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METHOD AND TEST CHAMBER FOR ACCELERATED AGING OF  
MATERIALS AND BONDS SUBJECT TO CORROSION RELATED  
DEGRADATION

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT (1) JOHN R. WELCH, (2) THOMAS S. RAMOTOWSKI AND (3) GERALD J. ROCHE, employees of the United States Government, citizens of the United States of America, and residents of (1) Bourne, County of Barnstable, Commonwealth of Massachusetts, (2) Tiverton, ~~County of~~ Newport, State of Rhode Island and (3) Freetown, County of Bristol, Commonwealth of Massachusetts, has invented certain new and useful improvements entitled as set forth above of which the following is a specification:

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1 Attorney Docket No. 84989

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3 METHOD AND TEST CHAMBER FOR ACCELERATED AGING OF MATERIALS AND  
4 BONDS SUBJECT TO CORROSION RELATED DEGRADATION

5

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

10

11 CROSS REFERENCE TO OTHER RELATED APPLICATIONS

12 Not applicable.

13

14 BACKGROUND OF THE INVENTION

15 (1) Field of the Invention

16 The present invention relates to the testing of polymer to  
17 metal bonds, and more specifically to a method and apparatus for  
18 demonstrating the durability of polymer to metal bonds in a  
19 cathodic environment by subjecting samples to accelerated  
20 cathode reactions that cause cathodic delamination.

21 (2) Description of the Prior Art

22 Polymer to metal bonds are increasingly used in vessels and  
23 devices designed for use in marine environments. It is vital  
24 that these bonds maintain their integrity while exposed to

1 saltwater. Of particular concern is the problem of cathodic  
2 delamination, which occurs when the metal hull of a marine  
3 vehicle is protected from corrosion by using a "sacrificial"  
4 anode system. In a situation where the anode is made of zinc,  
5 the reaction is  $2\text{Zn} \rightarrow 2\text{Zn}^{+2} + 4\text{e}^{-}$ . The cathodic reaction is  $\text{O}_2 +$   
6  $2\text{H}_2\text{O} + 4\text{e}^{-} \rightarrow 4(\text{OH})^{-}$ . Over a period of several months and years,  
7 the hydroxide ions  $(\text{OH})^{-}$  become highly concentrated at the  
8 cathode, creating a high alkalinity water environment  
9 destructive to polymer to metal bonds. In fact, cathodic  
10 delamination is the most commonly encountered failure for  
11 polymer to metal bonds in the marine environment.

12 In order to anticipate which polymer to metal bonds are  
13 most resistant to cathodic delamination, it is necessary to test  
14 the bonds in artificially created marine conditions. One prior  
15 art testing method and apparatus places the polymer to metal  
16 bond samples inside an open container filled with synthetic  
17 ocean water, and drill holes in the unbonded portion of the  
18 metal in order to suspend the samples from an electrically  
19 conductive rod. The water is heated using a stainless steel  
20 immersion heater. Any evaporated water is replaced with water  
21 of an approximate conductivity to the electrolyte contained in  
22 the open vessel. The emphasis on this testing method and  
23 apparatus is on water temperature based on the theory that the  
24 diffusion of water controls the degradation rate of polymers and

1 adhesives and therefore elevated temperatures will increase the  
2 rate of water permeation through the polymer thereby  
3 artificially accelerating the "aging" of the polymer to metal  
4 bond. There is no attention to dissolved oxygen or conductivity  
5 in this testing method.

6 Water, however, is not the only reactant that can affect  
7 the degradation rate of a bond. Cathodic delamination will not  
8 proceed if there is no dissolved oxygen in the water or if there  
9 are no electrons supplied to the cathode. In light of this,  
10 other prior art testing method and apparatus use a bubbling  
11 system in an attempt to maintain the dissolved oxygen in water  
12 at elevated temperatures. Such a system, however, is limited to  
13 maintaining the dissolved oxygen level that is physically  
14 allowable at the particular elevated water temperature.

15 There is currently no method and test apparatus to  
16 artificially accelerate the effect of cathodic delamination on  
17 polymer to metal bonds that also maintains the levels of  
18 dissolved oxygen in water and the levels of electrical current  
19 that would be encountered in the normal course by marine  
20 vehicles when the metal hull of the marine vehicle is protected  
21 from corrosion by using a "sacrificial" anode system. What is  
22 needed is a method and test apparatus that subjects different  
23 polymer to metal bonds to artificially accelerated cathodic  
24 delamination under typical marine conditions.



1 into the test chamber to maintain appropriate levels of  
2 dissolved oxygen in the heated synthetic ocean water.

3

4 BRIEF DESCRIPTION OF THE DRAWINGS

5 A more complete understanding of the invention and many of  
6 the attendant advantages thereto will be readily appreciated as  
7 the same becomes better understood by reference to the following  
8 detailed description when considered in conjunction with the  
9 accompanying drawings wherein:

10 FIG. 1 shows the test chamber where polymer to metal bond  
11 samples are placed;

12 FIG. 2 shows a diagram of the impressed current system in  
13 the test chamber.

14

15 DESCRIPTION OF THE PREFERRED EMBODIMENT

16 Referring now to FIG. 1 there is shown multiple bonding  
17 samples 10. The samples 10 are composed of a polymer bonded to  
18 a metal substrate. In the preferred embodiment, all of the  
19 samples are of the same dimensions. The samples 10 are placed  
20 inside a closed vessel that serves as the test chamber 12. In  
21 the preferred embodiment, the test chamber 12 is made of inert  
22 materials such as polypropylene, and nylon. The test chamber 12  
23 is partially filled with a fluid designed to approximate certain  
24 properties of natural ocean water as closely as possible

1 particularly with regard to salinity, and conductivity at  
2 various temperatures and pressures. For example, natural ocean  
3 water has an average salinity of 35 ppt at 15°C, 1 atm, and 43  
4 mS/cm. In the preferred embodiment, synthetic ocean water 14 is  
5 used to approximate natural ocean water, however the invention  
6 is not to be limited by the use of one particular fluid.

7 The synthetic ocean water 14 is heated using an external  
8 band heater 16. By increasing the temperature of the synthetic  
9 ocean water 14 in the test chamber 12 the effect of exposure on  
10 the bonding samples 10 is artificially accelerated. A  
11 thermometer 18 is used to monitor the water temperature.

12 The metal substrate of each polymer to metal bond sample 10  
13 is cathodically protected using an impressed current system as  
14 illustrated in FIG 2. The impressed current system includes a  
15 voltmeter 26 and current meter 28 joined to a power supply 30.  
16 A stainless steel plate is used as the anode 32. The power  
17 supply 30 removes the electrons from the steel anode 32 to a  
18 stainless steel cathode bus line 34. It is to be understood  
19 that the invention is not limited to the use of stainless steel  
20 for the anode and cathode. The cathode bus line 34 is used to  
21 electrically connect several bond samples 10 simultaneously.  
22 The cathode bus line 34 is then connected in parallel to  
23 maintain all bond samples 10 at a desired electrochemical  
24 potential relative to a reference cell 36. In a preferred



1 embodiment, the reference cell 36 is composed of Ag/Ag-Cl,  
2 however, any calibrated reference electrode could be used.

3 In the preferred embodiment, the desired electrochemical  
4 potential of each polymer to metal bond sample 10 relative to  
5 the reference cell 36 is -0.85 volt which is the voltage  
6 normally used to protect a steel hulled marine vessel that might  
7 naturally corrode at -0.600 volt. The current used to maintain  
8 the cathode bus line 34 at -0.85 volt relative to the reference  
9 cell 36 is dependent on the amount of wet surface area requiring  
10 cathodic protection. Approximately 10 mA is required to protect  
11 one square foot of wetted surface area.

12 Using an impressed current system requires an adjustment to  
13 the power supply 30 to account for the reduction in current as  
14 samples are removed from the test chamber 12. A zinc anode  
15 system for example would require a complete zinc anode resizing  
16 to ensure that the correct amount of current is being supplied  
17 to cathodically protect the remaining samples. Supplying too  
18 much current to the samples not only may cause an unknown effect  
19 in the cathodic delamination reaction, but changes the corrosion  
20 rate and also may cause the production of hydrogen gas in  
21 specific voltage regimes, which is highly explosive in a closed  
22 vessel containing pure oxygen. As more bonding samples 10 are  
23 removed from the test chamber 12 the required current will  
24 initially drop and then increase as the gradual delamination of

1 the polymer occurs and subsequently there is an increase in  
2 metal surface area exposed to the electrolyte.

3 As the band heater 16 increases the temperature of the  
4 synthetic ocean water 14 to artificially accelerate the exposure  
5 of the bonding samples 10, the level of dissolved oxygen will  
6 drop far below normal levels at lower temperatures. The  
7 dissolved oxygen level in 15°C natural ocean water is  
8 approximately 8 ppm. Maintaining this level of dissolved oxygen  
9 while at temperatures much higher than 15°C requires an increase  
10 in the partial pressure of oxygen in the atmosphere above the  
11 synthetic ocean water 14. A dissolved oxygen sensor 20 is used  
12 to measure the amount of dissolved oxygen in the synthetic ocean  
13 water 14. The level of dissolved oxygen is maintained at normal  
14 ocean temperature conditions (15°C) by injecting oxygen into the  
15 test chamber 12 through the pure oxygen inlet 24. A vacuum pump  
16 38 is used to evacuate all of the air in test chamber 12 after  
17 which the pure oxygen is injected into test chamber 12. To  
18 accelerate the dissolution of oxygen into the synthetic ocean  
19 water 14, a circulation pump 40 is used to create a turbulent  
20 mixing surface within test chamber 12. The circulation pump 40  
21 also creates a slight water velocity across the tip of the  
22 dissolved oxygen sensor 20. This is necessary to obtain an  
23 accurate measurement, because in stagnant water the sensor 20

1 would completely consume the dissolved oxygen in its immediate  
2 surroundings.

3 Leaving various types of polymer to metal bond samples 10  
4 in the vessel under the appropriate conditions as described  
5 above provides a determination as to which polymer to metal  
6 bonds are the most resistant to cathodic delamination. The  
7 period of test time that the bond samples 10 should be left in  
8 the vessel is derived through the use of the Arrhenius Equation  
9 which states that  $K = Ae^{-E/RT}$ , where K = specific reaction  
10 velocity (speed of the reaction), E = energy of activation  
11 (dependent on the type of reaction), A = constant (frequency  
12 factor), R = gas law constant (1.99 calories/degree-mole), T =  
13 temperature (absolute), and e = base of the natural logarithm.  
14 The reaction acceleration factor (RAF) for reaction velocities  
15 K1 and K2 for a given reaction at T1 and T2, where T2 > T1, is  
16 defined as  $RAF = K2/K1 = e^{E(T2-T1)/R(T1T2)}$ . The value of RAF is used  
17 to obtain the number of test days at the elevated temperature T2  
18 that will simulate 1 year of exposure at T1: Test Time (@T2) =  
19 365/RAF. The calculation of test time is highly dependent on  
20 the value of the energy activation E. Any inaccuracies in the  
21 estimation of the energy activation for the reaction will result  
22 in drastic inaccuracies in the calculation of test time. Past  
23 studies estimate 13,000 calories/mole as a composite energy of  
24 activation for water permeation through various elastomers.

1           The advantages of the present invention over the prior art  
2 are that the use of a closed vessel test chamber provides the  
3 ability to manipulate the environment that contains the polymer  
4 to metal bond samples 10 by for example creating a pure oxygen  
5 atmosphere to maintain appropriate dissolved oxygen levels in  
6 the synthetic ocean water 14. Prior art testing devices have  
7 ignored the decrease in dissolved oxygen concentration at the  
8 higher water temperature level at which a test is normally  
9 conducted. Lower than normal concentrations of dissolved oxygen  
10 in the synthetic ocean water 14 will actually slow the cathodic  
11 delamination reaction, thereby generating "false positive"  
12 results that seriously over-estimate the actual resilience of  
13 the bond samples 10 to cathodic delamination. Creating an  
14 excess of pure oxygen in the atmosphere above the synthetic  
15 ocean water 14 in the test chamber 12 ensures that the dissolved  
16 oxygen used up by the cathodic delamination reaction during the  
17 test is quickly replaced.

18           Prior art testing methods and apparatus have no provision  
19 for replacing the dissolved oxygen used up during a test. Some  
20 prior art testing methods and apparatus replace oxygen with  
21 forced air, which introduces large amounts of carbon dioxide  
22 into the synthetic ocean water 14. Carbon dioxide, which is  
23 much more soluble than oxygen in water, will react with water to  
24 form carbonic acid. The introduction of excess carbonic acid

1 into the synthetic ocean water 14 will affect the pH of the  
2 water. It could also react with the hydroxide ions generated by  
3 the cathodic delamination reaction thereby preserving the bond  
4 and ultimately compromising the testing.

5 The use of a closed vessel test chamber also ensures that  
6 little or no water is evaporated during the test and that the  
7 conductivity of the synthetic ocean water 14 remains constant.

8 The present invention uses an external band heater 16 to  
9 reduce "unknowns" created by adding an additional piece of metal  
10 into the test chamber 12 like an immersion heater.

11 The use of an impressed current system in the present  
12 invention rather than a zinc anode provides the ability to  
13 adjust the current level used to cathodically protect the metal  
14 substrates of the polymer to metal bond samples 10 with out the  
15 need of adjusting the size of the zinc anode or replacing it.  
16 It also avoids the build up of dissolved zinc in the test  
17 chamber 12 which can actually slow the cathodic delamination  
18 reaction or even cause it to reverse direction because of Le  
19 Chatilier's Principle.

20 Obviously many modifications and variations of the present  
21 invention may become apparent in light of the above teachings.  
22 For example: The temperature of the water inside the accelerated  
23 life testing chamber can be set to different temperatures to  
24 either speed up or slow down the rate of the cathodic

1 delamination reaction. The test chamber can be used to  
2 accelerate the aging of systems exposed to a variety of ocean  
3 water temperatures. A sodium chloride solution of the proper  
4 salinity and chlorine content can be substituted for synthetic  
5 ocean water. Sacrificial metal anodes (e.g. zinc) can be  
6 substituted for the battery employed in the impressed current  
7 system. A variety of different reference electrodes (properly  
8 calibrated) can be used to monitor the system. A variety of  
9 different metals/alloys can be used as the anode in the  
10 impressed current system. The closed vessel that is the test  
11 chamber 12 can be scaled up to hold larger size samples or a  
12 larger number of smaller samples.

13 In light of the above, it is therefore understood that  
14 within the scope of the appended claims, the invention may be  
15 practiced otherwise than as specifically described.

1 Attorney Docket No. 84989

2

3 METHOD AND TEST CHAMBER FOR ACCELERATED AGING OF MATERIALS AND

4 BONDS SUBJECT TO CORROSION RELATED DEGRADATION

5

6 ABSTRACT OF THE DISCLOSURE

7

8 A method and test apparatus for carrying out testing on a  
9 variety of samples of polymer bonded to metal wherein the  
10 samples are subjected to an accelerated cathodic reaction  
11 causing cathodic delamination of the samples. In particular,  
12 the method and test apparatus include a closed vessel that is  
13 partially filled with synthetic ocean water. An impressed  
14 current system is employed to protect the metal component of the  
15 samples. The synthetic ocean water is heated with an external  
16 band heater raising the temperature of the synthetic ocean water  
17 to thermal levels exceeding normal ocean temperatures in order  
18 to accelerate the reaction. Pure oxygen is then introduced into  
19 the closed vessel at a desired pressure to dissolve the oxygen  
20 into the synthetic ocean water to further simulate natural ocean  
21 conditions.

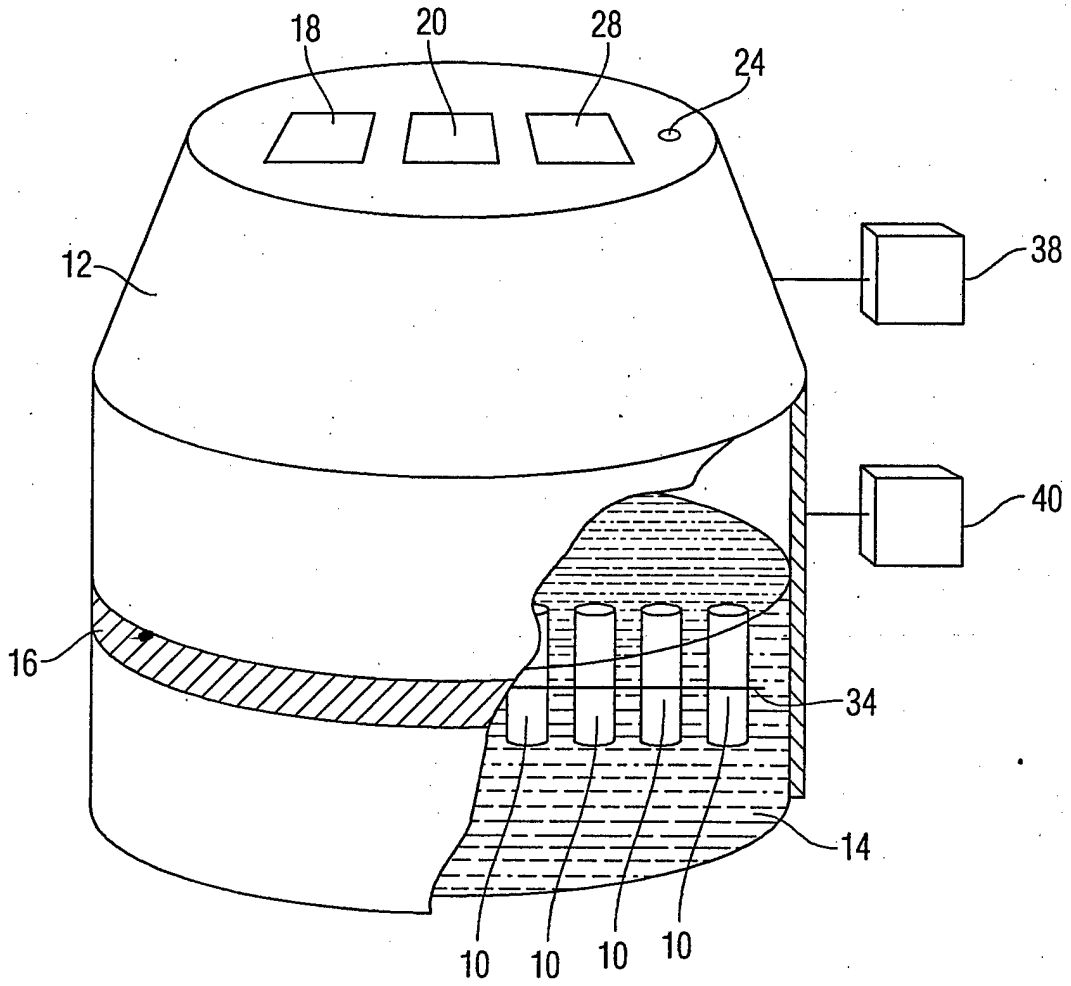


FIG. 1



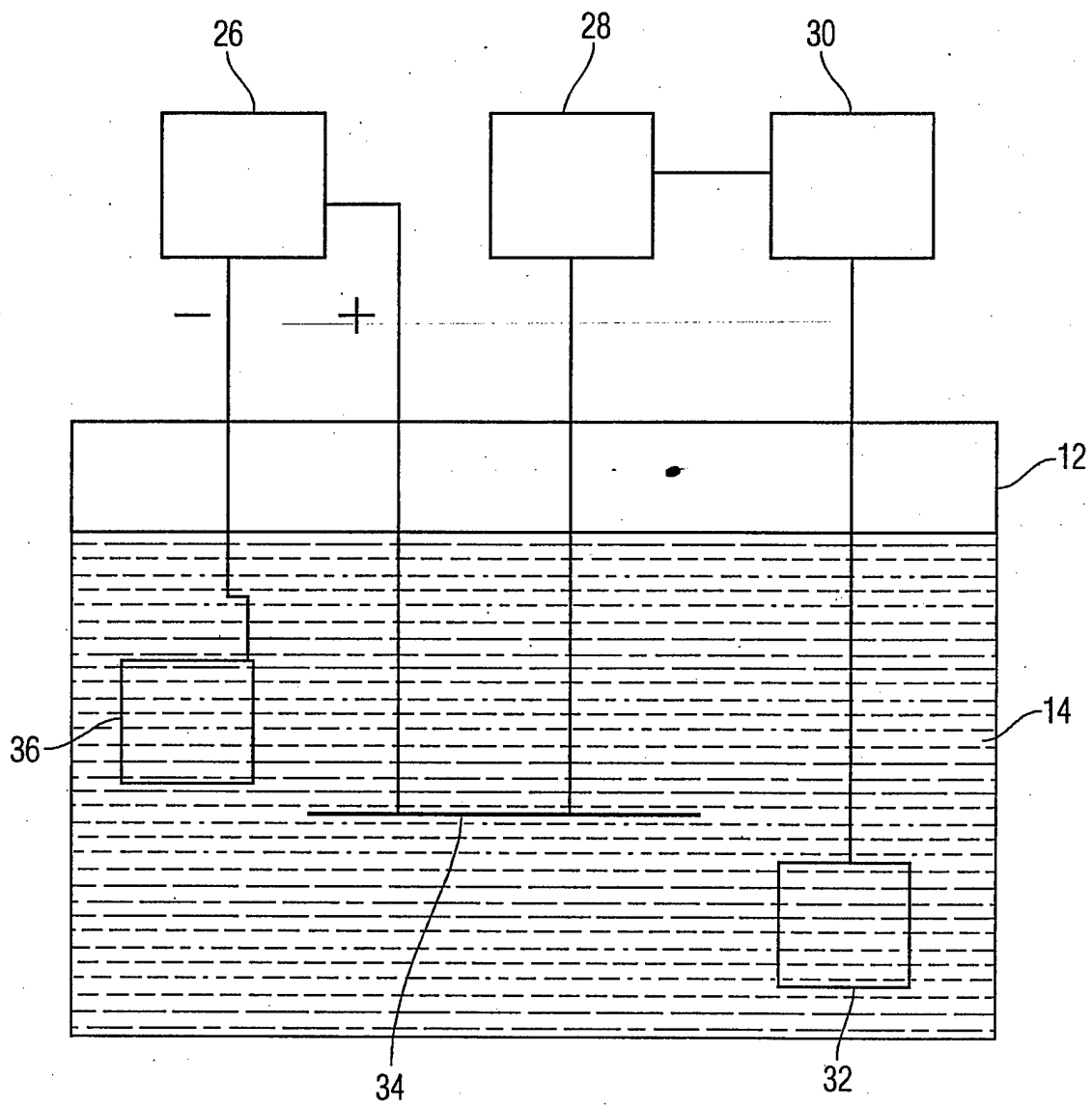


FIG. 2