained in the respective periods. The

following provides further explanation of various element used in measuring the foregoing elements:

[71] A typical ac impedance data (for coating H) obtained by the method of this invention can be described in Fig 10. The impedance data was obtained using a  
5 frequency scan from 100000 Hz to  $10^{-2}$  Hz. This plot is called Nyquist plot with a minus imaginary part as Y axis and a real part as X axis. The shortcoming of this plot is that the frequency is not explicitly expressed in the plot. Since the impedance, as noted earlier, is frequency dependent, the impedance is changed when the frequency is changed. By the impedance data at various frequencies (normally from  
10 100000 Hz to  $10^{-2}$  Hz), the resistance component and capacitance component can be separated and obtained respectively. For example, on the far left hand of Figure 10 which is expanded as Figure 11, a solution resistance in the start up period,  $^{Sta}R_{Sol.2}$ , can be obtained by selecting the real part of the impedance at 100000 Hz. On the far right hand of Figure 10, which is expanded as Figure 12, a start up resistance  $^{Sta}R_{Sta.2}$   
15 can be obtained by selecting the real part of the impedance at  $10^{-2}$  Hz. The value of ( $^{Sta}R_{Sta.2} - ^{Sta}R_{Sol.2}$ ) is also showed in Figure 10, which can be used to calculate the corrosion resistance of the coating tested.

[72] The corrosion resistance data obtained by the corrosion evaluator of the present invention and a conventional cyclic corrosion test is shown in Figure 13.  
20 From Figure 13, one can readily observe that there was substantial correlation between the convention carrion test method and the corrosion test method of the present invention. The correlation coefficient of these two methods can be calculated by using the conventional definition of Pearson product-moment correlation coefficient. The Pearson product-moment correlation coefficient is a well-known  
25 correlation coefficient indicating the strength and direction of a linear relationship between two random variables. The correlation coefficient of these two methods was 74%, which is very high compared to the correlation coefficient between any other two conventional coating evaluation methods, which is less than 55%. Therefore, the accelerated corrosion resistance evaluator correlates very well with the conventional  
30 corrosion test method.

[73] The discrepancy observed in the coating evaluation tests is primarily due to the difficulty in preparing the coated samples with the exactly same quality and the subjective nature of the evaluation methods used in the conventional corrosion tests.

[74] The discrepancy observed on E-coating G can be explained in the following  
35 manner:

[75] For the same E coating formulation, the pretreatments should be ranked from the best to the poorest as Zn phosphate > iron phosphate > none. This ranking is

well known based on the prior experience and the knowledge of corrosion science. It was shown from Figure 13 that both methods can correctly identify this ranking (compare coating A, B, and C in one group and compare coating F, G, and H in the second group). Also from Figure 13 and Table 1 below, it can be seen that most of the data showed that for the same pretreatment, E-coating 2 performs better than E-coating 1 (compare coating F to coating A, coating G to coating B, coating H to coating C, and coating I to coating D). The corrosion evaluation method of the present invention identified such a trend with 100% accuracy while the conventional cyclic corrosion methods identify this trend with only one exception of coating G. Therefore, it is highly likely that the data of the coating G obtained by the method of the present invention is more accurate and more trustable.

**Table 1**

E-coated coupons for the correlation test

Label	Pretreatment	E-coating	Bake Time and Temperature
A	None	E-coating 1	10 minutes at 360°F
B	Iron phosphate	E-coating 1	10 minutes at 360°F
C	Zn phosphate	E-coating 1	10 minutes at 360°F
D	Zn phosphate	E-coating 1	18 minutes at 310°F
E	None	E-coating 2	10 minutes at 360°F
G	Iron phosphate	E-coating 2	10 minutes at 360°F
H	Zn phosphate	E-coating 2	10 minutes at 360°F
I	Zn phosphate	E-coating 2	18 minutes at 310°F

### Claims

What is claimed is:

1. A process for evaluating corrosion resistance of an anode coating applied over a surface of an anode and corrosion resistance of a cathode coating applied over a surface of a cathode comprising:
  - (i) sealably positioning said anode in an anode holder located on a chamber of a corrosion resistance evaluator, said chamber containing an electrolyte therein such that a portion of said anode coating is exposed to said electrolyte, said portion of said anode coating having an anode defect thereon;
  - (ii) sealably positioning said cathode in a cathode holder located on said chamber such that a portion of said cathode coating is exposed to said electrolyte, said portion of said cathode coating having a cathode defect thereon;
  - (iii) directing a computer of said evaluator through computer readable program code means residing on a usable storage medium located in said computer and configured to cause said computer to perform following steps comprising:
    - a) subjecting said portions of said anode coating and said cathode coating to a start-up period;
    - b) directing an impedance measurement device in communication with said computer and is connected to said cathode and said anode to measure n1 set of impedances A during said start-up period at preset intervals, wherein each said set of ac impedances A are measured at preset frequencies ranging from 100000 to  $10^{-6}$  Hz of AC power at desired AC voltages with an amplitude ranging from 10 to 50 mV supplied by an alternating current variable power generator in communication with said computer, said alternating current variable power generator having AC output leads that connect to said cathode and anode;
    - c) determining start-up solution resistances ( $^{Sta}R_{sol,n1}$ ) by selecting a real part of said impedance A at a start-up solution frequency selected from 500 to 100000 Hz from each said set of said impedances A;
    - d) determining start-up resistances ( $^{Sta}R_{Sta,n1}$ ) by selecting a real part of impedance A at a start-up frequency selected from  $10^{-1}$  to  $10^{-6}$  Hz from each said set of said impedances A;
    - e) directing a direct current variable power generator to apply n2 preset DC voltages in a stepwise manner for n2 preset durations, wherein said direct current variable power generator is in communication with said computer and is connected to said cathode and said anode; and wherein said direct current measurement device in communication with said computer and

connected to said cathode and said anode is used to measure said preset DC voltages;

f) directing said impedance measurement device to measure a set of impedances B at the end of each of said preset duration at said preset frequencies of AC power with said amplitude supplied by said alternating current variable power generator to produce n2 said sets of said impedances B;

g) determining stepped-up solution resistances ( $^{Stp}R_{Sol.n2}$ ) by selecting a real part of said impedance B at stepped-up solution frequency selected from 500 to 100000 Hz from each said set of said impedances B;

h) determining stepped-up resistances ( $^{Stp}R_{Stp.n2}$ ) by selecting a real part of impedance B at a stepped-up frequency selected from  $10^{-1}$  to  $10^{-6}$  Hz from each said set of said impedances B;

i) subjecting said portions of said anode coating and said cathode coating to n3 preset recovery periods in between each of said preset durations;

j) directing said impedance measurement device to measure a set of impedances C at the end of each of said preset recovery periods at said preset frequencies of AC power with said amplitude supplied by said alternating current variable power generator to produce n3 said sets of said impedances C;

k) determining recovery solution resistances ( $^{Rec}R_{Sol.n3}$ ) by selecting a real part of impedance C at a recovery frequency selected from 500 to 100000 Hz from each said set of said impedances C;

l) determining recovery resistances ( $^{Rec}R_{Rec.n3}$ ) by selecting a real part of impedance C at recovery frequency selected from  $10^{-1}$  to  $10^{-6}$  Hz from each said set of said impedances C;

m) calculating corrosion performance resistance ( $R_{perf}$ ) of said anode and said cathode pair by using the following equation:

$$R_{per} = [ \sum^{Sta} f_{n1} (^{Sta}R_{Sta.n1} - ^{Sta}R_{Sol.n1}) ] / n1 + [ \sum^{Stp} f_{n2} ( ^{Stp}R_{Stp.n2} - ^{Stp}R_{Sol.n2} ) ] / n2 + [ \sum^{Rec} f_{n3} ( ^{Rec}R_{Rec.n3} - ^{Rec}R_{Sol.n3} ) ] / n3, \text{ wherein } n1, n2, n3 \text{ and } n3 \text{ range from } 1 \text{ to } 100; \text{ and } ^{Sta}f_{n1}, ^{Stp}f_{n2}, \text{ and } ^{Rec}f_{n3} \text{ range from } 0.0000001 \text{ to } 1; \text{ and}$$

n) causing computer 40 to direct a computer monitor 52 to:

(n1) display the corrosion performance resistance ( $R_{perf}$ ),

(n2) direct a printer 54 to print the corrosion performance resistance ( $R_{perf}$ ),

(n3) transfer the corrosion performance resistance ( $R_{perf}$ ) to a remote computer 56 or a remote database, or

(n4) a combination thereof.

2. The process of claim 1 wherein said cathode and said anode are made of steel.

3. The process of claim 1 wherein said anode coating and said cathode  
5 coating results from a multilayer coating composition comprising an automotive OEM paint, an automotive refinish paint, a marine paint, an aircraft paint, an architectural paint, an industrial paint, a rubberized coating, a polytetrafluoroethylene coating, or a zinc-rich primer.

4. The process of claim 1 wherein said chamber is surrounded by a thermal  
10 jacket to maintain temperature of said electrolyte at a desired temperature ranging from 0.5°C to 99.5°C.

5. The process of claim 1 wherein two or more of said chambers are surrounded by a thermal jacket to maintain temperature of said electrolyte in each of said chambers at a desired temperature ranging from 0.5°C to 99.5°C.

6. The process of claim 1 wherein said anode coating is identical to said  
15 cathode coating.

7. The process of claim 1 or 6 wherein said anode defect is identical to said cathode defect.

8. The process of claim 1 or 6 wherein said anode defect comprises a  
20 plurality of circular openings disposed on said coating that expose said underlying surface of said anode to said electrolyte.

9. The process of claim 1 or 6 wherein said cathode defect comprises a plurality of circular openings disposed on said coating that expose said underlying surface of said cathode to said electrolyte.

10. The process of claim 9 wherein said cathode or anode defect comprises  
25 circular openings each having a diameter in the range of from 5 micrometers to 3 millimeters, each said circular opening being uniformly separated from one another by 10 to 1000 times the diameter of said circular openings.

11. The process of claim 10 wherein said cathode or anode defect comprises  
30 in the range of from 1 to 100 of said circular openings per square centimeter of said cathode or anode, said circular opening being uniformly separated from one another, and wherein said circular opening has a diameter in the range of from 5 micrometers to 3 millimeters.

12. The process of claim 1 wherein said electrolyte comprises:

35 (a) an aqueous solution containing sodium chloride at a concentration of 3 parts by weight based on 100 parts by weight of said aqueous solution,

(b) an aqueous solution that simulates acid rain, or

(c) a corrosive chemical solution.

13. The process of claim 1 wherein said anode holder and said cathode holder each form a leg of an inverted 'Y' to permit any gas generated during use to escape readily from said chamber.

5 14. The process of claim 1 wherein said anode holder and said cathode holder are positioned at the opposite ends of said chamber to permit any gas generated during use to escape readily from said chamber.

15. The process of claim 1 wherein said start-up period ranges from half an hour to one thousand hours.

10 16. The process of claim 1 wherein said preset interval ranges from half an hour to ten hours.

15 17. The process of claim 5 wherein said cathodes have different types of cathode coatings applied thereon and said anodes have different types of anode coatings applied thereon for comparing delamination of one type of said cathode coating to the other type of said cathode coating, and to compare corrosion resistance of one type of said anode coating to the other type of said anode coating.

18. The process of claim 17 wherein in each said chamber said cathode coating and said anode coating is the same.

20 19. The process of claim 18 wherein thickness of said cathode coating and said anode coating in each of said chambers is the same.

1/14

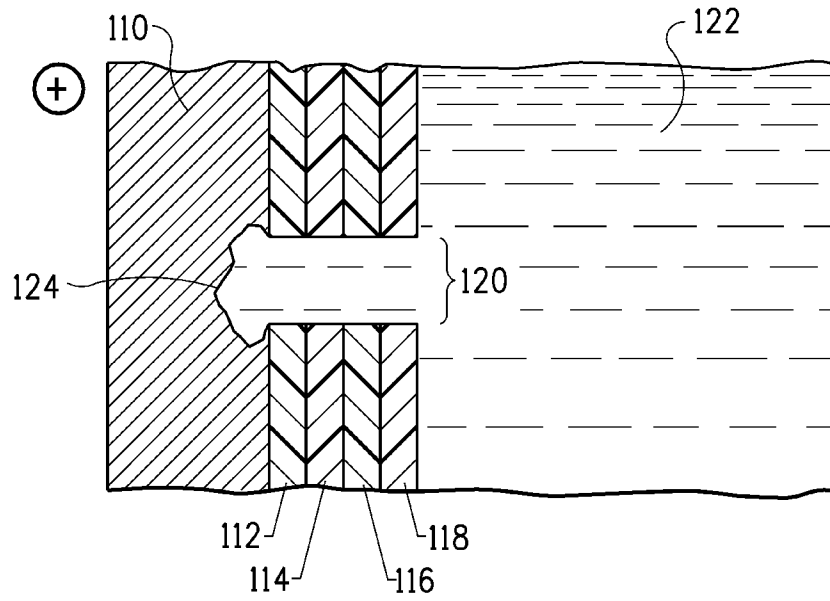


FIG. 1

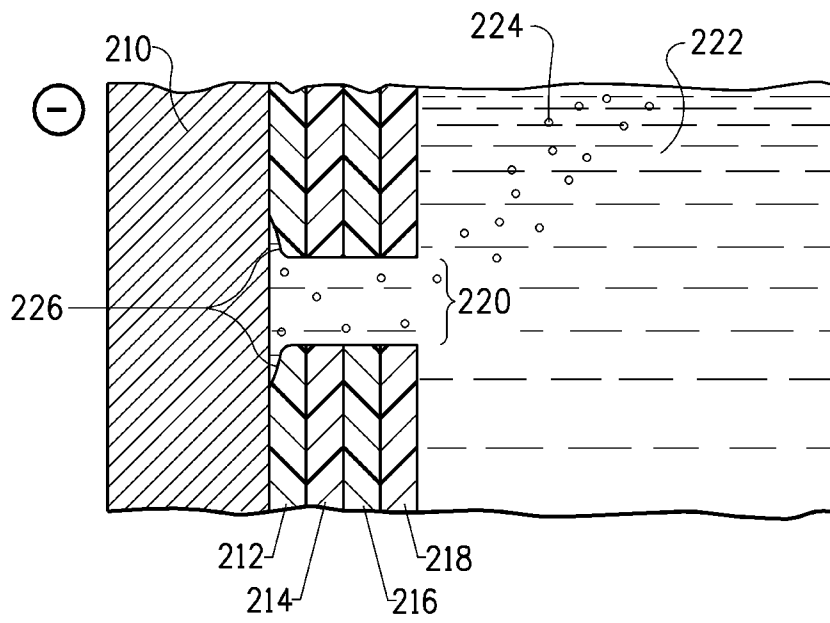
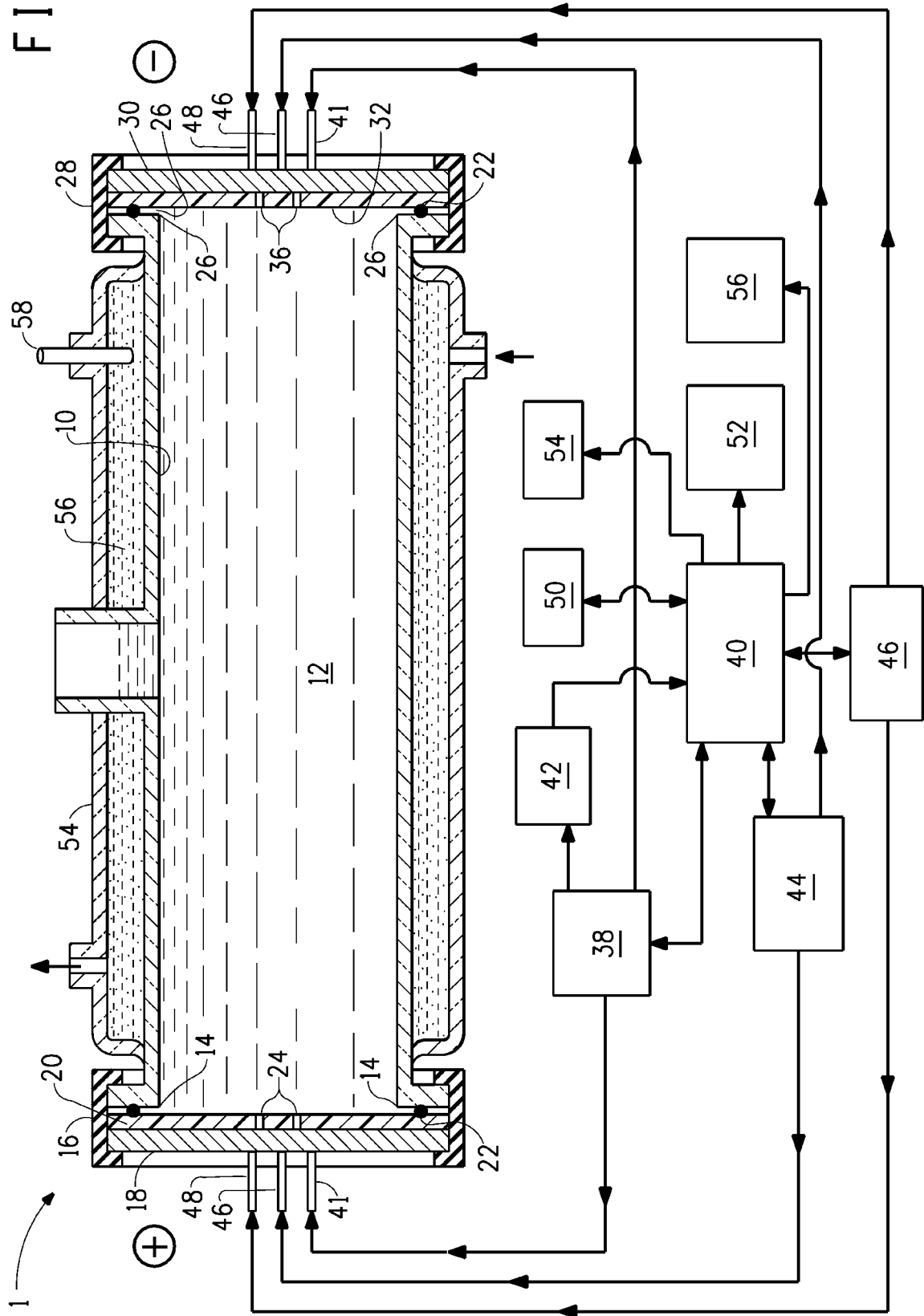


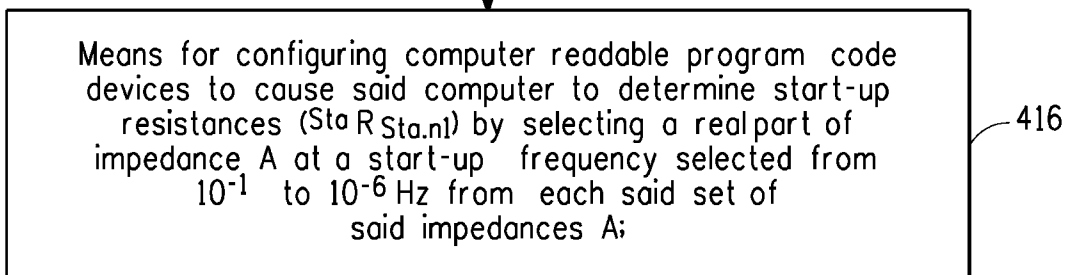
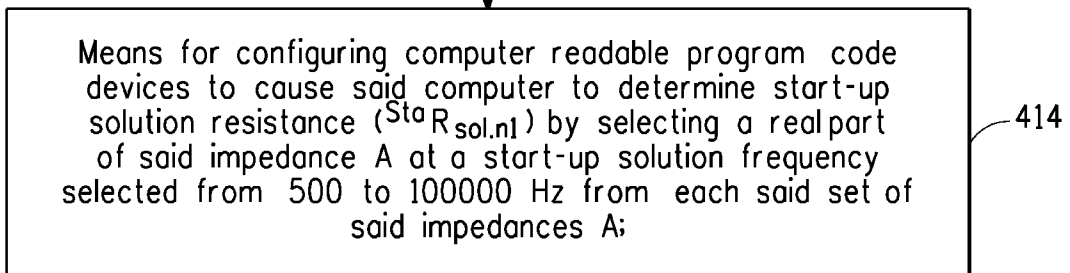
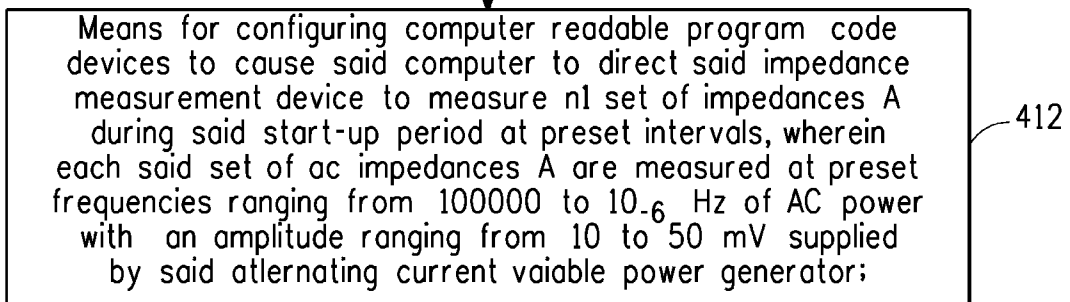
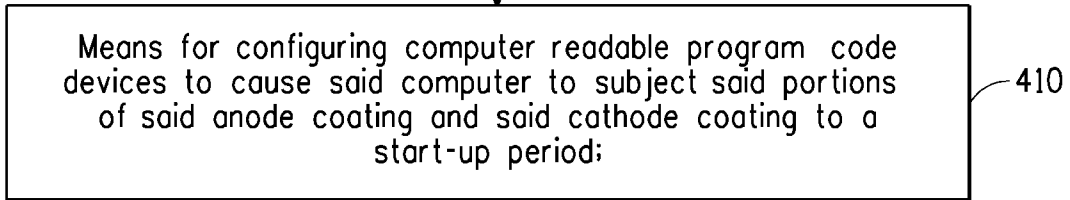
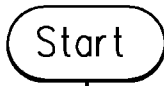
FIG. 2

FIG. 3



3/14

400

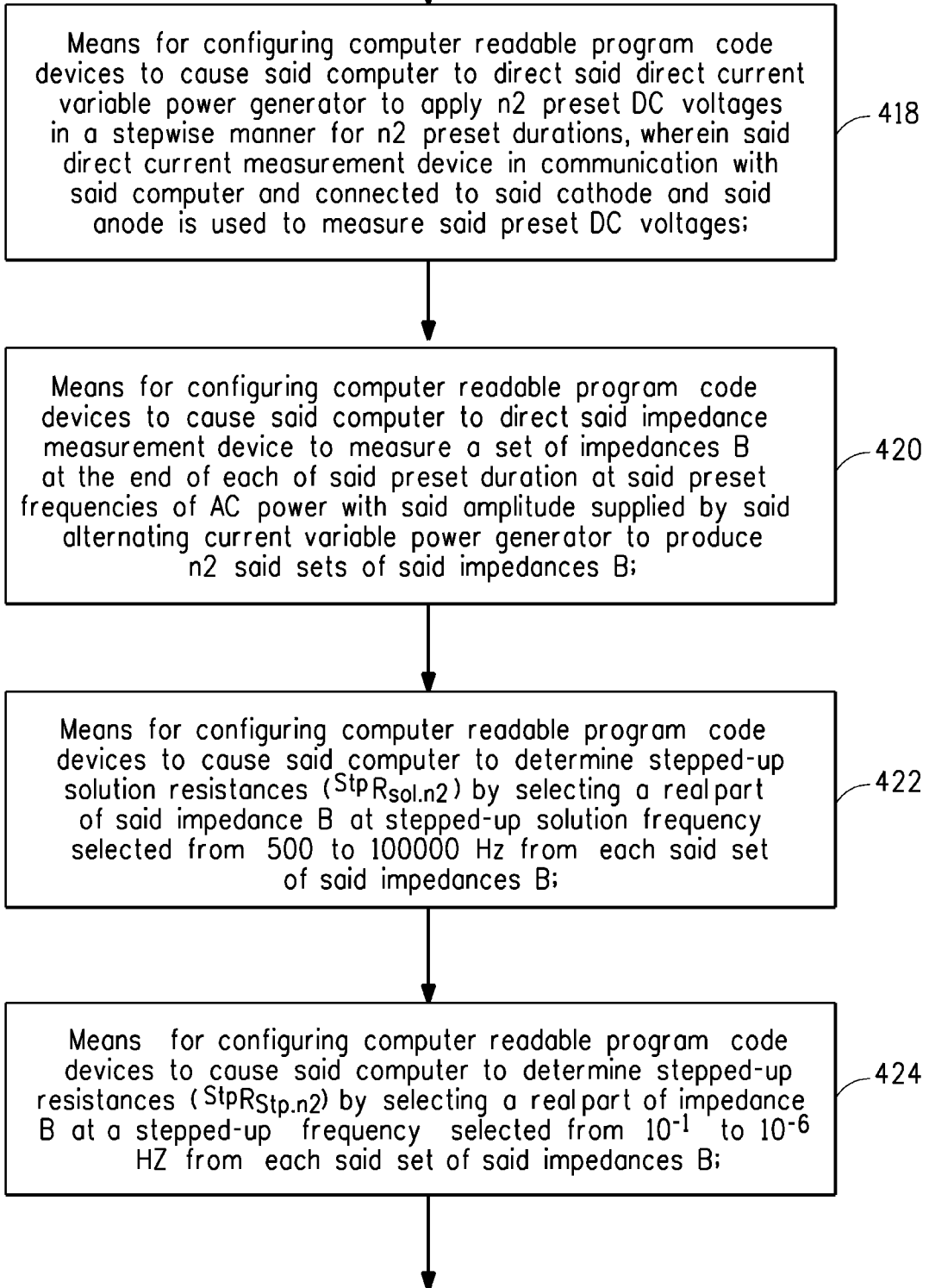


Continued on Fig. 4B

FIG. 4A

4/14

Continued from Fig. 4A

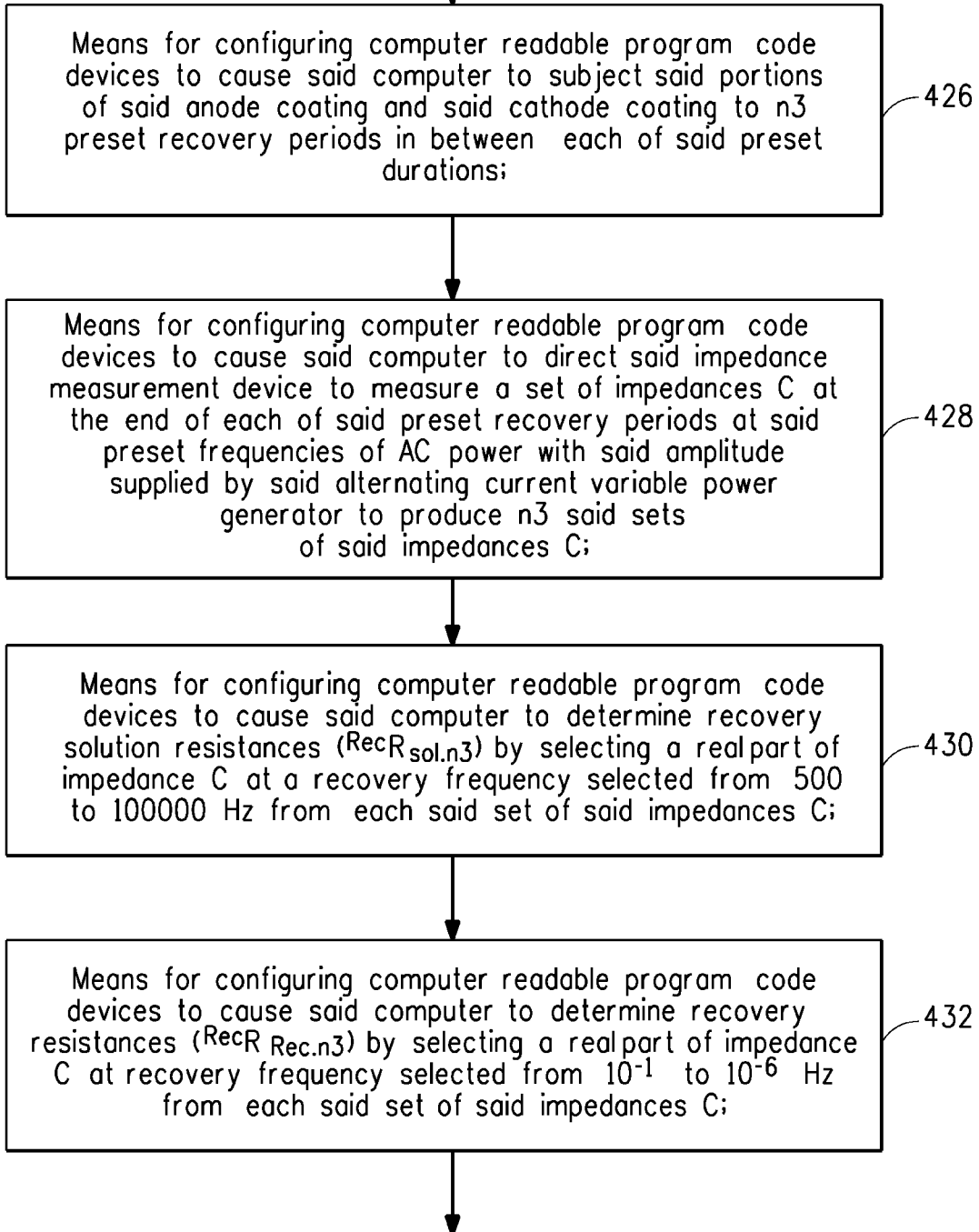


Continued on Fig. 4C

FIG. 4B

5/14

Continued from Fig. 4B



Continued on Fig. 4D

FIG. 4C

Continued from Fig. 4C

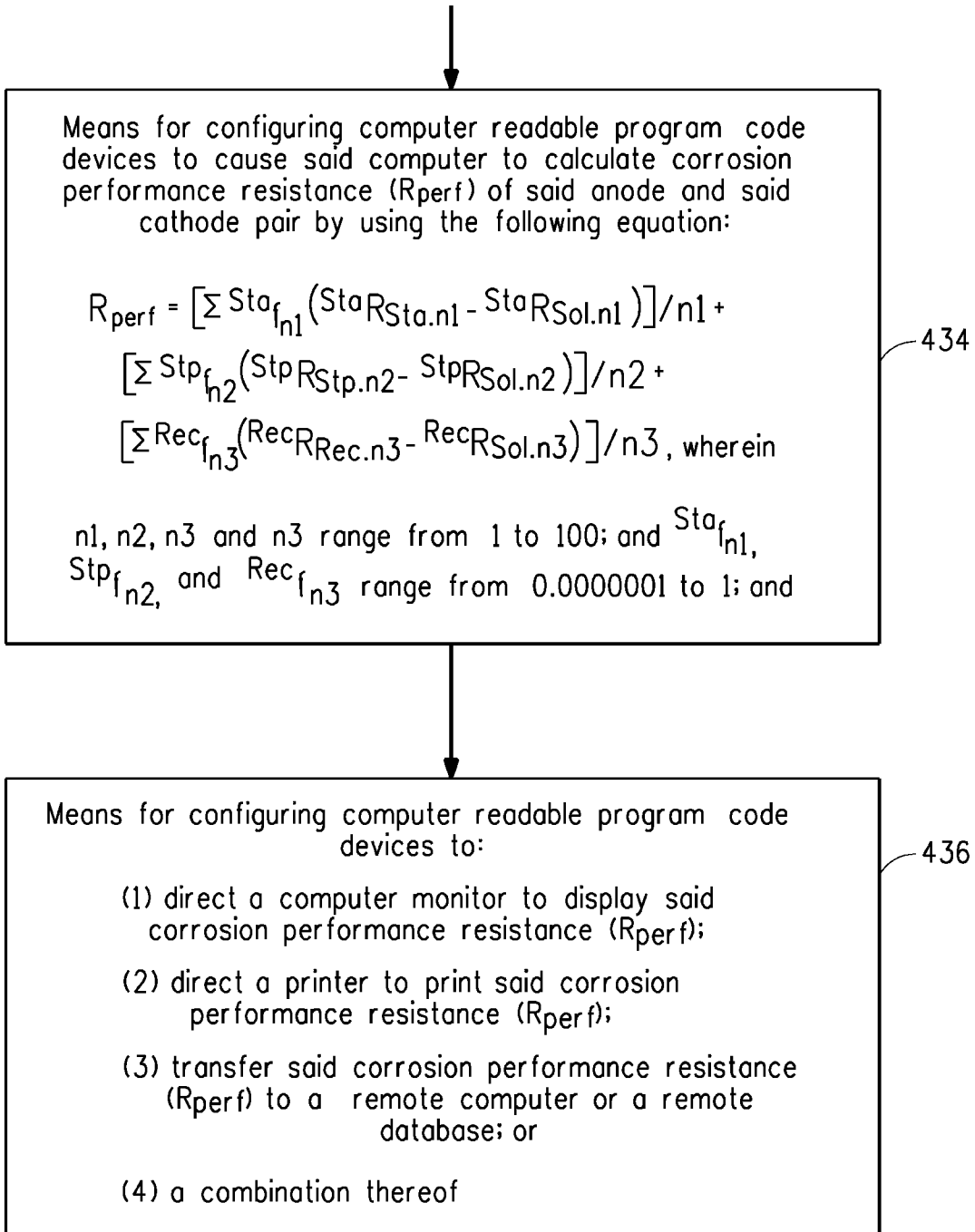


FIG. 4D

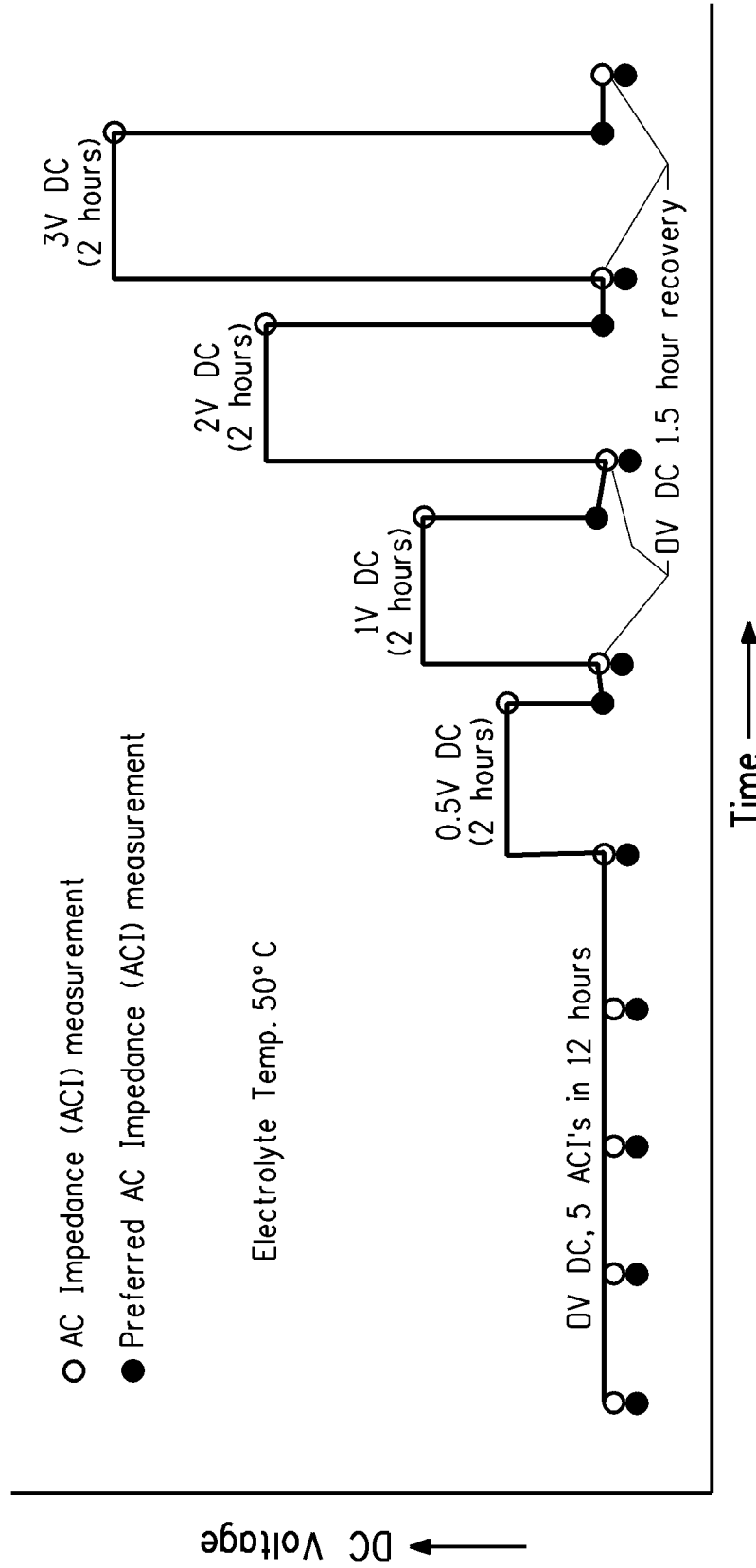


FIG. 5

8/14

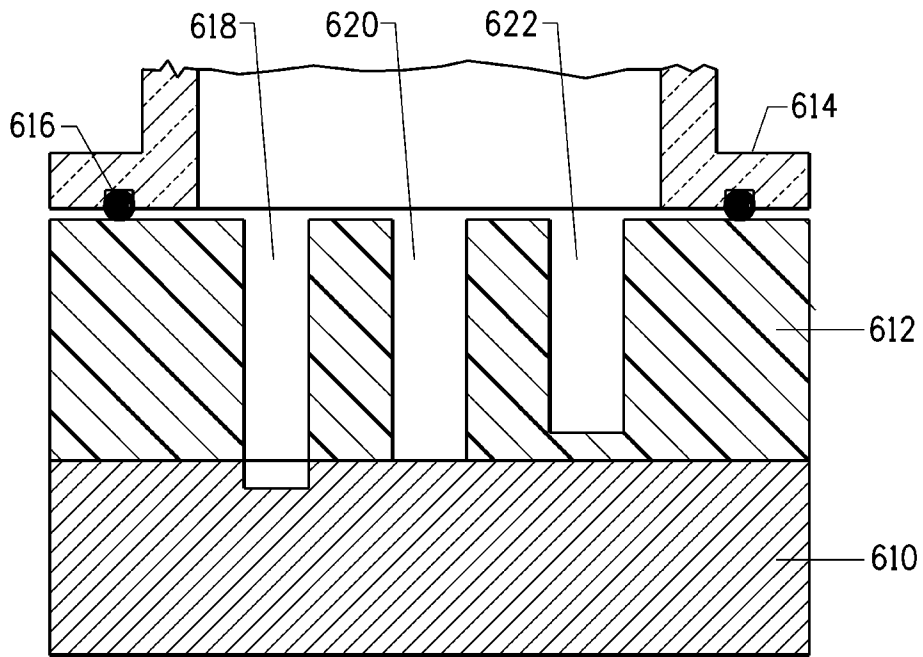


FIG. 6

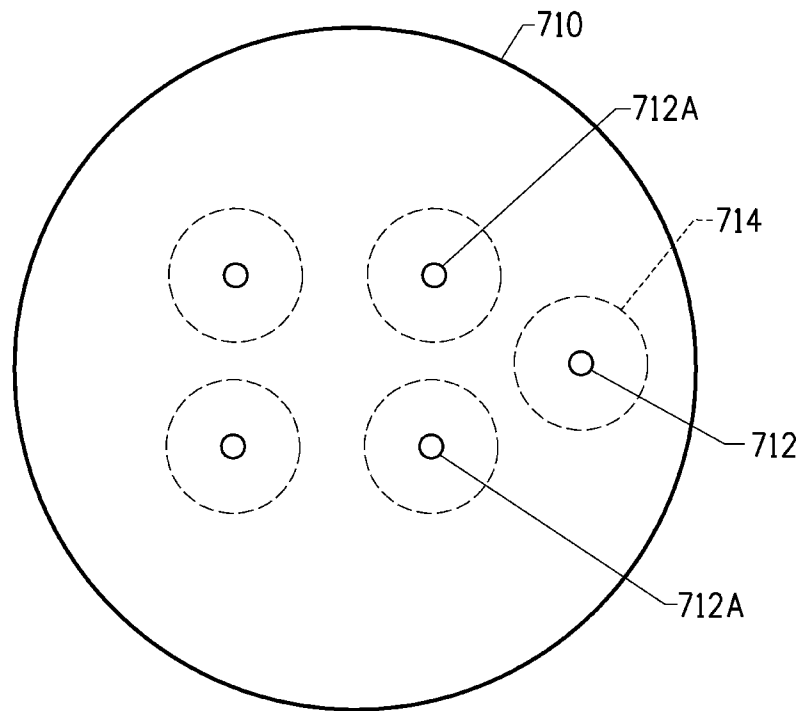


FIG. 7

9/14

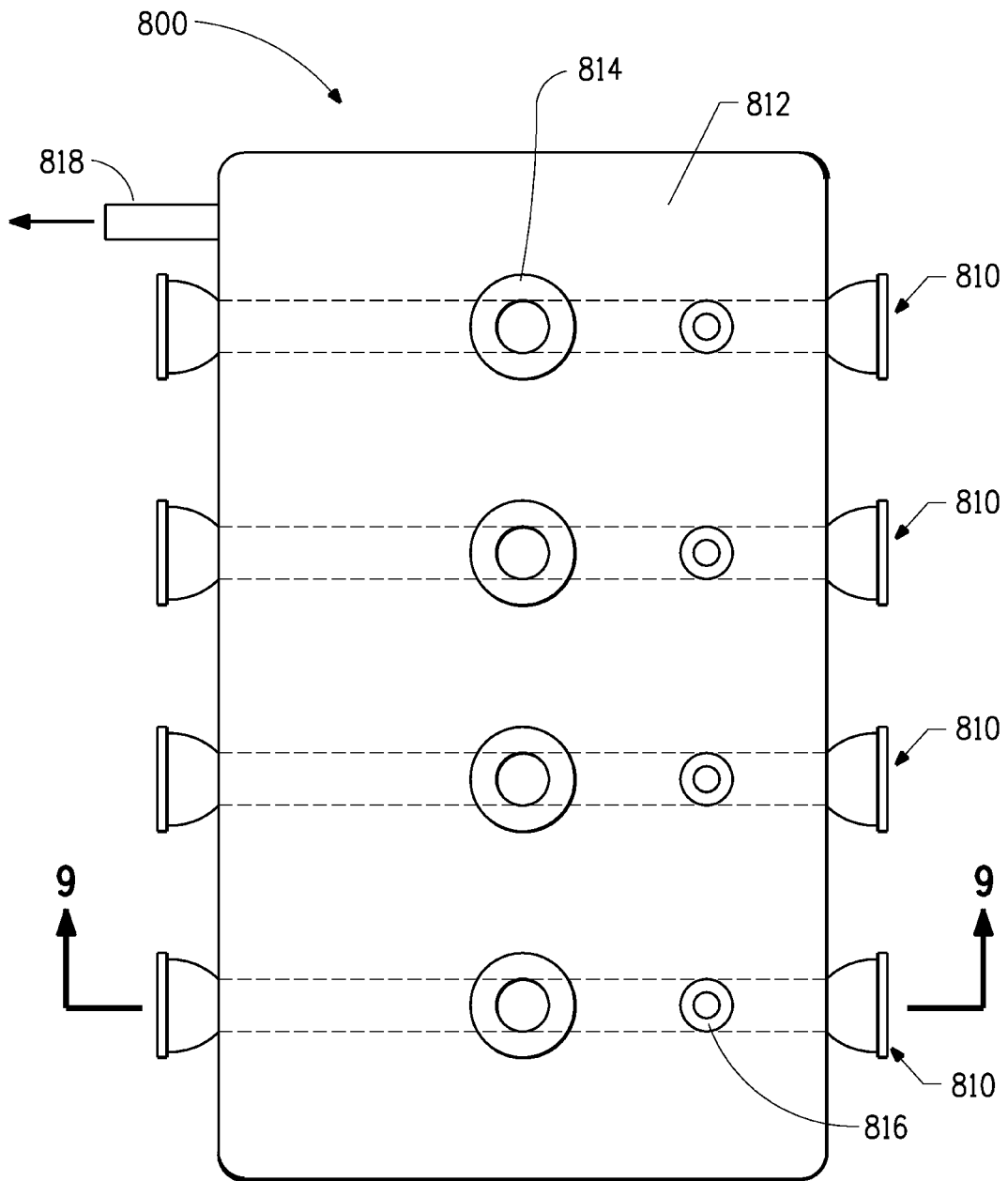


FIG. 8

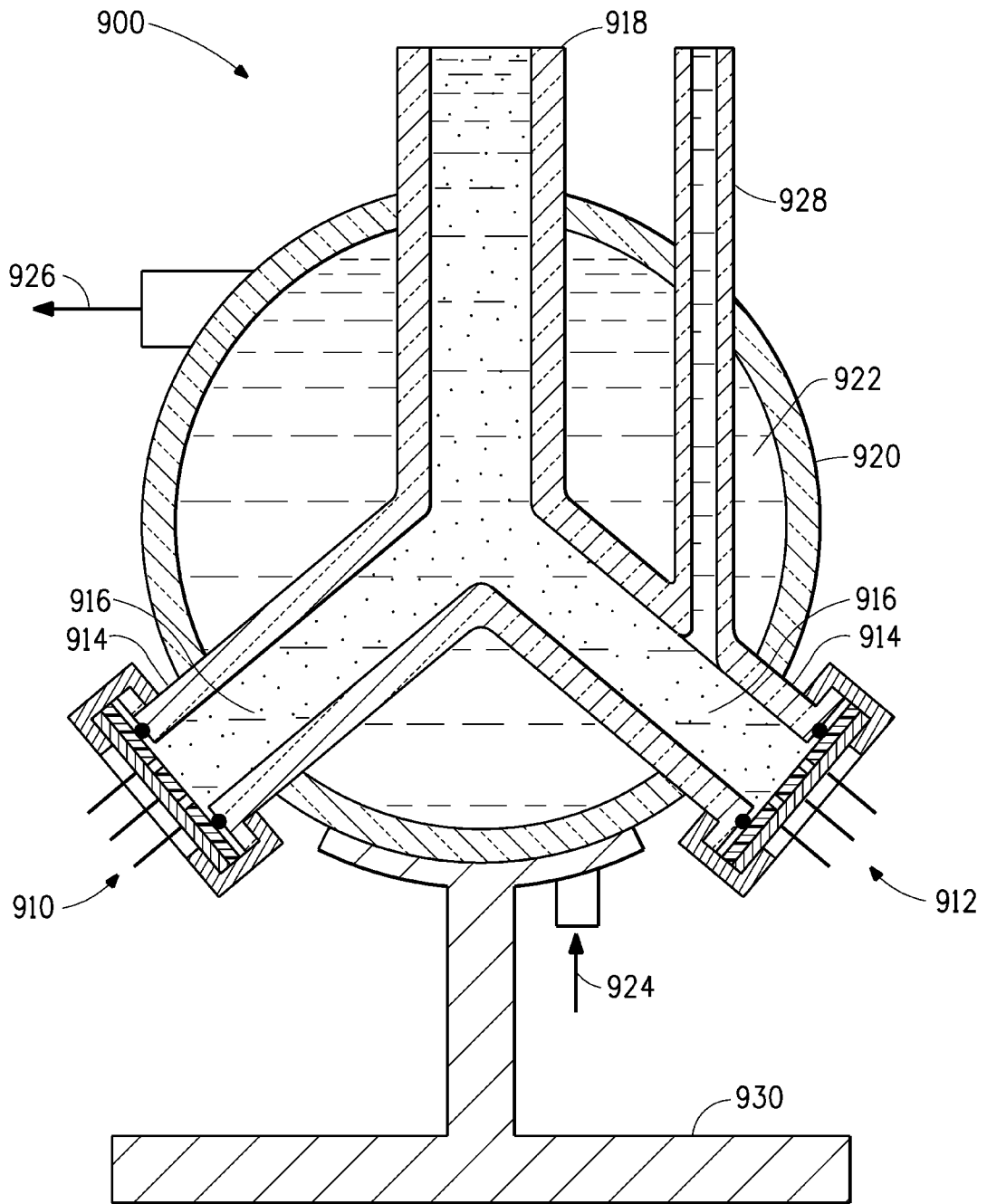


FIG. 9

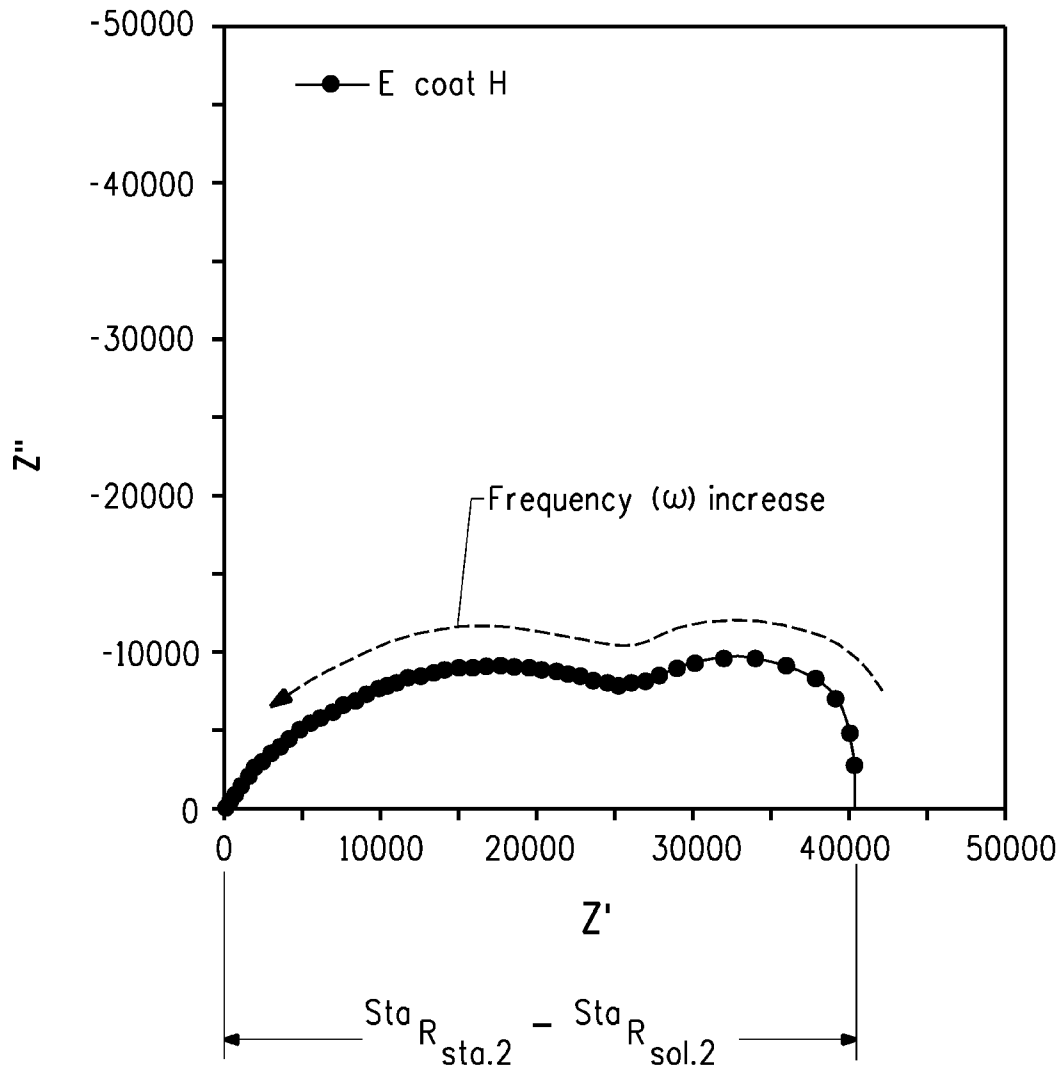


FIG. 10

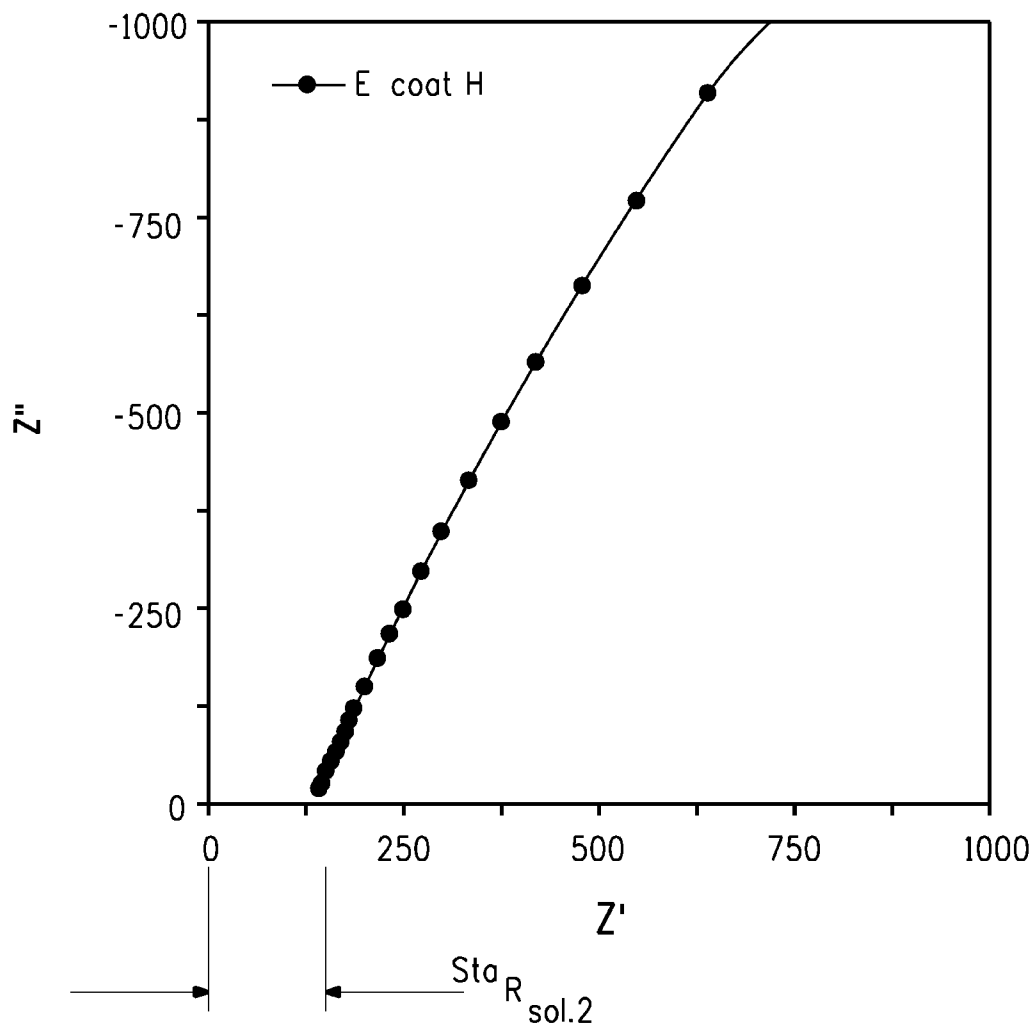


FIG. 11

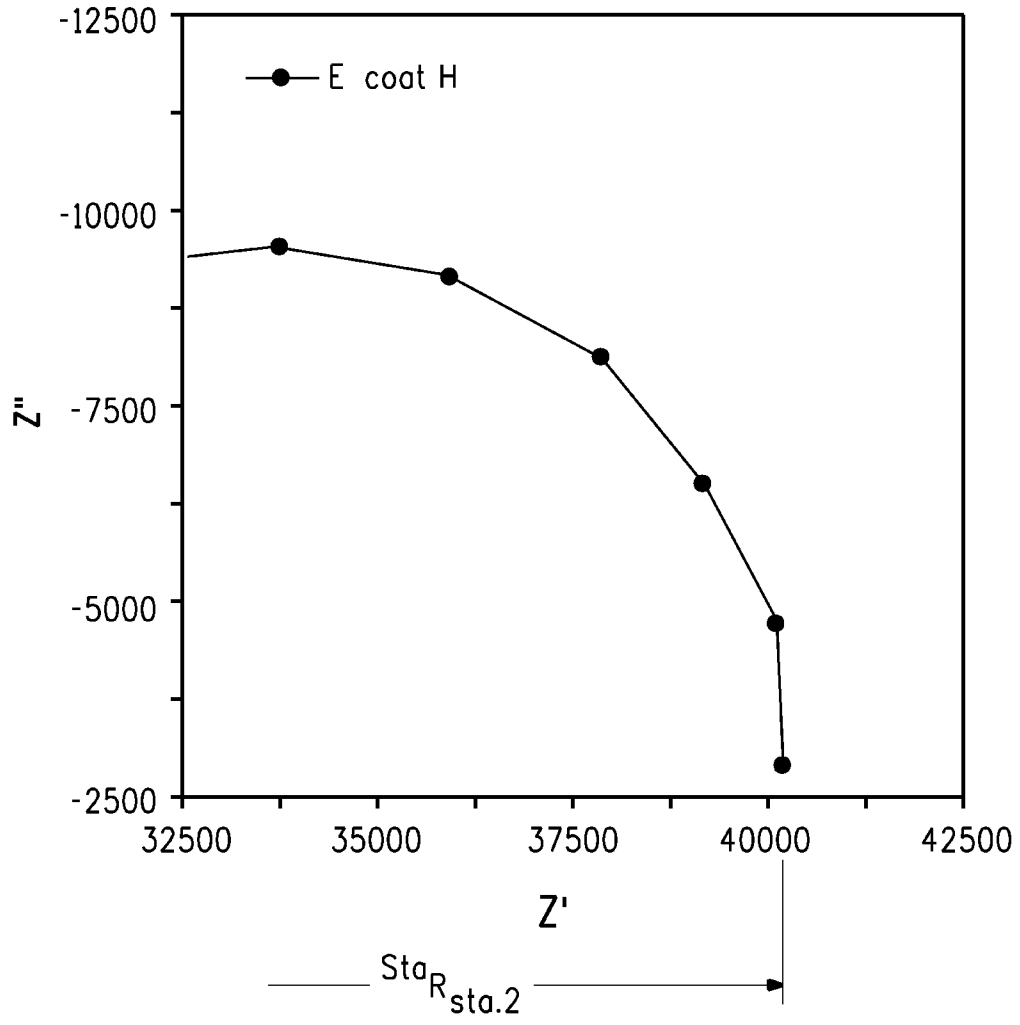


FIG. 12

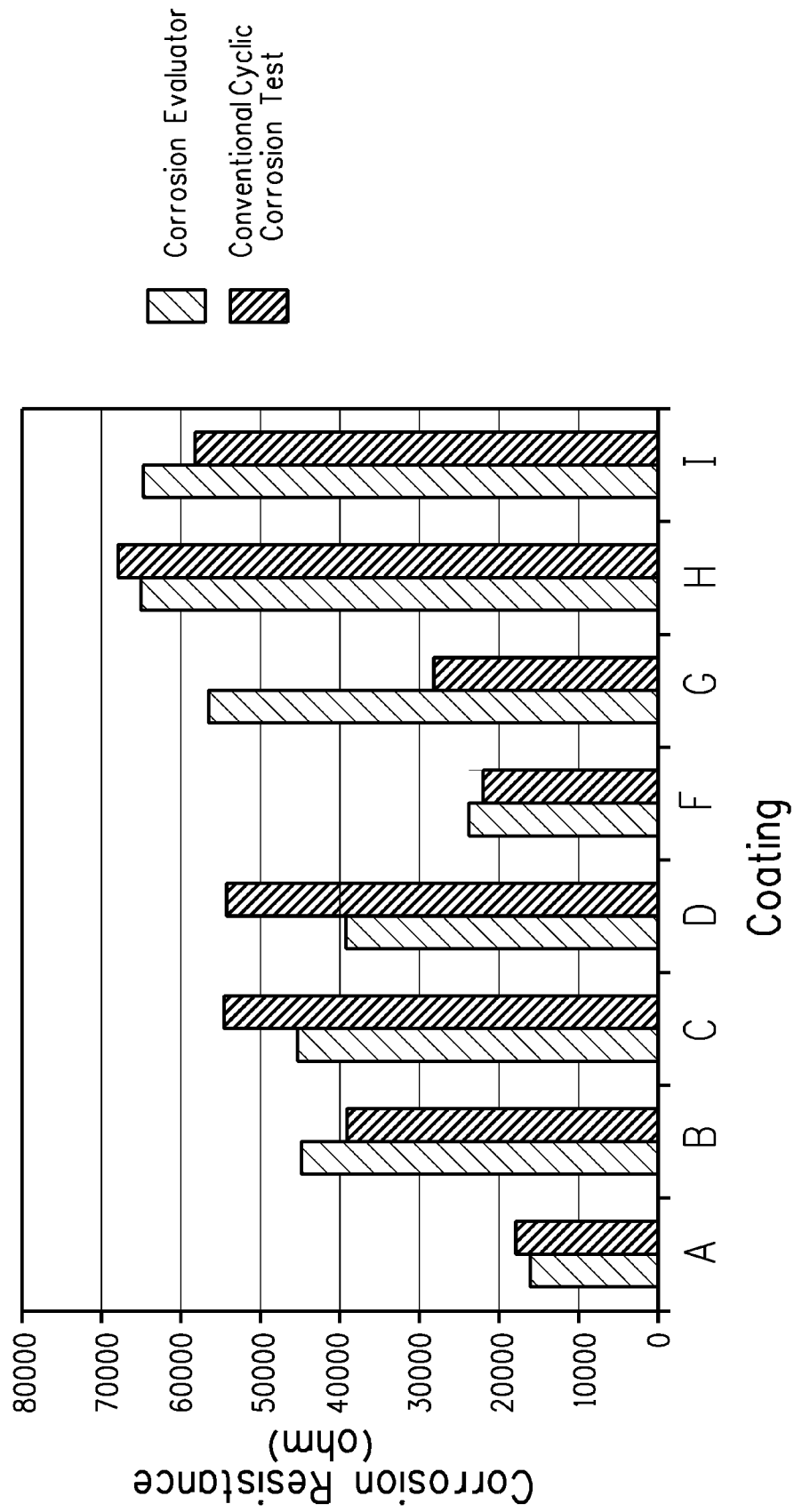


FIG. 13

**A. CLASSIFICATION OF SUBJECT MATTER***G01N 17/00(2006.01)i, G01N 17/02(2006.01)i, G01N 27/26(2006.01)i*

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

G01N 17/00; C23F 1/00; G01N 17/02; G01N 27/26; G01N 3/30; G01N 31/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models  
Japanese utility models and applications for utility models  
(Chinese Patents and application for patent)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) &amp; Keywords: "corrosion resistance", "coating", "evaluate"

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 60-088358 A (NIPPON PAINT CO., LTD.) 18 May 1985 See claim 1; figure 2.	1-19
A	JP 2007-178238 A (UNIV. OF FUKUI) 12 July 2007 See abstract, figure 1.	1-19
A	EP 0760473 A1 (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.) 05 March 1997 See abstract; column 10, line 18 - line 43.	1-19
A	US 2006-0217895 A1 (IWAWAKI, HIROHITO) 28 September 2006 See abstract; paragraph [0016] - paragraph [0035].	1-19
A	EP 0693680 A2 (HITACHI, LTD.) 24 January 1996 See abstract; claims 1-3.	1-19
A	EP 0591802 A2 (HITACHI, LTD.) 13 April 1994 See column 18, line 46 - column 19, line 7.	1-19
A	JP 2008-261813 A (NIPPON STEEL CORP.) 30 October 2008 See abstract.	1-19

 Further documents are listed in the continuation of Box C. See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family


Date of the actual completion of the international search

28 APRIL 2010 (28.04.2010)

Date of mailing of the international search report

**29 APRIL 2010 (29.04.2010)**

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2010/020029**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 60-088358 A	18.05.1985	JP 1653374 C JP 60-088358 A	30.03.1992 18.05.1985
JP 2007-178238 A	12.07.2007	JP 2007-178238 A	12.07.2007
EP 0760473 A1	05.03.1997	DE 69630493 D1 DE 69630493 T2 EP 0760473 B1 JP 03-340317 B2 JP 09-304325 A JP 3340317 B2 KR 10-1997-0013166 A US 5820746 A1	04.12.2003 06.05.2004 29.10.2003 16.08.2002 28.11.1997 05.11.2002 29.03.1997 13.10.1998
US 2006-0217895 A1	28.09.2006	JP 2006-266955 A US 7585677 B2	05.10.2006 08.09.2009
EP 0693680 A2	24.01.1996	EP 0693680 A3 JP 02-938758 B2 JP 08-021793 A JP 2938758 B2 US 5901071 A1	15.07.1998 11.06.1999 23.01.1996 25.08.1999 04.05.1999
EP 0591802 A2	13.04.1994	EP 0591802 A3 JP 03-061707 B2 JP 06-201635 A JP 3061707 B2 US 5519330 A1	08.06.1994 28.04.2000 22.07.1994 10.07.2000 21.05.1996
JP 2008-261813 A	30.10.2008	JP 2008-261813 A	30.10.2008