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EFFECTS OF INHIBITING WASHES ON THE CORROSION BEHAVIOR OF METALS IN DILUTED SEAWATER ENVIRONMENTS

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ABSTRACT

Several commercial products are suggested for use as freshwater rinse additives to enhance salt removal and to provide a residual protective film that can retard the rate of metal corrosion in seawater environments. These products have become increasingly attractive to the military as they face stronger demands to reduce the high costs of corrosion related repairs and extend the lifetimes of ground vehicles and other equipment operating in harsh marine environments. Presently, however, there have been few studies in which the additive performance has been demonstrated for various controlled conditions simulating those likely to be encountered in service. In this study the inhibitive performance of rinse water additives is assessed for conditions in which salinity is a moderating variable. Weight loss measurements are used to determine inhibitor performance for both aluminum and steel samples. Results are discussed in terms of the potential benefits and optimal conditions for their use.

Keywords: corrosion control, inhibiting washes, military equipment, marine environments, steel, aluminum.

INTRODUCTION

Operational maneuvers for military ground transport vehicles routinely include submersion in seawater and prolonged exposures to saltspray. Residual salt deposits combined with humidity during downtimes or storage promote the accelerated deterioration of metal components. As a result it has been shown that the operational lifetimes of military vehicles can be reduced by more than 30% and the costs for replacing individual damaged parts can be as much as 10% of the initial cost of the equipment. For example, replacement of steel frame rails on Marine Corps HMMWV's costs between $5000 to $7000 per vehicle.[1] As equipment ages maintenance and life cycle costs become significant.

In order to remedy the problems associated with corrosion, maintenance facilities on military bases are now exploring the use of commercial inhibitor additives to augment the recommended procedure of fresh water rinses following exposures. It should be noted that fresh water rinses are not always practical for the military either because of the time constraints of an active military operation or the limited availability of fresh water. Selection of appropriate treatments is complicated by the fact that it is very difficult to construct a "typical" set of conditions for usage of military equipment in order to determine the quantitative benefits from maintenance rinses. In addition, both aluminum and steel are used in large portions of military ground vehicle constructions. In an attempt to establish a baseline for the effects of water rinses on metal corrosion, Bieberich and Sheetz have measured the weight loss of steel and aluminum panels having a crevice of known geometry exposed to a marine environment.[2] These panels were subjected to fresh water washdown at one or two week intervals for one year. The results showed a decrease of up to a 30% in the corrosion rate of steel when it was washed down with fresh water with the corrosion rate being lower for the more frequent rinse cycle. With somewhat less certainty Bieberich's work showed that the depth of pits on aluminum was lower as a result of fresh water washes. This study went on to evaluate the effects of rinse water additives on the corrosion rates for the same conditions of exposure.

In previous work at the Naval Research Laboratory (NRL), the corrosion rates of steel and aluminum exposed to seawater rinses were tested for five inhibitor additives.[3] Tests were designed to reduce the complexity of the problem by directly studying the ability of each type of inhibitor to retard corrosion of aluminum and steel specimens under conditions of total seawater immersion. Under these conditions manufacturer claims for providing protection from seawater corrosion were verified and ranked for metals typically found in vehicular constructions. At that time no attempt was made to evaluate performance under conditions where intermittent drying and repeated immersion occurs or for saltspray environments. In addition, the study did not consider the effects of inhibitors on the paints used for vehicular camouflage and first line protection. Corrosion becomes a problem when there is some level of paint deterioration and the metals are exposed.

It is significant to note that the conditions of the experiments at NRL were not meant to mimic field conditions. It is expected that field conditions are inherently characterized by high levels of variability which would in turn influence the effectiveness of any given inhibitor. One objective of the analysis was to isolate experimental conditions that are controllable, or minimally variable, and representative of a relatively optimal situation for inhibitor activity. That is to say, experimental conditions where a given metal is known to be in the presence of inhibitor species being tested. In so doing, it was expected that the results of the study would provide figures of merit for the purposes of correlating the effects of inhibiting washes on the corrosion behavior of metals. In this study it was shown that, in general, the additives tested had a deleterious effect on the corrosion of aluminum, increasing the size and number of pits relative to the control. For steel immersed in seawater individual additives reduced corrosion rates from 11 to 83%.

In the present study, we returned to the problem of scarcity of fresh water during washdown procedures. Three of the most promising additives from the earlier work were selected for testing in diluted seawater to determine the effects on corrosion rates. The idea being that using the additives in watered-down seawater may prove beneficial. This concept was tested under the same conditions of our previous work.

EXPERIMENTAL

Materials:

Three commercial corrosion control products, designated ADD 1, ADD 2 and ADD 3,[1] that showed beneficial results in our earlier work were tested in this study. Weight loss measurements during full immersion in seawater doped with the additives were used to determine corrosion rates. The manufacturers and descriptions of each product are shown in Table I along with the dilutions used in this study. These dilutions are what the manufacturer recommends for preparing fresh water rinse solutions.

Test samples were 1 inch (2.54 cm) x 2 inch (5.08 cm) coupons cut from 1/8th inch (0.32 cm) Aluminum alloy 6061 and AISI Grade 1018 steel panels. These alloys represent materials that are typically used for military ground vehicle constructions. One eighth inch (0.32 cm) diameter holes were drilled on one end of the coupons to accommodate nylon threads used for suspension in 200 ml jars containing test solutions. All samples were rinsed sonically in methanol and then in water. The samples were then dried, weighed, and stored in a desiccator until the tests were started.

Procedures:

The manufacturer recommended dosage of inhibitor was added to stock solutions of artificial seawater[4] diluted to half and quarter strength with distilled water. Two hundred milliliters of the trial solutions were added to the test jars and the metal samples were immersed by suspension from plastic lids. Triplicate samples were used for each trial. Contact with ambient air was assured through the half-inch holes that had been drilled in the jar lids. After twelve weeks the metal samples were removed from solution, rinsed, and then the corrosion products were removed according to standard procedures.[5] The samples were than reweighed to determine corrosion rates. Figure 1 shows an example of the test set up.

RESULTS AND CONCLUSIONS

Observations concerning steel:

Shown in Figure 2 are the results of our accelerated corrosion tests for steel. Several observations follow from these results. The corrosion rate of steel is reduced nearly 50% when the seawater concentration is diluted 50% but remains relatively constant for further dilution to 25%. The trends in weight loss with seawater dilution for ADD 1 are about the same as for undiluted seawater. This additive showed the least benefit in reducing the corrosion rate of steel relative to the others tested. A difference of 22% between ADD 1 and seawater is observed relative to maximum seawater strength. ADD 2 and ADD 3 show the greatest reduction in the corrosion of steel at all concentrations. Reductions of 58% and 78% for ADD 2 and ADD 3, are observed for full strength seawater The corrosion rates are not observed, however, to decrease significantly with seawater dilution for ADD 2 and ADD 3.

Conclusions concerning steel:

Our observations support several conclusions. In the presence of ADD 2 and ADD 3 there are significant reductions in the corrosion rate of steel. Significant reductions in corrosion rates are realized in seawater diluted to half strength. Some benefits can be achieved by rinsing steel with diluted seawater. No significant changes occur upon further dilution. Use of ADD 2 and ADD 3 results in significant reductions in corrosion rates of steel. The corrosion rates observed are under optimum control conditions, which are representative of situations where the metal is known to be in the presence of the inhibitor. This is in contrast to relatively less controlled conditions where samples experience

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[1]ADD 1, ADD 2 and ADD 3 represent Chlorid, Cortec VCI-416 and Salt Away, respectively

multiple exposures to saltwater or rain. These results support the conclusion that saltwater rinses which include ADD 2 and ADD 3 can be effective in reducing rates of corrosion.

Observations and conclusions concerning aluminum:

Shown in Figure 3 are the results of our accelerated corrosion tests for aluminum. Several observations and conclusions follow from these results. Essentially no change in corrosion rate is observed for aluminum with seawater dilution. These results were not surprising based on our present understanding of the role of chloride ions in the pitting of aluminum. The corrosion rates of aluminum are markedly increased in the continued presence of ADD 1 and ADD 3 (by factors of 24 and 28, respectively). More numerous, larger and deeper pits are observed on the aluminum in these situations (see Figure 4 for example). Somewhat fewer pits are observed on aluminum in the presence of ADD 2 as compared to seawater. Rinses with ADD 1 and ADD 3 should be avoided for aluminum samples. It is significant to note that although the overall corrosion rates are increased in the presence of ADD 1 and ADD 3, reductions in corrosion rates are again realized in diluted seawater. The singular trend observed in Figure 3 for seawater doped with ADD 1 supports the conclusion the point of maximum dilution is a statistical outlier requiring further sampling.

Correlation of results to those of other tests:

As mentioned earlier, Bieberich and Sheetz[2] have reported results of corrosion tests which include evaluation of some of the washdown additives considered in this study under conditions of marine environment exposure. In particular, their study showed some reduction in the corrosion rates of new steel rinsed in seawater followed by a rinse with fresh water containing additives (as per the manufacturer recommended levels of dilution). This result can be correlated with the trend shown in Figure 3 for seawater without additives. Our results are in agreement with their observations which support the recommendation that for steel the use of ADD 1 not be pursued for practical application to USMC vehicles. It is significant to note that for steel, however, our results do support the use of ADD 3 which they have not recommended. In the case of aluminum our results are consistent with their observations concerning the relative effectiveness of ADD 1 and ADD 3.

SUMMARY

The objective of this work was to examine the intrinsic capacity of commercial rinse additives to affect corrosion rates of aluminum and steel specimens representative of materials of construction for Marine Corps vehicles. Controlled laboratory exposures were designed to afford the maximum potential of the additive to reduce corrosion rates. That is, the experiments were such that it was clear that the additive could make contact with the metal surfaces or be able to affect the process leading to corrosion. This approach represents an initial step towards a quantitative assessment of whether, in fact, rinse additives have the potential to reduce corrosion rates on operational vehicles and an attempt to rank their effects for various seawater environments.

Based on the trends in our experimental results the following observations can be made.

1. The corrosion rate of steel is reduced as seawater is diluted to half strength and this rate is maintained with further dilution. This suggests that for situations where fresh water is scarce, rinses of exposed steel surfaces with diluted seawater may prove beneficial.

2. ADD 1 provides poor protection to steel in seawater, however significant reductions in corrosion rates are observed for ADD 3 and ADD 2, in that order. It is important to note that for the other two additives the action of the inhibitor seems to overcome that of the seawater.

3. In the case of aluminum, pitting is significantly increased in seawater containing ADD 1 and ADD 3 for all seawater concentrations. Rinses containing these additives should be avoided for aluminum parts. In the presence of ADD 2 aluminum pitting is about the same as for seawater.

4. A significant, and yet somewhat subtle, result of this analysis is that it supports an increased confidence level concerning the overall concept of using inhibitor additives or reductions in seawater concentration as viable methods of corrosion control. The results shown in Figures 2 and 3 demonstrate a high degree of sensitivity to differences in the types of washdown additives, and further, a marked and statistically reliable reduction in corrosion due to either the presence of inhibitor or reduction in seawater concentration.

5. The effects of the additives tested show some correlation with long-term marine exposure results.

6. Using the results from this study as a base-line, follow-up work should examine the adherence of rinse additives to dried metal surfaces for temporal and mechanical applications of rinsing solutions containing these additives.

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Table 1 Rinse Water Additives

ADDITIVE	DESCRIPTION	DOSAGE
ADD 1	Water additive for salt removal and corrosion inhibition	23.4 ml/L
ADD 2	Water based cleaner and degreaser that deposits a corrosion resistant film on metals	10.2 ml/L
ADD 3	Water additive for salt removal and corrosion inhibition	23.4 ml/L

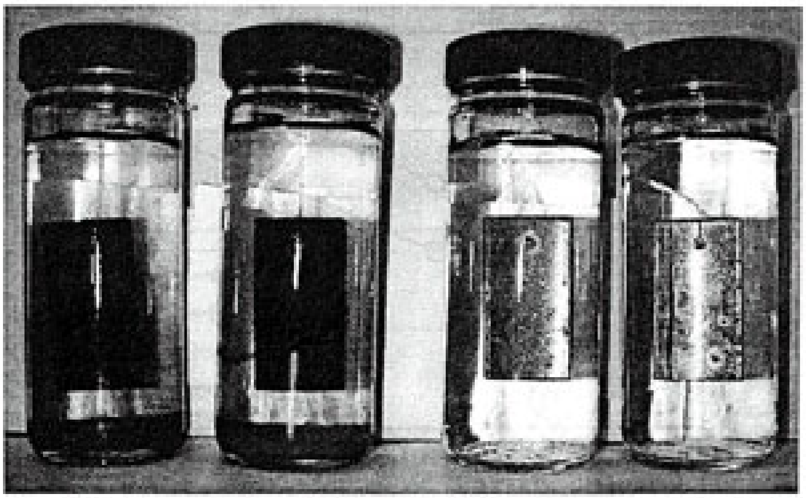

FIGURE 1: Sample bottles from left to right, steel in 1/4 and 1/2 strength sea water, aluminum in 1/4 and 1/2 strength sea water.

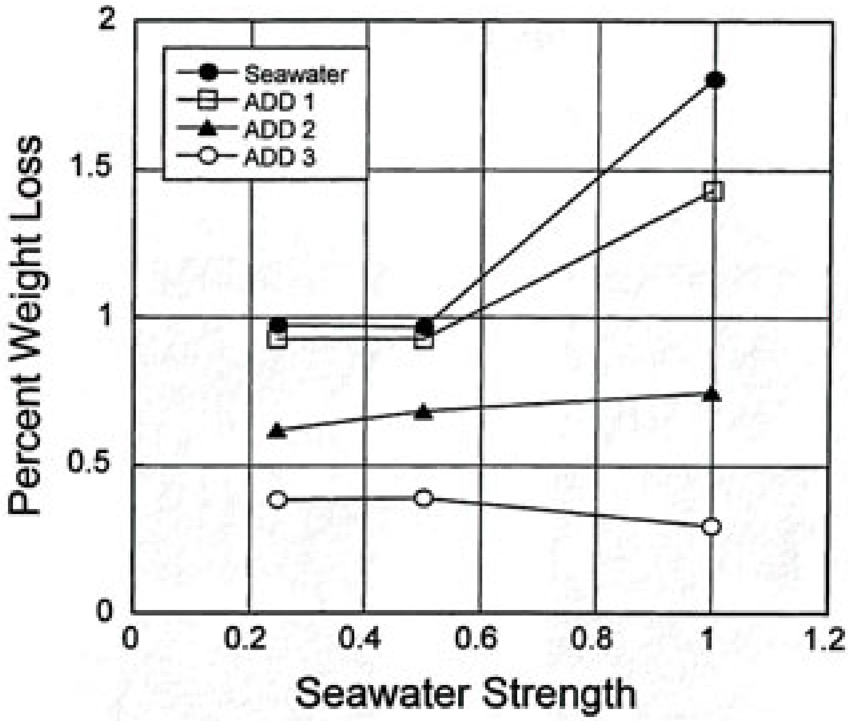

FIGURE 2: Plot of percent weight loss of steel as a function of seawater strength for various inhibitors.

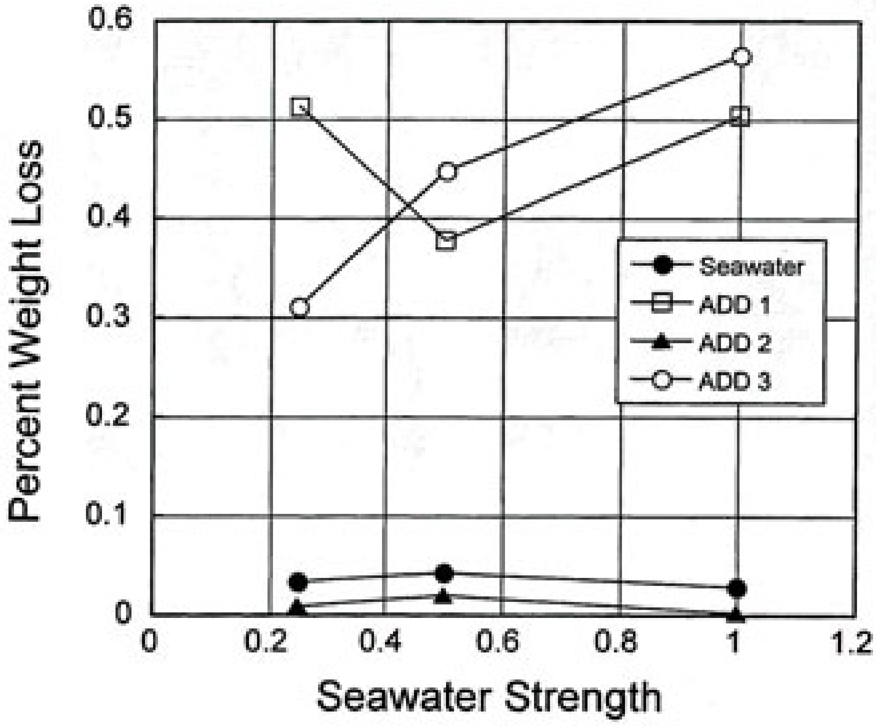

FIGURE 3. Plot of percent weight loss of aluminum as a function of seawater strength for various inhibitors.

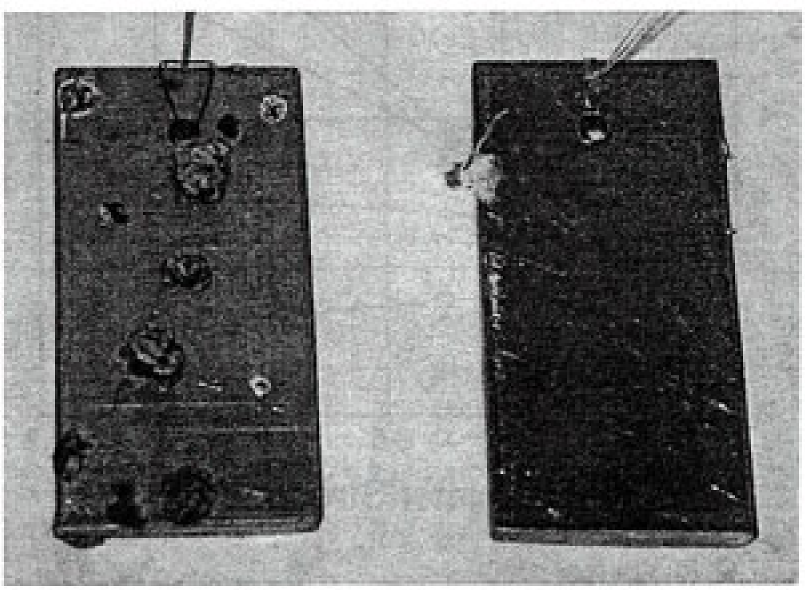

FIGURE 4: Comparison of the extent of pitting on aluminum samples following immersion in seawater containing ADD 3 (left) and seawater without an additive (right).