Cathodic Debonding of Undersea Electronic Cable Connectors: Delamination Kinetics When Primers and Encapsulants Are Bonded Directly to Bare Metal Connector Backshells

Thomas S. Ramotowski, Wayne C. Tucker, and Matthew A. Rice
Naval Undersea Warfare Center, Division Newport
Naval Sea Systems Command, U.S. Navy
Newport, RI, 02841
thomas.ramotowski@navy.mil

Abstract— **When undersea cable connectors are attached to receptacles that are part of a cathodically protected vessel hull, the encapsulants applied over the connector backshells to protect the interior of the connector from seawater ingression often rapidly debond from the backshell, thereby compromising the interior of the cable and connector. This process is called "cathodic delamination" or "cathodic disbondment" and it is believed to be caused by the generation of highly alkaline conditions at the metal-encapsulant bondline due to the reduction of dissolved oxygen and the subsequent generation of hydroxyl (OH^-) ions. An investigation into the kinetics of this process for the case where encapsulants and their associated primers are bonded directly to bare metal connector backshells was undertaken to develop better accelerated life testing techniques for marine hardware subject to cathodic delamination. Two different commercial encapsulation systems were investigated: PR-420 primer/PR-1547 polyurethane (PRC-DeSoto) and AD-1146 primer/EN-1556 polyurethane (Cytec). Small sacrificial zinc anodes were used to provide the proper cathodic polarization for the test samples. This testing revealed that cathodic debonding preferentially proceeds from exposed edges/bondlines inward, rather than through the encapsulant. Some primer/encapsulant systems (e.g., the PRC-Desoto system) are inherently more resistant to cathodic delamination that other systems. The rate at which the debonding proceeds was found to be diffusion controlled and was linear when plotted versus the square root of elapsed time. Debonding rate data were used to determine the Arrhenius activation energy for the cathodic delamination of both encapsulation systems (8.4 kcals/mole for the PRC-DeSoto system and 2.6 kcals/mole for the Cytec system), which are quite different from the experimentally determined Arrhenius activation energies for the diffusion of water through the various encapsulants (3.1 kcals/mole and 3.9 kcals/mole, respectively). These results suggest that the cathodic delamination process for undersea electronic cable connectors is controlled by the rate of water and dissolved species diffusing along the disrupted bondline, rather than by water the rate of water and oxygen diffusing through the encapsulant.**

Keywords—cathodic delamination, cathodic disbondment, cable connectors, accelerated life testing, adhesion, activation energy

I. INTRODUCTION

The hulls and outboard machinery of most U.S. Navy vessels require some form of cathodic protection (either sacrificial anodes or an induced current cathodic protection – ICCP- system) to prevent corrosion damage. While these cathodic protection methods prevent metal in contact with seawater from corroding, an unfortunate side-effect of their use is the destruction of metal to polymer bonds referred to as "cathodic delamination" or "cathodic disbondment". Hardware not directly connected to the cathodic protection system itself can become cathodically polarized by being connected directly to a protected hull, or to any other metal object that is connected to the hull. Cathodic delamination is thought to cause hundreds of millions of dollars of damage to marine hardware every year.

Cathodic delamination is known to cause paint to debond from metal hull walls, and polymeric encapsulants to debond from metal surfaces on specialized pieces of hardware (e.g., sensors and connectors). The process was recognized over 80 years ago [1] for paint debonding from steel. The key chemical reaction during the cathodic disbondment of a polymer from a cathodically polarized metal substrate is the reduction of dissolved oxygen in water to generate hydroxyl ions [2,3]:

$$2H_2O + O_2 + 4e^- \rightarrow 4(OH^-) \qquad (1)$$

The reduction of oxygen is the major cathodic reaction that occurs when the cathodic polarization of the metal substrate is below -1020 mV versus the saturated Calomel electrode (SCE). The electrons in the reaction come sacrificial anodes or an ICCP system anode. The hydroxyl ions are generated at the metal-polymer interface where they create an extremely alkaline/high pH environment that weakens and degrades most metal-to-polymer bonds, eventually causing their failure.

Our research has focused on developing a better understanding of the cathodic delamination process as it affects the metal-polymer bonds typically encountered on outboard electronic cable connectors. We are interested in both the kinetics and the mechanism of the key degradation reactions that occur during the cathodic delamination of polymers bonded to connector backshells so that better and more reliable accelerated life testing (ALT) techniques for hardware subject to cathodic delamination can be developed. These new ALT techniques and methods will help ensure that premature, cathodic delamination induced hardware failures while in Fleet service are minimized, thereby lowering the total ownership/lifecycle cost of outboard cables

II. Experimental Set-Up

A. Materials

Although other cable connector backshell alloys are in use, our experiments exclusively used monel 400 alloy as the metal substrate. Monel 400 is a nickel-copper alloy that exhibits moderate corrosion resistance when immersed in seawater. Monel 400 flat-bar stock was machined into rectangular coupons 4 x 1 x 0.25 inches in size. A small threaded hole was made on the flat side of the coupon opposite the bonding surface for the attachment of sacrificial zinc anodes.

Two primer/encapsulant systems were studied. All components of the first system were manufactured by PRC-DeSoto and included PR-420 primer and PR-1547 (amber) polyurethane as the encapsulant. All components of the second system were manufactured by Cytec and included AD-1146-C-1 primer and Conathane EN-1556 polyurethane as the encapsulant.

For experiments used to measure the uptake of water into the polyurethane encapsulants, all samples were immersed in distilled water. For the cathodic delamination experiments, the samples were immersed in salt solution (3.5% sodium chloride by weight). The zinc anodes attached to some samples were standard zinc boat rudder anodes (slightly "domed", disc-like shapes approximately 1.5 inches in diameter and 0.25 inches thick at the top of the "dome").

B. Sample Manufacture

The center two square inches of the monel 400 coupons were sandblasted with 80 grit aluminum oxide and then rinsed/cleaned with acetone prior to primers being applied to their bonding surfaces.

Samples made using the PRC-DeSoto system had their bonding surfaces painted with PR-420 primer. The PR-420 primer was allowed to air-dry for 2-4 hours before the samples were placed into a specially-designed metal mold (that made nine samples at a time) and the PR-1547 (amber) polyurethane was applied. The samples were then heated at 80°C for a minimum of 16 hours to cure the polyurethane.

Samples made using the Cytec system had their bonding surfaces painted with a coat of AD-1146-C-1 primer, which was allowed to air dry at room temperature for 30 minutes. A second coat of AD-1146-C-1 primer was then painted over the first coat and also allowed to air dry at room temperature for 30 minutes. The sample coupons were then placed in an oven and heated at 80°C for two hours, after which they were allowed to cool to room temperature and were placed in the metal mold. The Conathane EN-1556 polyurethane was mixed and poured into the mold (which made 9 samples per batch). The samples were then placed into an 80°C oven for a minimum of 16 hours to cure the polyurethane.

This work was funded by the NUWC Division Newport ILIR Program and the Office of Naval Research's Corrosion Research Program.

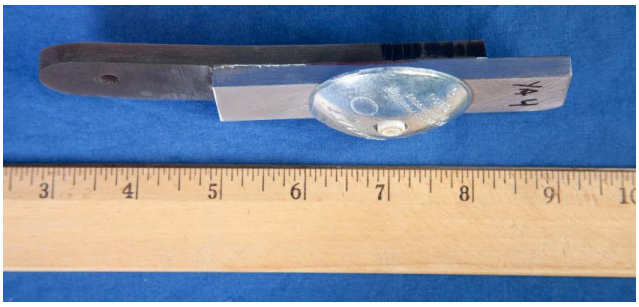

Fig. 1. Peel sample ready for testing. This sample has a sacrificial zinc anode attached to its backside. Note the overhang of the polyurethane substrate over the back of the metal substrate. Only the center two square inches of the sample are bonded together.

Fig. 2. A set of twelve individual peel samples hung by their tails from metal rods fitted into slots on top of the acrylic holder-racks, before immersion in a salt water test tank.

Once the polyurethane had been cured, the samples were removed from the metal mold, cut apart using a band-saw, and their edges were sanded flush so that no primer or polyurethane extended over the edges. A small hole was drilled into the polyurethane "tail" of the samples to allow them to be suspended from a metal bar attached to an acrylic rack used to hold them upright in the salt water filled test tank. Samples that were going to be exposed to cathodic delamination conditions had small zinc sacrificial anodes attached to their backsides (via a nylon screw) before they were placed into the holder racks; figures 1 and 2). These samples are referred to as "peel samples" because their ultimate fate, after environmental conditioning, was to be peeled to destruction on an Instron machine.

Samples of polyurethane used for the water absorption/diffusivity measurements were cut from 3 mm thick

sheets of each polyurethane that had been cured for a minimum of 16 hours at 80°C. The samples were cut into discs 6 cm in diameter.

C. Experimental Procedures

Water absorption experiments were conducted by placing each polyurethane disc into its own beaker containing 300 ml of distilled water. The discs rested on a bed of glass marbles to ensure water was in contact with all sides of the sample. The beakers were covered with a polyethylene bag that was secured with a rubber band. The samples were randomly divided into three equal batches (three samples each) and these batchers were maintained at three different temperatures for the duration of the experiment. Periodically, the polyurethane discs were removed from their beakers, patted dry with a paper towel, and then weighed. Once weighed, the samples were returned to their beakers. The periodic weighing of the samples continued until each sample's weight gain versus time plot leveled off (i.e., the sample had become saturated with water).

Diffusion constants for each sample set were calculated using two different methods [4,5]. The results from the two methods agreed well with each other. To obtain the activation energy for the diffusion of water through the two polyurethanes, the natural log form of the Arrhenius equation was used:

$$\ln D = -(Ea/RT) + \ln C \qquad (2)$$

As the equation indicates, a plot of the natural log of diffusion constants versus 1/T (temperature in Kelvin) should be linear with a slope of –(Ea/R) (the activation energy divided by the gas constant) if the process being studied follows Arrhenius kinetics.

Fig. 3. Experimental set-up for peel samples and test racks maintained at elevated temperature. Samples in air are on top; samples in the salt solution without sacrificial anodes are in tank on the left, and samples in the salt solution with sacrificial anodes attached are in the tank on the right.

Conditioning of the peel test samples was conducted at three different temperatures (23°C, 40°C, and 55°C). A total of 72 samples were used for each temperature studied. For each temperature, 24 samples were placed in a holder rack which remained in air; 24 samples (without sacrificial zinc anodes attached) were placed in a holder rack that was submerged in the 3.5% NaCl solution, and 24 samples (with sacrificial zinc anodes attached) were placed in a holder rack and submerged in the 3.5% NaCl solution (figure 3). Every other day, pure oxygen gas was bubbled into the salt solution tanks to maintain the dissolved oxygen content of the solutions. Each week, three samples were removed at random from the test racks and pulled to failure on an Instron machine in accordance with reference [6]. The average peel strength and failure mode for each sample were recorded.

III. EXPERIMENTAL RESULTS

A. Water Diffusion Activation Energies

Once the polyurethane discs in the water absorption experiments became saturated with water, diffusion constants were calculated [4,5] and the Arrhenius activation energies for the diffusion of water through the polyurethanes were determined. Using the method of Crank [4], the activation energy values were 3.5 kcal/mole for both polyurethanes; using the method of Aminabhavi *et al*. [5], the activation energy values were 2.7 kcals/mole for the PR-1547 (amber) polyurethane, and 4.4 kcals/mole for the Conathane EN-1556 polyurethane. The average values for the two materials were:

PR-1547 (amber):	3.1 ± 0.5 kcals/mole
Conathane EN-1556:	3.9 ± 0.7 kcals/mole

B. Peel Sample Degradation Modes

Peel samples were maintained under three different conditions (in air; in the salt solution without sacrificial anodes, and in the salt solution with sacrificial zinc anodes attached) so that the effects of the conditioning on sample performance could be determined. The average peel strength values for the samples maintained in air and in the salt solution without sacrificial anodes attached at all three test temperatures exhibited a small drop over time (the experiments ran for eight weeks). The magnitude of the peel strength decrease varied from about 5% to 35% depending upon the sample type and environmental conditions. The observed failure modes also varied depending upon sample type and the environmental conditioning; approximately 40% of the samples exhibited cohesive failure/tearing of the polyurethane substrate, while the remaining 60% of the samples exhibited an adhesive failure (typically between the primer and the polyurethane).

Only the samples placed into the salt water solution tanks with sacrificial zinc anodes attached experienced cathodic delamination conditions. The first set of samples tested were made using the PRC-DeSoto system, and all of the samples exhibited what resembled a "window-frame" debonding pattern. The samples debonded from their exposed edges inwards so that as time in the test tank increased, the amount of primer/polyurethane still bonded to the metal surface decreased. Eventually, the "window-frame" of debonded primer/polyurethane increased in width to encompass the entire test coupon. Figure 4 is an example of a peel test coupon that exhibits the "window-frame" failure mode described above. In all cases where the "window-frame" failure mode was

observed, the primer debonded from the metal substrate. This type of failure was only observed on samples subjected to cathodic delamination conditions, and it is considered to be characteristic for the cathodic disbondment of peel samples with exposed edges.

Fig. 4. Example of a peel test coupon exposed to cathodic delamination conditions for 7 weeks at 23°C. This sample was made using the PRC-DeSoto system. Note the "window-frame" debonding pattern.

C. Cathodic Delamination Kinetics

Because the width of the "window-frame" debonded region increased as a function of time, the width of the "window-frame" region could be used as a variable to calculate the debonding kinetics for samples exposed to cathodic delamination conditions (figure 5). The rate at which the width "window-frame" region increased could be plotted as a function of time, and the slope of such a graph could be used to determine the rate at which the cathodic delamination process was proceeding.

Fig. 5. Increase of the width of the debonded, "window-frame" region as a function of time for peel samples made using the PRC-DeSoto system and kept under cathodic delamination conditions at 40°C for a period of 8 weeks. Each sample represents one week of elapsed time moving from left to right.

Plots of the width of the "window-frame" debonded region versus the square root of time are presented as figures 6 and 7. These plots are quite linear for all of the temperatures used in our cathodic delamination experiments – their R^2 values are greater than 0.957. In all cases, the lines do not intercept the X-axis of the graphs at zero. This indicates that the debonding process has an "incubation" time (i.e., the debonding process takes a while to begin). The magnitude of this "incubation time" is different for different temperatures and different primer/polyurethane systems.

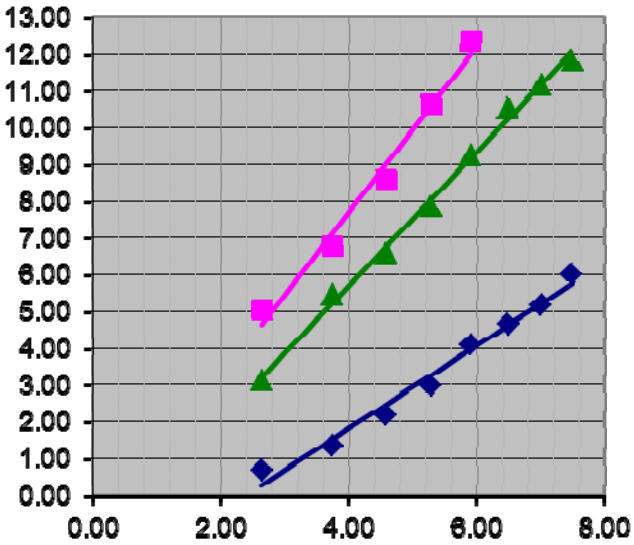

Fig. 6. Plot of the width of the debonded, "window-frame" region (in mm) versus the square root of elapsed time (in days$^{1/2}$). The pink data are for samples maintained at 55°C; the green data are for samples maintained at 40°C, and the blue data are for samples maintained at 23°C. These data are for samples made using the PRC-DeSoto system.

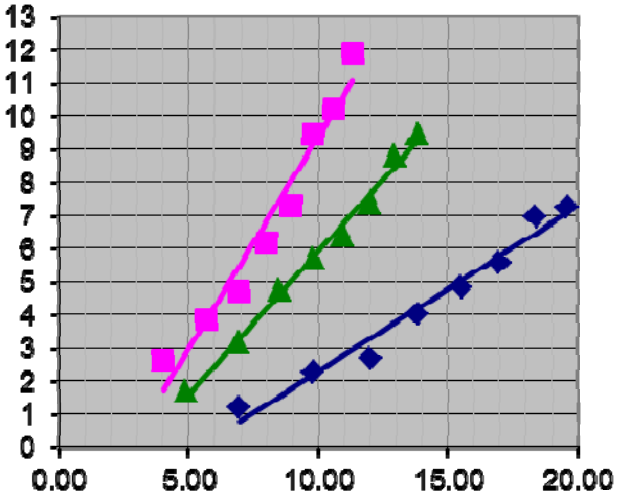

Fig. 7. Plot of the width of the debonded, "window-frame" region (in mm) versus the square root of elapsed time (in hours$^{1/2}$). The pink data are for samples maintained at 55°C; the green data are for samples maintained at 40°C, and the blue data are for samples maintained at 23°C. These data are for samples made using the Cytec system.

The slopes of the data trends for each temperature in figures 6 and 7 were squared to obtain units of area/time. These squared slopes were then used in the natural log version of the Arrhenius equation (equation 2) to obtain the activation energy for the cathodic delamination process for each primer/polyurethane system. The results obtained were:

PRC-DeSoto system:	8.4 kcals/mole
Cytec system:	2.6 kcals/mole

IV. Discussion of Results

As expected, the two different primer/polyurethane systems exhibited different behavior under cathodic delamination conditions. The PRC-DeSoto system performed better (exhibited a slower debond rate) at all test temperatures than the Cytec system. In fact the Cytec system failed so quickly under cathodic delamination conditions that the samples maintained at the lowest test temperature (23°C) completely debonded within two weeks! That failure time was so fast that an insufficient amount of data were collected from the samples (recall, the initial experimental parameters required three peel samples to be removed from the test racks each week). The data presented in figure 7 are from a second trial of cathodic delamination samples made using the Cytec system, but in that case, three samples were removed from the test approximately every day rather than every week.

The implications of the above observations are that the PRC-DeSoto primer/polyurethane system performs significantly better under cathodic delamination conditions than the Cytec primer/polyurethane system; therefore, if one wants his/her outboard cable connectors or any kind of marine hardware to last longer when exposed to cathodic delamination conditions, the PRC-DeSoto primer/polyurethane system should be used instead of the Cytec system. The observed differences in behavior presumably result from difference in the chemical structure of the primers and polyurethanes. The Cytec system primer, AD-1146-C-1, is phenolic resin based, and phenolic resins are not recommended for use in high pH/alkaline conditions. The PRC-DeSoto primer is based upon a heavy metal complex that is apparently more resistant to degradation under high pH conditions.

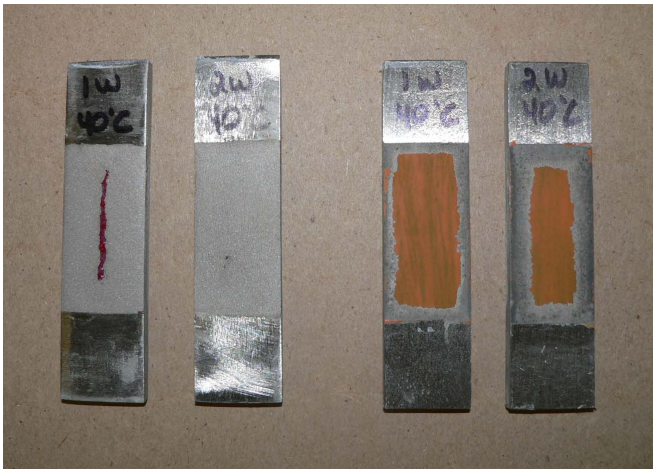

Fig. 8. Example of the difference in cathodic delamination resistance between the Cytec primer/polyurethane system (red color, leftmost samples) and the PRC-DeSoto primer/polyurethane system (orange color, rightmost samples). These metal coupons come from the 40°C test tank (cathodic debonding conditions). The first (leftmost) sample of each set was representative of one week of conditioning in the test tank; the second (rightmost) sample of each set was representative of two weeks of conditioning in the test tank. After two weeks, the Cytec system was completely debonded, while the PRC-DeSoto system was about 40% bonded to the metal substrate.

The results of this study also indicate that the "dry" performance of peel samples (or even the "wet" performance under non cathodic delamination conditions) cannot be used to predict how such samples will perform under cathodic delamination conditions. For example, the Cytec primer/polyurethane system performed better that the PRC-DeSoto system when dry and when exposed to salt water (but not under cathodic delamination conditions). It had higher peel values and more frequent incidents of polyurethane cohesive failure (ripping/tearing). Once the peel samples were subjected to cathodic delamination conditions, however, the performance of the two primer/polyurethane systems reversed; the PRC-DeSoto system was by far the best performer.

The testing also revealed that cathodic delamination propagates through/via exposed bondlines. This mode of attack leads to the "window-frame" pattern of debonding observed on all samples subjected to cathodic delamination. This pattern was so consistent that a "window-frame" debonding pattern should be considered to be characteristic for cathodic delamination for rectangular peel samples such as these with exposed bondlines on their edges. Samples subjected to cathodic delamination conditions that appear to have 100% adhesive failure between the metal substrate and the primer were found (by additional testing) to be examples of "window-frame" like debonding that had occurred so fast that it had completely debonding the primer from the sample before the sample was pulled to destruction on the Instron machine. Another defining characteristic of cathodic delamination is that it debonds everything from the surface of the metal substrate. Finally, the rate at which the debonded region increases in width for the cathodic delamination process was found to be linear when plotted versus the square root of time. This implies that cathodic delamination is a diffusion controlled process that follows Fick's laws for diffusion. Exactly what is diffusing along the bondline/delamination front during cathodic disbondment is a topic that will be investigated in future experiments. However, because cathodic delamination follows Fickian behavior, slopes derived from experiments such as those described in this document (figures 6 and 7) can be used to estimate how long it will take the delamination front to travel a given distance. This gives scientists and engineers another tool to use to predict how long a given piece of hardware subject to cathodic delamination at a given temperature would be expected to last.

The above facts have important implications for real outboard cable connectors. One would expect real connectors to fail from cathodic delamination from the exposed polymer-metal bond line in the vicinity of the connector nut down into the body of the connector. The fact that cathodic delamination is diffusion-controlled and follows the relationship

$$x^2 = t \qquad (3)$$

where "x" is the length of the debonded region and "t" is time means that connectors with longer backshells would be expected to survive longer under cathodic delamination conditions. This may also explain why connectors with multiple concentric grooves machined into their backshells also last longer under cathodic delamination conditions – because the grooves lengthen the path the delamination front must travel to allow water access to the interior of the connector. Finally, if someone suspects, but is not sure that his/her connector failed due to cathodic delamination, one way to tell would be to look at the surface of the metal backshell. That

surface should be free of any primer/polyurethane up to the point where the delamination front has reached. There may be some salt residue and/or calcareous deposits (carbonates precipitate from seawater under high pH conditions), but for the most part, cathodic disbondment leaves a bare metal surface in the wake of its delamination front. Connector debonds in which the primer remains bonded to the backshell metal surface are unlikely to have been caused by cathodic delamination.

The Arrhenius activation energies have implications for individuals wishing to conduct accelerated life tests on cable connectors (or any other kinds of hardware) subject to cathodic delamination. First, the magnitudes of the activation energies are consistent with diffusion controlled processes and are too low for chemical reaction controlled processes. Second, the two different primer/polyurethane systems had significantly different activation energies for the same basic process (cathodic delamination). This proves that there isn't just one activation energy for the "cathodic delamination process"; although some basic parameters of the cathodic delamination process may be similar from system to system, the different chemistries of the different systems will affect the rate at which each system debonds. The activation energy was low for the Cytec system; this implies that it will be difficult to accelerate the debonding process for that system using higher temperatures (as in a standard Arrhenius ALT). This makes sense, however, because our experiments indicated that cathodic delamination occurs quite fast with the Cytec system (even at room temperature). A process that occurs rapidly at lower temperatures should have a fairly low activation energy, and that is just what our experiments indicated for the Cytec system. The higher activation energy value for the PRC-DeSoto system suggests correctly that cathodic delamination does not proceed as quickly with this system as with the Cytec system. However, the higher activation energy also implies that cathodic delamination of the PRC-DeSoto system can be accelerated reasonably in a standard Arrhenius ALT (using heat as the accelerant). It is important to maintain the proper conditions for cathodic delamination within the ALT tank – especially the dissolved oxygen level, because the fundamental cathodic delamination reaction (equation 1) requires dissolved oxygen to be present for the reaction to occur.

V. CONCLUSIONS

Because cathodic protections systems of various designs are in widespread use throughout the U.S. Navy and the marine industry in general, many pieces of marine hardware, including ouboard cable connectors, suffer from cathodic delamination, a process that compromises metal-to-polymer bonds. Our research has confirmed that cathodic delamination preferentially begins at exposed metal-polymer bondlines. The delamination process is diffusion-controlled and its progress can be modeled using Fick's laws of diffusion. Cathodic delamination conditions produce a localized environment with a very high high pH, and these high pH conditions are responsible for the destruction of the metal-polymer bonds. The two most commonly used commencial primer-polyurethane systems for overmolding outboard cable connectors exhibited significantly different debonding behaviors when exposed to cathodic delamination conditions. When used directly on sandblasted metal surfaces, the PRC-DeSoto system (PR-420 primer and PR-1547 (amber) polyurethane) resisted cathodic disbondment for a longer period of time than did the Cytec system (AD-1146-C-1 primer and Conathane EN-1556 polyurethane). The ability of these two systems to resist cathodic delamination was reflected in the Arrhenius activation energies calculated for the delamination process from experimental data. The moderately high activation energy value for the PRC-DeSoto system (8.4 kcal/mole) was reflective of the system's resistance to cathodic delamination, while the rather low activation energy value calculated for the Cytec system (2.6 kcals/mole) is indicative of a system that is not very resistant to the delamination process. The activation energy values for cathodic delamination for both systems are different from the activation energy values for water diffusing through the two polyurethanes, thereby suggesting that the cathodic delamination process does not occur through thick encapsulant layers; instead, it preferentially attacks exposed metal-polymer bondlines.

ACKNOWLEDGMENTS

The authors thank Dr. R. Brown, Department of Chemical Engineering, University of Rhode Island, for many helpful discussions related to this work. A. Duszkiewicz (University of Rhode Island) assisted with the manufacture of many of the peel test samples, and M. Leff (NUWC Division Newport) analyzed all of the peel test samples using his Instron Machine.

REFERENCES

[1] Evans, U. R., "The Electrochemical Conversion of Painted Steel with Special Reference to the Alkaline Peeling of the Coat," *Transactions of the Electrochemcial Society*, vol. 55, 1929, pp. 243-248.

[2] Koehler, E. L., "The Mechaniism of Cathodic Disbondment of Protective Organic Coatings – Aqueous Displacement at Elevated pH," *Corrosion*, vol. 40, no. 1, 1984, pp. 5-8.

[3] Hamade, R. F., and D. A. Dillard, "Cathodic Weakening of Elastomer to Metal Adhesive Bonds: Accelerated Testing and Modeling," *Journal of Adhesion Science and Technology*, vol. 17, no. 9, 2003, pp. 1235-1264.

[4] Crank, J., *The Mathematics of Diffusion, 2nd Edition*, Oxford University Press, Oxford, UK, 1975.

[5] Aminabhavi, T. M., R. W. Thomas, and P. E. Cassidy, "Predicting Water Diffusivity in Elastomers," Polymer Science and Engineering, vol. 24, no. 18, 1984, pp. 1417-1420.

[6] "ASTM-D-429-08: Standard Test Methods for Rubber Property – Adhesion to Rigid Substrates, Method B" American Society for Testing and Materials International, 2008.