Accelerated Life Testing of Marine Cables and Connectors: Problems, Pitfalls, and Suggestions for Improvements

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Abstract- The ability to scientifically predict the performance, degradation resistance, and usable lifetime of marine cables and connectors is highly desired and valued by design engineers and program managers. The costs associated with these items failing prematurely in their end-use applications can be quite high. On the other hand, significant savings can be realized if the service life of such hardware can be reasonably extended beyond several repair/refit cycles. Historically, the most frequently encountered failure mechanism for marine cables and connectors has been delamination of the polymeric overmolding compound from metal connector backshells. Most outboard cables are connected to cathodically protected metal surfaces which induce a cathodic potential within metal connector backshells. Corrosion reactions occurring on cathodically polarized metal surfaces then cause metal-polymer adhesion failure by a variety of mechanisms. Over the years, several testing protocols have been developed either by or for the U. S. Navy to use increases in temperature to accelerate this so-called "cathodic delamination" process. The purpose of these accelerated life test (ALT) protocols is to determine the resistance to degradation of various metalprimer-polymer combinations used on cables and connectors in a marine environment. Unfortunately, many of the existing ALT protocols exhibit technical and/or scientific deficiencies that compromise their ability to provide meaningful data for the prediction of service life, and the understanding of the cause(s) of hardware failure in the marine environment. These problems include, but are not limited to: choice of failure mechanism model; differences in activation energy for materials/reactions/processes; maintenance of the proper corrosion current density and voltage; and maintenance of the proper ALT fluid medium chemistry. All of these issues are important for the successful completion of an ALT, yet ALTs are often conducted without addressing one or more of these critical issues.

I. INTRODUCTION AND BACKGROUND

Reductions in the U.S. Navy's operations and maintenance budget after the end of the cold war have caused USN program managers to insist that new naval hardware last for ever longer periods of time in the marine environment. For many systems, a fifteen-year service life requirement is the norm and calls for a thirty-year service life are becoming more common. Accelerated life testing is a valuable tool for ensuring that these ambitious service life goals are met. Various protocols exist for setting up and running an accelerated life test (ALT) [1,2]. These protocols vary in detail depending upon the type of material/item being tested and the expected degradation mechanism. In all cases, the rate at which certain degradation reactions occur is increased by various means to cause degradation to occur much faster in the laboratory than it does in the actual service environment. Thus, an ALT can simulate many year's worth of service in a hostile environment in a matter of weeks or months, thereby enabling rapid and accurate predictions of the time-to-failure (TOF) of items to be made.

Cathodic delamination refers to a process in which certain chemical reactions occur on a cathodically-protected metal surface in an aqueous environment. These reactions tend to degrade/destroy polymer to metal bonds. The functioning of many pieces of USN hardware (transducers [3,4,5], hull penetrators, cable connectors [6,7,8], etc.) can be seriously compromised by polymer-metal bond failures. Indeed, the cathodic delamination process is thought to be responsible for the majority of the premature failures experienced by outboard USN hardware. Accelerated life testing protocols exist for the cathodic delamination process, but in a number of respects, these existing protocols are inadequate. The purpose of this paper is to point out inadequacies in the current cathodic delamination ALT protocols, and to offer suggestions as to how these protocols can be improved to ensure they provide meaningful predictions of a component's useful service life in environments where cathodic delamination is favored.

II. THE CATHODIC DELAMINATION PROCESS

Most of the accelerated life testing protocols developed for components subject to cathodic delamination in a marine environment are based upon the Arrhenius equation:

$$K = A e^{-E/kT}$$

In this equation, K is the reaction rate; A is a constant characteristic of the reaction mechanism; E is the activation energy of the reaction; T is the absolute (Kelvin) temperature at which the reaction is occurring; and k is Boltzmann's

constant. A detailed discussion of how the Arrhenius equation is used to develop ALT protocols is beyond the scope of this paper; a detailed discussion of the process involved can be found in the literature [1,2]. All Arrhenius-based ALT protocols use an increase in temperature to accelerate the degradation reaction of interest. All of the accelerated life testing performed by/for the U.S. Navy to date on components subjected to cathodic delamination have utilized heated sea water; most have also used applied voltages [3,4,5] or sacrificial zinc anodes coupled to the items undergoing testing [6,7,8,9,10, 11,12].

The chemical basis of the cathodic delamination process is fairly well understood [13,14, 15,16,17]. The steel hulls of USN submarines and surface craft are protected from corrosion by sacrificial zinc anodes. These sacrificial anodes ensure that the hulls (and any metal object directly attached to the hull made from metals/alloys more noble that zinc or magnesium) will be cathodically polarized. At voltages lower than -0.5 volts (versus the standard calomel electrode, SCE), the following reactions will occur on cathodically-polarized metal surfaces exposed to sea water:

$$O_2 + 2H_2O + 2e^- \rightarrow HOOH + 2OH^-$$

Between -0.7 V to -1.2 V (versus SCE), hydrogen peroxide (HOOH) can be broken down:

$$HOOH + 2e^- \rightarrow 2OH^-$$

Some surfaces do not support the production of hydrogen peroxide; in those cases, the product of the first reaction will be four hydroxide ions rather than two hydroxide ions and one hydrogen peroxide molecule. Finally, at voltages more negative than -0.6 V (versus SCE), hydrogen ions can be reduced directly to molecular hydrogen and thence to hydrogen gas:

$$2\mathrm{H}^{\!\!+}+2\mathrm{e}^{\!\!-}\!\rightarrow 2\mathrm{H}\rightarrow\mathrm{H}_2$$

All of these reactions will cause the pH of the liquid layer immediately above the cathodically polarized surface to increase [17], in some cases to values as high as 14 [13]! The last reaction (reduction of hydrogen ions) is not commonly encountered in shipboard environments, because (by design) the potential is not allowed to drop to the levels needed to sustain it. The generation of atomic hydrogen at/near a metal surface is undesirable, because it can lead to hydrogen stress cracking and/or hydrogen embrittlement.

Although there is general agreement that the above are the corrosion reactions that initiate the cathodic delamination process, there is considerable debate regarding the mechanism by/through which the newly generated hydroxide ions and/or hydrogen peroxide molecules degrade the crucial metal-to-polymer bonds. Hydrogen peroxide is a very strong oxidizer and might directly degrade the polymer surface at the bond line via an oxidative mechanism. In addition, hydrogen peroxide is a good solvent, and might actually

dissolve portions of the polymer that are directly bonded to the metal surface. The presence of hydroxide ions will significantly increase the pH at/near the bond line. Some polymers [18,19] can be saponified or hydrolyzed directly by hydroxide ions. In other cases, an increase in hydroxide ion concentration at the polymer-metal interface is thought, via osmotic pressure, to trigger the formation of water-filled blisters that can physically delaminate the metal/polymer interface [17,19,20]. Yet another possibility is that the rise in pH triggered by the formation of the hydroxide ions causes the metal oxide layer to which the polymeric component is typically bonded to become unstable and dissolve [13,19,21].

III. CRITICAL PARAMETERS FOR AN ALT

In an ALT (and in real life) an electrochemical cell must be in operation for cathodic delamination to occur. There are four critical conditions necessary for the operation of any electrochemical cell: (1) an anode - a location where electrons are generated; (2) a cathode - a location where electrons are consumed: (3) a pathway for electrons to flow from the anode to the cathode; and (4) a medium to supply corrosion reaction reactants and absorb corrosion reaction products. If any one of these four items is missing, the cell will not operate. Thus, an ALT that successfully accelerates the cathodic delamination process must ensure that all four of the above conditions are met and maintained. In and around U.S. Navy ships and submarines, sacrificial zinc anodes are directly connected (electron pathway) to steel hulls (cathodes) in the presence of sea water (the electrolyte/medium). In some cases, the sacrificial zinc anodes are replaced by an impressed current source. The equivalent to that in an ALT would be to attach a battery or electrical power supply directly to the samples to provide the required cathodic polarization.

Because the cathodic delamination process is electrochemical in nature, the potential of the cathodic surface is a very important variable that has not been properly worked into the existing USN cathodic delamination ALT protocol for cables and connectors. Past attempts [3,4,5] to apply a voltage to the metal substrate have not always produced the expected results or properly reproduced the failure mechanism(s) observed in failed components returned from the Fleet. Perhaps as a result of these problems, voltages have not been applied to the metal substrates of components subject to cathodic delamination in more recent ALTs [7,8]. Instead, the metal substrates were physically connected to sacrificial zinc anodes while immersed in heated seawater. This technique had also been utilized in the past with mixed results [6]. Possible reasons for these problems include: (1) improper scaling of the experiment; (2) failure to ensure the zinc was electrically connected at all times to the ALT samples; or (3) a buildup of zinc ions in solution. The first issue is important, because the cathodic delamination reactions consume electrons and are, thus, sensitive to both voltage and current. If the current density on the cathodic surface is not correct (typical of the real-life situation) the rate of the delamination reaction will change. If, at any time during the ALT, the zinc anodes are not shorted to the samples, the electrochemical cell will shut down. Finally, as the reaction progresses, the concentration of zinc ions in the ALT fluid medium will increase. In accordance with Le Chatelier's principle, as the concentration of zinc increases, the reaction at the anode,

$$Zn \rightarrow Zn^{+2} + 2e^{-1}$$

will slow down, and possibly reverse. This problem can be avoided by replacing the ALT fluid medium from time to time, or by using a battery or power supply as the source of electrons for the cathodic delamination reaction.

Although in theory, the attachment of sacrificial zinc anodes to the metal substrate of a component in an ALT should ensure that metal substrate is cathodically polarized, unexpected things can happen once the temperature of the ALT fluid medium (sea water or a sodium chloride solution) is raised. Two of the more modern ALT protocols have specified water temperatures of 58°C [7] and 70°C [8]. As the temperature of the ALT fluid medium is raised, it is possible for the zinc-metal substrate potential to reverse [22]. Once the reversal occurs, the metal substrate will no longer be cathodically polarized, and the cathodic degradation reaction(s) will cease. The temperature at which the potential reversal will occur depends upon the presence and concentration of certain dissolved ions, especially bicarbonates, carbonates, and nitrates. Certain concentrations of bicarbonate can even affect the potential reversal at room temperature! The presence of other dissolved ions (chlorides and sulfates) tend to counteract the effects of the ions which trigger the potential reversal, but the interplay between the various dissolved species is complex. One would think that seawater, with its high chloride content, might not support the conditions necessary for the reversal to occur, but, unfortunately, such is not the case. The author has observed a potential reversal between a brass/inconel galvanic couple in a sea water ALT being conducted at 60°C. Even though the two metals were directly connected to each other, the brass showed no evidence of corrosion (contrary to what was happening in real life) at the end of the ALT. In addition, the surface of the brass part was covered with a whitish encrustation, later determined to be calcium carbonate by Xray diffractometry. Carbonates will only precipitate from seawater in a high pH environment (such as that found immediately above a cathodically polarized surface).

The generation of hydrogen peroxide and/or hydroxide ions on a cathodically polarized surface during an ALT consumes oxygen dissolved in the fluid medium. Most ALTs are carried out in small tanks. The water or seawater within these tanks can become depleted in dissolved oxygen rather quickly during an ALT, because the solubility of oxygen in water is very low. Once the dissolved oxygen is depleted, the reaction will stop, and the samples will no longer be subject to cathodic delamination. Samples in such an ALT might, therefore, appear to have survived the ALT without debonding when, in reality, they survived because the composition of the ALT fluid medium changed such that it could no longer support cathodic delamination reactions. Thus, it is very important to maintain the dissolved oxygen content of the fluid medium throughout the duration of the ALT. The best way to do this is to bubble pure oxygen through the fluid medium at all times.

The issue of carbonate precipitation needs to be addressed in cathodic delamination ALT protocols. The high pH environment that exists immediately above the cathode surface can trigger the precipitation of carbonates from seawater. In some (but not all) cathodic delamination ALTs, air is bubbled through the seawater in which the parts undergoing the testing are immersed. Air is bubbled through the water to prevent the water from becoming de-oxygenated. Unfortunately, air contains some carbon dioxide, and that gas is significantly more soluble in water than oxygen gas. Once dissolved, the carbon dioxide can form bicarbonate or carbonate ions, which then can precipitate out on the surface of the cathode. Once carbonates form on the surface of the cathode, the cathodic delamination reactions of interest will be greatly hindered, if not stopped altogether. One possible way to avoid/greatly lessen the carbonate precipitation problem would be to bubble pure oxygen in the ALT solution rather than air. The use of oxygen vice air would keep the disturbance of the carbonate/bicarbonate chemistry of the ALT solution to a minimum. Substitution of a sodium chloride solution of the proper salinity for seawater might also help because, in such a solution, there would be essentially no carbonate/bicarbonate ions present at the start of the ALT. At least one cathodic delamination experiment [23] utilized a carbon dioxide trap to address the carbonate precipitation problem.

The heating of the ALT fluid medium significantly decreases its concentration of dissolved oxygen. The solubility of oxygen gas is affected by the chlorinity of the solution in addition to its temperature [24]. From 0°C to 50°C, oxygen gas solubility in water drops by a factor of 3 for 0 chlorinity and by a factor of 2.5 for 25 chlorinity (note: chlorinity is salinity divided by 1.80655). Dissolved oxygen is consumed in the chemical reactions that trigger cathodic delamination; a significant decrease in its concentration in the ALT fluid medium would be expected to slow the rate at which cathodic delamination proceeds. None of the extant cathodic delamination ALT protocols address this issue. Thus, it is possible that a part undergoing ALT testing might exhibit "resistance" to cathodic delamination simply because of the decreased availability of dissolved oxygen in the test solution. The only way to resolve this problem would be to lower the ALT temperature, but that would significantly lengthen the amount of time required to complete the ALT.

One final issue of concern for ALT protocols for cathodic delamination is related to the mechanism by which the metalto-polymer bonds fail during the test. The Arrhenius equation (and ALT reaction acceleration factors derived therefrom) include and activation energy term, E. Although it is rarely stated in ALT protocols, E is usually the activation energy for the diffusion of water into the connector overmold material [17]. It is important to verify that the value of E used in an ALT protocol to convert time spent at an elevated temperature into time spent at the normal service temperature is correct for the actual overmolding material used to encapsulate the connector. Different polymers have different values of E for water diffusion. Even small errors in the value of E can be problematic because of the exponential relationship between E and the ALT reaction acceleration factor. It is also possible that under some conditions, and with certain materials, a completely different reaction or process will be the rate-determining step for the debonding process. In such instances, the activation energy for a process other than the diffusion of water into a polymer should be used to calculate the correct accelerated age of the ALT samples. One should not simply assume that the activation energy value used for accelerated age calculations in a "generic" ALT protocol is the correct one for any specific set of materials and conditions.

IV. CONCLUSIONS

At the present time, a significant amount of money and effort are being spent by industry and the U.S. Navy on nonconductive ceramic (NCC) coatings to prevent cathodic delamination on outboard cable connectors [8]. In order to realistically evaluate the long-term effectiveness of these rather expensive coatings, properly designed ALTs need to be run. To date, the ALT protocol [25] used to estimate the longterm performance of connectors exhibits a number of the shortcomings discussed in this paper. A new and improved ALT protocol is needed for the evaluation of all outboard hardware expected to be subjected to cathodic delamination. At a minimum, the new protocol needs to address: (1) the possibility of zinc/cathode metal potential reversals; (2) the possibility of carbonate precipitation on the cathode surface; (3) the need to continually replenish the dissolved oxygen consumed by the cathodic delamination reactions; (4) the decreased solubility of oxygen gas as the temperature of the test solution is increased; and (5) differences in activation energy for the diffusion of water into different overmolding compounds.

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