A Comparative Study of Corrosion Inhibitors for the Treatment of Archaeological Copper and Copper Alloys

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ABSTRACT

The performance of two different corrosion inhibition solutions and two different immersion times for the treatment of archaeological copper and copper alloys was evaluated. The corrosion inhibitor solutions examined were a standard benzotriazole (BTA) in ethanol solution and a combination solution containing both benzotriazole (BTA) and 5-amino-2-mercapto-1,3,4-thiadiazole (AMT) in ethanol. Non-inventoried archaeological fragments were used as test samples and were immersed in the test solutions for periods of one and 24 hours. After treatment the test samples were aged using high humidity and the performance of the corrosion inhibitors was compared based on when the test samples began to corrode and the number of the test samples that corroded in each test group. The one-hour simple immersion of artifacts in BTA was found to perform better than the 24 hour immersion, but more data is needed to evaluate the performance of the BTA and AMT combination.

INTRODUCTION

Corrosion inhibitors have been used in conservation to prevent the continued corrosion, and often, rapid deterioration of archaeological copper and copper alloy artifacts after their removal from the burial environment. Both patinas and corrosion products result from the chemical interaction between the burial environment and the metal surface (Scott 2002; Carroll 1997). Corrosion can be defined as a destructive or discontinuous surface that obscures the original form of the object while a patina is a "continuous layer that preserves detail and shape" (Scott 2002: 10). The corrosion layers and patinas on archaeological artifacts are often a mixture of products due to the complex chemistry and numer-

ous variables involved. As a result, the study of the performance of corrosion inhibitors can be challenging and the results difficult to interpret, especially when conducted on original artifacts. Although testing on artificially corroded samples may allow for the elimination of unknown variables, the results can markedly differ from the testing on original artifacts (Golfomitsou 2006; Uminski and Guidetti 1995). Both methods have been employed to evaluate the performance of corrosion inhibitors used on copper and copper alloy artifacts to prevent bronze disease.

The term, bronze disease is used to describe a type of corrosion that is particularly destructive to archaeological copper alloys artifacts. It refers to progressive and extreme deterioration resulting from the conversion of nantokite (cuprous chloride) to basic copper chlorides (paratacamite, atacamite, and botallackite) through exposure to moisture and oxygen. These corrosion products are frequently identified by their appearance, as nantokite is a waxy, very soft, grey corrosion product and basic copper chlorides are pale green and powdery (Scott 1990, 2002; Carroll 1997). Based on previous analysis of copper alloys by numerous researchers, the resulting basic copper chlorides on most archaeological artifacts are a mixture of predominantly paratacamite and atacamite (Scott 1990). This reaction has the potential to be highly destructive due to the mobility of chloride anions. In the burial environment these anions can penetrate deep into the metal core of an object as they are drawn in to balance the charge of ongoing electrochemical reactions occurring as the copper metal is converted to copper cations. The presence of the chloride ions within the artifact allows nantokite to form under the outer zone of the patina, within the metal core of the object, or at the base of corrosion pustules (Scott 2002). Nantokite is insoluble in

water and stable under certain conditions allowing it to remain dormant for extended periods of time depending on the storage conditions of the excavated artifact (Carroll 1997; Scott 1990). However, when it is exposed to moisture and oxygen it becomes unstable and reacts to form a basic copper chloride causing severe damage due to its location beneath the patina of the object. This damage is caused by the stresses that result from the expansion in volume as the nantokite is converted to basic copper chlorides and takes the form of pitting, cracking, and fragmentation (Scott 1990, 2002; Carroll 1997).

The corrosion inhibitors used in conservation were adapted from applications in industry. These chemical treatments were developed to be applied on cleaned metal surfaces, rather than already corroded surfaces as are found on archaeological artifacts. For this reason, their application has been heavily tested over the years in attempts to find compounds that meet the criteria for a conservation material on archaeological artifacts (Faltermeier 1999; Sease 1978; Ganorkar *et al.* 1988; Golfomitsou 2001; Golfomitsou and Merkel 2007; Golfomitsou 2006). The corrosion inhibitors that have been examined typically form a protective layer over the object and interfere with the anodic side of the corrosion reaction, the cathodic side of the corrosion reaction, or both (Faltermeier 1999; Scott 2002; Sease 1978; Ganorkar *et al.* 1988). The effect this treatment has on the visual appearance of the object is also a critical factor in the selection of corrosion inhibitors for use in conservation (Faltermeier 1999; Golfomitsou 2006). The two most widely studied corrosion inhibitors have been benzotriazole (BTA) and 5-amino-2-mercapto-1,3,4-thiadiazole (AMT), with only the former having been widely utilized in practice for the treatment of copper and copper alloys.

CORROSION INHIBITORS IN CONSERVATION

BENZOTRIAZOLE

Benzotriazole (BTA) has the longest history of use in conservation (Sease 1978; Scott 2002). Typically, objects are immersed in a dilute BTA solution (in distilled water or ethanol) under vacuum (Faltermeier 1999; Scott 2002; Sease 1978;

Drayman-Weisser 1994; Kaye, Cole-Hamilton, and Morphet 2000; Golfomitsou 2006). BTA is a nitrogen heterocycle derivative with three nitrogen atoms. There are two long pairs of electrons associated with the nitrogen ring which allows this compound to form coordination complexes (Sease 1978). BTA has been found to complex specifically with copper but with a range of possible Cu-BTA complex structures resulting depending on the conditions of the treatment. The predominant complex that forms is inert, insoluble in water and most organic solvents, and appears to be polymeric in nature (Sease 1978; Scott 2002; Ganorkar *et al.* 1988). However, the Cu-BTA complexes are still not entirely understood (Scott 2002; Sease 1978). The electrochemical properties of the complex indicate that it not only blocks corrosion through the formation of a protective film but that it also interferes with the anodic and or the cathodic reaction during oxidation of copper and reduction of oxygen (Sease 1978).

Despite its recognized effectiveness on corroded surfaces, BTA has some important limitations. Not all artifacts are stabilized by treatment and re-treatment has often found to be necessary (Drayman-Weisser 1994; Scott 2002; Faltermeier 1999; Carroll 1997). Research into this problem has found that the formation of a protective film is influenced by pH, and that low pH environments are not favorable to its formation. In particular, exposed nantokite (cuprous chloride) may not be stabilized by the BTA treatment, as it can have a pH of 3.5-4, and in chloride pits the pH is likely to be even lower (Scott 2002; Faltermeier 1999; Golfomitsou 2006). Another issue with BTA is that it does alter the appearance of the object by darkening the surface (Faltermeier 1999; Golfomitsou 2006).

In addition to these issues, there are a number of safety concerns associated with BTA based on two papers in *Studies in Conservation* by Oddy where he discusses the existing medical testing and the need for additional testing (1972, 1974). The main health concerns with BTA are that it is toxic if ingested and may be a carcinogen (Scott 2002; Sease 1978; Faltermeier 1999; Oddy 1972, 1974). Since Oddy's publications, BTA has been the subject of numerous studies to determine its carcinogenicity in both short term and long-term studies in the United States. These studies have been inconclu-

sive (National Toxicology Program 2010; National Cancer Institute 1978). Current information from Material Safety Data Sheets available for BTA consistently label it as harmful if inhaled or swallowed but offer no additional information on its carcinogenicity (Fischer Scientific 2007; J.T. Baker 2008; Science Lab.com 2008). Whether BTA is carcinogenic or not, the health and safety guidelines outlined by Oddy for the use of BTA are easily achieved in any laboratory and should remain recommended practices for the use of BTA in chemical treatments of copper and copper alloy artifacts. He suggests that care should be taken not to inhale the dry powdered BTA when preparing solutions, gloves should be worn during treatment, that the solution should not be allowed to evaporate to dryness during treatment, and that glassware should be cleaned thoroughly after treatment. Finally he also recommends that BTA should never be heated as it sublimes at 98°C (Oddy 1972). These safety precautions have become standard methods in BTA treatment protocols and are consistent with those used at Kaman Kalehöyük.

5-AMINO-2-MERCAPTO-1,3,4-THIADIAZOLE

Due to the limitations of BTA in low pH environments, 5-amino-2-mercapto-1,3,4-thiadiazole (AMT) has been proposed as an alternative as it does complex in low pH environments. Furthermore, AMT can function as both a corrosion inhibitor and as a cleaning agent. In the initial studies using AMT on archaeological artifacts it was found to form a complex film over the metal while simultaneously cleaning the objects treated. The objects were immersed in an aqueous solution of AMT with a few drops of acid under vacuum. This process resulted in the formation of a yellowish precipitate, which was removed by washing the object in distilled water (Ganorkar *et al.* 1988). The cleaning action results from the formation and removal of the yellow precipitate. This precipitate is the byproduct of the reaction between AMT and nantokite, and has not occurred in other studies using alternative methodologies unless nantokite was exposed during mechanical cleaning prior to immersion in an corrosion inhibitor (Faltermeier 1999). The main reason for the limited application of AMT has been the concern associated with the potential cleaning action of this corrosion

inhibitor. Retention of surface patinas and corrosion layers is preferable in some cases as information from the burial environment can be obtained from these layers (Scott 2002). Furthermore AMT has been found to cause surface darkening and to be less effective than BTA (Faltermeier 1999).

TREATMENT OF COPPER AND COPPER ALLOYS AT KAMAN-KALEHÖYÜK

Kaman-Kalehöyük has been a center of research and experimentation in the treatment of archaeological copper and copper alloy artifacts since the 1980's. The documentation of these treatments available in the treatment database demonstrate the usefulness of this type of documentation for the reevaluation of treatments as well as a record of the shifting and ever developing approaches to chemical and preventive treatment of archaeological copper and copper alloys.

Currently at Kaman-Kalehöyük, chemical treatment of copper and copper alloys has been abandoned. Beginning in the 2010 field season, objects were cleaned mechanically and then stored using the Revolutionary Preservation System (RP System). This method works through the removal of the reactive components of the storage environment (water and oxygen) by sealing the artifacts using an enclosure with good impermeability to gas exchange such as ESCAL (linear low density polyethylene), along with a desiccant and an oxygen scavenger (Mathias, Ramsdale, and Nixon 2004).

Prior to this shift, the standard treatment of copper and copper alloys at Kaman-Kalehöyük has been chemical treatment using BTA. The concentration of the BTA solution has changed over time, with the most recent standardized chemical treatment being immersion under vacuum in a 0.25M solution of BTA in ethanol (Treatment Protocols).

Original research into developing improved methods for the application of corrosion inhibitors has also been conducted using artifacts excavated from Kaman-Kalehöyük. In 2000 and 2001 Golfomitsou oversaw treatment of 220 of the small find excavated from Kaman-Kalehöyük as part of her PhD dissertation studying the synergistic effects

of additives with BTA (Golfomitsou 2006). The treatments were selected based on preliminary and extensive testing conducted in the lab on artificially corroded metal coupons of known composition and included evaluation of a range of corrosion inhibitor solutions, treatment times, and treatment methods. The artifacts selected in her study ranged in form, historical period, and excavation date. The treatments were evaluated based on accelerated aging through 24 hour exposure to 100% RH by suspending the object over water in a sealed chamber. This was followed by an annual survey of the objects for the long term evaluation of their stability (Golfomitsou 2006). The data from the long-term study, although not included in her dissertation, remains on file in the conservation lab at Kaman-Kalehöyük. The performance of the treatments was evaluated on a graded system based on the number and severity of points of corrosion on each artifact. Among Golfomitsou's findings is that the immersion time of a treatment is more critical than whether the treatment was conducted under vacuum. For this reason, she abandoned vacuum impregnation during the second season of treatments (Golfomitsou 2006). In her tests comparing BTA treatments, she found that a BTA solution of 0.25M in ethanol for one hour, was more effective than longer treatment times and than other BTA concentrations (Golfomitsou 2006, 2001). In addition, she found that BTA and AMT in combination had a synergistic effect with the combination of 0.1M BTA and 0.01M AMT being the most effective corrosion inhibitor overall in both the short term and the long-term evaluation of the treatments (Golfomitsou 2006).

COMPARISON OF BTA AND THE BTA/AMT COMBINATION AS CORROSION INHIBITORS

METHODOLOGY

The present study was devised to compare the performance of a standard BTA treatment to the combination treatment using BTA and AMT developed by Golfomitsou as part of her PhD research and to confirm her previous results (Golfomitsou 2006). Two rounds of testing were conducted each with slightly different methodologies. The second round of testing was conducted principally to eliminate certain issues of contamination that will be discussed below. The test samples for test one were selected from non-inventoried artifacts excavated in 1999. The test samples for test two were also selected from non-inventoried artifacts excavated in 2005. The artifacts in both rounds of testing represented a range of historical periods, and dimensions. These were mostly unidentifiable fragments, which is why they were non-inventoried and each test sample consisted of one of these non-inventoried fragments. In all likelihood, the test samples represented a range of copper alloy compositions as well. Avoiding this variable at Kaman would be exceedingly difficult as previous research has found that even artifacts with the same form, and from the same period can have a range of compositions (Masubichi and Nakai 2003). The test samples were initially selected based on visual examination. Artifacts with pale green powdery corrosion typical of 'bronze disease' were separated out from the season's finds as possible candidates for testing. To confirm the presence of basic copper chlorides samples of the powdery corrosion were taken from each of the artifacts and tested for chlorides using the silver nitrate test as described in *Material Characterization Tests for Objects of Art and Archaeology* (Odegaard, Carroll, and Zimmit 2005). Those that tested positive were set aside. Of those that tested positive there were a number of fragments which clearly had little to no remaining metal core based on their relative light weight and in some cases, hollow cross-section. These artifacts were also eliminated and the 25 test pieces were selected from the largest remaining artifacts. It was not possible for both tests to be conducted on materials from the same season, as there were insufficient fragments that fit the necessary criteria from a single season for two rounds of testing. These 25 test samples were numbered and then divided into five test groups of five test samples each.

In both rounds of testing, after the test samples were selected, they were cleaned using a glass bristle brush and a scalpel to remove soil from the burial environment and the powdery green corrosion. This was done to facilitate observations during testing, so that new corrosion would be more readily apparent.

The test samples for both rounds of testing were divided into five different test groups: standard BTA

treatment for one hour, standard BTA treatment for 24 hours, BTA/AMT combination treatment for one hour, BTA/AMT combination treatment for 24 hours, and a control group. The control group received no treatment. The test groups, excluding the controls, were degreased in acetone prior to treatment for 15 min. The test samples were then allowed to dry and were then immersed in the corrosion inhibition solutions for either one or 24 hours. The standard BTA treatment was based on the solution concentration recommended in the lab manual in the conservation lab, and consisted of treatment using a 0.25M BTA in ethanol solution. The BTA/AMT combination treatment involved immersion in a 0.1M BTA and 0.01M AMT in ethanol corrosion inhibition solution. Treatment was not conducted under vacuum based Golfomitsou's findings (2006).

In test one, the stock solution of ethanol was used to prepare the corrosion inhibition solutions. During the preparations for the first round of testing there were some concern that the stock ethanol was either not very pure or contaminated. This concern arose when one of the artifacts excavated in the 2010 season and undergoing treatment in the conservation lab, began to corrode while immersed in the stock solution of ethanol. As no other ethanol was available at the time, a different container of the stock solution was used to prepare the corrosion inhibitors. To ensure that this solution would not cause additional problems during testing, one of the artifacts meeting testing criteria, but not selected for testing, was placed in the stock ethanol overnight. No corrosion was observed during this period. For this reason it was felt that the ethanol could be used. However, during the second round of testing a high-grade ethanol arrived in the lab (ethanol absolute, 99.8% ethanol) and so this was used to prepare the corrosion inhibition solutions during the second round of testing.

Once the test samples were removed from the corrosion inhibition solutions they were allowed to dry. Each test group was then placed into a humidity chamber consisting of a sealed clear plastic container with a data logger, and a saturated salt solution, forming five humidity chambers. Previous research on accelerating aging of metals has found that there is a correlation between the rate of corrosion of protec-

tive-coated metals (coatings were applied as the rate of corrosion was based on leakage of current through an organic insulator) and the sum of the RH and the temperature (in °C). A typical method of exposing samples to high RH is through the use of a saturated salt solution. This is because the concentration of water vapor in equilibrium with a saturated salt solution is constant although temperature dependent (Feller 1994). After testing was completed, the information from the data loggers was exported to Excel and the conditions for each chamber were graphed and compared to ensure that the aging conditions were consistent between the chambers. The data loggers were set to collect two readings a day, one in the morning and one in the afternoon, and recorded the temperature and the relative humidity at that time. For the first round of testing a saturated sodium chloride solution in water was used. Previous researchers have used sodium chloride to obtain RH levels around 73% at 100°C (Feller 1994). A high value was expected during testing, as the temperature in the chambers would be the ambient temperature in the lab, and well below 100°C.

After the initial round of testing it was felt that the sodium chloride solution may be a source of contamination, creating an environment far more corrosive to the metal surfaces than desired. For this reason a different salt solution was selected for the second round of testing. Unfortunately, the only other available option in the lab was potassium iodide, which has been found to yield a much lower relative humidity. Previous researchers using potassium iodide have found it gave an RH around 56% at 100°C (Feller 1994). Again it was expected that the RH would be above 56% in the chambers as the temperature would be ambient, and therefore below 100°C. Although this RH was significantly lower than the one used in the first round, it was still deemed acceptable based on previous research and recommended storage environments for copper alloys. Corrosion rates have been found to rapidly increase above 55% RH and it is recommended that copper alloys should be stored at below 46% RH (Scott 1990). Again the saturated salt solution was placed into each of the humidity chambers. Another difference between the two rounds of testing was the length of time that the test samples were left in the humidity chambers. In the first round of

testing, the test samples were aged for 8 days, while in the second round the test samples were aged for 10 days. Observations of the test samples were conducted through the clear plastic and the date at which visible corrosion appeared on the surface of each test sample was recorded during both rounds of testing.

Prior to and throughout testing, the test samples were documented photographically. In test one and two, overall images of the test samples were taken before cleaning, after cleaning, after treatment, and after aging. In addition, digital photomicrographs of two areas on each artifact were taken after cleaning, and after aging. In the first round of testing digital photomicrographs were also taken before cleaning, but this was not found to be helpful for analysis and so was not continued for the second round of testing. Digital photomicrographs were taken after treatment only in cases where the appearance of the object was noticeably altered by the corrosion inhibition treatment (darkening, and in some cases formation of BTA crystals on the surface which were removed by localized swabbing with ethanol).

The performance of the corrosion inhibition treatments was evaluated by comparing the number of test samples in each group exhibiting active corrosion at both the mid point of aging and the end point of aging. The method used by Golfomitsou, where performance was evaluated based on number of corrosion points, could not be used due to the small size of the test samples used in this study.

All of the digital photography was conducted using a 27 mm Olympus Camedia C-5060 wide zoom digital camera (5.1 Megapixel). The digi-tal photomicrographs were also taken using this camera with a mount constructed in the lab to allow for the images to be captured through the ocular of a binocular microscope. The microscope used was a Carton DSZT44. All images included a scale in mm, as the exact magnification could not be determined.

RESULTS

First Round of Testing

All of the graphs produced from the data gathered by the data loggers in the humidity chambers during aging of the test samples showed regular and consistent daily cycles. The plotted data of the relative humidity (RH) showed a similar pattern in all of the chambers as well with a rapid increase in RH followed by a gradual decrease in RH over time. This gradual decrease is likely due to leakage of humidity from the chambers. The average temperatures and RH can be seen in Table 1 along with the minimum and maximum temperatures and RH recorded (the initial RH reading was excluded as this reading was taken shortly before the chambers were sealed and is not reflective of the relative humidity during aging). The temperatures are comparable in all of the chambers with averages all between 26°C and 25°C. The RH was comparable in most of the chambers with all but one group having averages between 80.2% RH and 81.6% RH. The exception is the chamber containing the test samples treated in BTA for one hour. This chamber had lower maximum and minimum RH values and so has a lower average as well.

Table 1 Environmental Conditions in the 5 Humidity Chambers in the 1st Round of Testing

Test samples contained in the humidity chamber	Average Temperature (°C)	Temperature range (°C)	Average Relative Humidity	RH max and min (excluding the initial reading)
Control (no treatment)	25.6	26.8-24.4	80.6%	86.1-78.6
BTA 1 hour	25.5	26.8-24.4	78.3%	83.7-73.7%
BTA 24 hours	25.7	27.1-24.4	81.2%	87.9-78.9%
BTA/AMT 1 hour	25.6	27.3-24.4	80.2%	86.2-77.9%
BTA/AMT 24 hour	25.6	26.9-24.4	81.6%	85.7-80.51%

Furthermore, the relative humidity was slower to rise in this chamber after it was sealed compared to the others, likely indicating a poorer seal as compared to the other groups.

All of the test groups had at least two test samples with active corrosion by the end of the accelerated aging within their respective humidity chambers (8 days). A difference in the susceptibility to corrosion can be seen by comparing the number of test samples, out of the five in each of the five test groups, that exhibited active corrosion after 4 days of accelerated aging and after completing accelerated aging at 8 days in the humidity chamber. After 4 days exposure to high humidity three test samples in the control group exhibited corrosion, none of the test samples treated in BTA for one hour had any corrosion, two of the test samples treated in BTA for 24 hours had active corrosion, four test samples treated in the BTA/AMT combo for one hour had active corrosion, and one test sample treated in the BTA/AMT combo for 24 hours had corrosion. At the end of the 8 day accelerated aging period, all five of the control test samples had active corrosion, four of the test samples treated in BTA for one hour had active corrosion, all five of the test samples treated in BTA for 24 hours had active corrosion, all five of the test samples treated in BTA/AMT combo for one hour had active corrosion, and two out of the test samples treated in the BTA/AMT combo for 24 hours had active corrosion.

Second Round of Testing

All of the graphs produced from the data gathered by the data loggers in the humidity chambers during aging of the test samples showed regular and consistent daily cycles. The plotted data of the relative humidity (RH) showed a similar pattern in all of the chambers as well with a rapid increase in RH followed by a gradual decrease over the testing period followed by a rapid drop after the chambers were opened. The chambers were all more tightly sealed in the second round as there was less variability between chambers and there was less of a decrease in RH over time. The average temperatures and RH can be seen in Table 2 along with the minimum and maximum temperatures and RH recorded (the initial RH reading and the final reading were excluded as these were taken shortly before the chambers were sealed and after they were opened and are not reflective of the relative humidity during aging). The conditions within all of the chambers were comparable with average temperatures ranging from 27.5°C to 27.8°C, and average RH ranging from 66.1% to 67.0%.

All of the test groups exhibited at least two test samples with active corrosion by the end of the accelerated aging within each group's respective humidity chamber (10 days). There was little change in the test samples (five test samples per each group) after the initial 5 days of aging as the majority of the test samples, which exhibited corrosion at the completion of the experiment, had corroded by 5 days in the chamber. There is possibly a slight difference in the observed susceptibility of the test samples to corrosion despite the lower relative humidity in the second round of testing. After 5 days in the humidity chamber four of the test samples in the control group had active corrosion,

Table 2 Environmental Conditions in the 5 Humidity Chambers in the 2nd Round of Testing

Test samples contained in the humidity chamber	Average Temperature (°C)	Temperature range (°C)	Average Relative Humidity	RH max and min (excluding the initial reading and the final reading)
Control (no treatment)	27.5	28.7-26.3	66.4%	67.3-63.1%
BTA 1 hour	27.6	28.8-26.3	67.0%	69.2-65.6%
BTA 24 hours	27.8	29.1-26.4	66.6%	68.3-64.7%
BTA/AMT 1 hour	27.8	30.3-26.4	66.1%	67.6-64.3%
BTA/AMT 24 hour	27.6	29.4-26.3	67.0%	69.0-65.1%

one of the test samples treated in the BTA for one hour had corrosion, two of the test samples treated in BTA for 24 hour had active corrosion, three of the test samples treated in the BTA/AMT combo for one hour had active corrosion, and three of the test samples treated in the BTA/AMT combo for 24 hours had active corrosion. After 10 days in the humidity chambers four of the test samples in the control group exhibited active corrosion, two of the test samples treated in BTA for one hour had active corrosion, three of the test samples treated in the BTA for 24 hours had corrosion, three of the test samples treated in BTA/AMT combo for one hour had corrosion, and three of the test samples treated in the BTA/AMT combo for 24 hours had corrosion.

DISCUSSION

In the present study the selection of the top performing corrosion inhibitor treatment was based on the test groups: on performance within the first half of accelerated aging and overall. As was expected the control group with no treatment performed the worst in both rounds of testing. Based on the results in the first round of testing with test samples exposed to the much higher relative humidity the test samples treated in the BTA for one hour performed the best in the first half of the aging period, but by completion of the accelerated aging in the humidity chamber, the BTA/AMT combo for 24 hours had the least number of corroded test samples. It should be noted that the BTA for one-hour test samples were exposed to a slightly lower RH in the humidity chamber during aging as compared to the other test groups. This difference in aging conditions is likely due to an incomplete seal of the chamber, especially as the temperatures recorded were fairly consistent across the test groups.

In the second round of testing the BTA treatment performed better in the initial half of aging, and continued to perform better than the other test samples throughout the experiment. In the first round of testing the BTA/AMT combination for one hour performed the worst and only slightly better than the control group with no treatment. In the second round of testing there is less clear differ-

ence between the BTA/AMT for one hour and 24 hour treatment, as both performed equally poorly. The differences between the different test groups in general in the second round of testing was slight likely as a result of the much lower relative humidity used in this round of testing.

Although there were concerns about contamination from the sodium chloride solution used in the humidity chamber, all of the test samples would have been exposed to similar levels of chloride contamination and so the results can still be used as a form of evaluation for the performance of the corrosion inhibitors, especially as in the second round of testing so little difference in behavior was apparent. Furthermore, as the test samples treated with the corrosion inhibitors in the first round of testing all performed better than the test samples with no treatment and the use of the high grade ethanol in the second round seems not to have markedly improved the corrosion inhibitor effectiveness overall, it is unlikely that the use of the stock ethanol in the first round of testing had any strong effect on the results. Even so, there are some common features in both rounds of testing. In both rounds the BTA treatment for one hour performed better than the BTA for 24 hours, which is consistent with Golfomitsou's findings. However, the BTA/AMT combination treatment for one hour did not consistently perform better than the standard BTA treatment in the present study contrary to the previous findings by Golfomitsou.

There are a number of reasons why there may be the difference in behavior between the testing in this study as compared to the study conducted by Golfomitsou. One of these differences is the method of exposure to high humidity. In the previous study objects were exposed to much higher RH for a shorter period of time. This was then followed by long-term evaluation. The longer exposure in this study to a high RH may have resulted in the difference in the performance. Other studies conducted at Kaman examining the effectiveness of BTA have found that the accelerated aging tests do not always yield the same conclusion as long term studies where samples are allowed to age naturally in storage (Carroll 1997). It is possible that exposure to brief periods of high humidity does not accurately predict the long term stability of artifacts treated with

corrosion inhibitors, especially as in storage at many sites artifacts are exposed to cycles of low and high humidity and temperature.

Another critical difference in this study as compared to Golfomitsou's study is the difference in sample selection and sample condition. The samples used by Golfomitsou, while heavily corroded, were still in sufficiently good condition as to be identified, classified, and inventoried as a result. Furthermore, these objects were much larger than the test samples used in the present study. This allowed for a different method of evaluation of the behavior of the corrosion inhibitors, whereby samples were graded on the number of points of corrosion. However, in the present study the test samples were two small to be evaluated in this fashion. In some cases, for example, a single point of corrosion covered roughly one third of the objects surface. Furthermore, the difference in condition may have had an effect on the results. Corrosion reactions are complex and the behavior of a corrosion inhibitor is dependent on its ability to complex with the artifact. The more corroded surface of the test samples used here may have affected the complex formation and so affected its performance.

CONCLUSION

The results of this study, while not supporting all of the conclusions reached by Golfamitsou in her PhD dissertation, demonstrate the challenges associated with testing on actual artifacts. Furthermore, this study reveals a need for further testing of the use of BTA and AMT in combination before this method can be accepted as a standard treatment method. A possible avenue for future research would be a long-term study focusing only on the performance of BTA at different immersion times and the BTA/AMT combination also at different immersion times without exposure of the artifacts to high humidity. This is a more time consuming method, but the results will most accurately reflect the likely long-term behavior of treated objects. Furthermore, additional testing focusing only on the comparison of samples treated for the same amount of time but with or without vacuum impregnation may also be advisable. Due to the complex nature of corrosion behavior on archae-

ological artifacts studies focused on improving single features of the treatment methodology may yield more easily repeatable results.

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