The International Journal of Nautical Archaeology

NAUTICAL ARCHAEOLOGY

Volume 25
Number 1

Contents

Editorial

History and archaeology of HM Floating Duck, Bermuda
The cannon from Dunwich Bank, Suffolk
A folk boat from north-western Louisiana, USA

Technical Communications

An improved copper-based corrosion inhibitor-coating system for ferrous artefacts
Odyssey (5.234-5) and Hellenic ship construction: a clarification
A three-hole stone anchor with wood remains from Crusader Arad (Afula), Israel

News Reports

Maritime archaeology in Northern Ireland: an interim statement
Archaeological intertidal surveys in North Munster, Republic of Ireland 1995

Reviews

F Foisier, Itinerario Generale: Itinerario delle Embiezazioni di Venezia alla Fulatione dei Mediteranei (P. Van Der Meer)
P Mantell, Ships of the Ports of London: First in Eleventh Centuries AD (English Heritage: Archaeological Report No. 3) (P. Brown)
D Ganszark, Zemianu Brezhankic Gama (Shore Ethnography no. 4) (D. Goddard)
J Morrison (Ed.), The Age of the Galley: Mediterranean Naval Vessels since Pre-Classical Times (Conway History of the Ship Series) (W. M. Murray)
C G Codell, Medieval Ship Archaeology (J. McKeeford)
R Coles, Wetland Management - A Survey for English Heritage (WARP Paper 9) (V. Heal)
M Boud (Ed.), The Archaeology of Ships of War (The International Maritime Archaeology Series, vol 11) (P. Marsden)
L F Pearson, Lighthouses (Shore Album 312) (R. G. W. Prescott)

Cover design: Drawing of a gold model 4.5 m long from the tomb of Queen Ahhotep of Egypt, mother of Ahmose I (1552-1527 BC) and published in the British Museum Press' Egyptian Bookshelf volume The Royal Boat of Ahmose I (1552-1527 BC). The boat is purple in shape with looking platforms on fore- and after-decks and is rowed by six men and a dog on a four-wheeled box-wagon. (Drawing after K. H. Dietmann, MBIR 10, 1943, 66)
Technical Communication

An improved tannin-based corrosion inhibitor-coating system for ferrous artefacts

Worth Carlin and Donald H. Keith
Ships of Discovery, Corpus Christi Museum, 1900 N. Chaparral St. Corpus Christi, TX 78401, USA

Introduction
Artefacts recovered from the sea in the late 1960s and early 1970s were re-examined in 1993 to determine their present condition, to evaluate the effectiveness of the original treatment, and to re-treat those exhibiting symptoms of active corrosion. Originally conserved by mechanical cleaning, electrolytic reduction, and coating in microcrystalline wax, after 20 years the artefacts were in good condition, but the microcrystalline wax coating was thin and no longer impermeable to air penetration. In some places, slow corrosion was taking place. More than 350 16th-century wrought-iron items were re-treated with the experimental tannic acid solution described below followed by a tannin-derived coating which is impervious to air and moisture.

The Padre Island 1554 Plate Fleet collection
A collection of 16th-century artefacts salvaged from two ships wrecked in the Gulf of Mexico in 1554 is currently housed in the Corpus Christi Museum of Science and History (Arnold, 1992). They were recovered at intervals between 1967 and 1973, and conserved at the Texas Archaeological Research Laboratory at the University of Texas at Austin from 1969 to 1976 (Arnold & Weddle, 1979; Olds, 1975). When recovered, most of the wrought-iron artefacts were heavily encrusted with calcareous marine deposits. Following mechanical removal of the encrustation, they were cleaned electrolytically to remove corrosive chlorides, then washed with deionized water, dehydrated in alcohol, air-dried and immersed in molten microcrystalline wax (Hamilton, 1976). To the authors' knowledge, this is the oldest, largest collection of wrought-iron artefacts conserved by electrolytic reduction.

An inspection in 1993 determined that most of these were in good condition after 20 years, with less than 5% of the collection showing any trace of rust. The overall excellent condition of the collection attests to the effectiveness of this method of conservation. Investigators who have been convinced that it is preferable to strip iron to bare metal, removing all corrosion products, should reconsider the advantages of treatments which strive to preserve and pacify an artefact's 'rind' as well as its metallic core.

During the passage of more than 20 years, many of the objects had been exposed to a variety of less-than-optimum environmental conditions; part of the collection was exhibited in a travelling exhibit and other artefacts were loaned to other museums for temporary exhibit and some changes had taken place. The original
microcrystalline wax coating was very thin, and susceptible to water vapour penetration and some new corrosion was beginning. Each artefact was examined closely and it was noted that a few of the smaller items, such as bolts, had developed small cracks perpendicular to their long or wrought dimension. The cracks indicated that a dimensional change was occurring consistent with continuing oxidation.

In order to quantify the physical difference between surface and core, samples were taken from a bolt (41WY3-1530). A dental pick was used to separate a flake from the outer oxidized surface of a bolt, removing a fragment approximately 0.32 cm thick by 1.0 cm wide by 2.0 cm in length. A sample of the underlying metal was obtained by drilling into the bolt below where the flake had been removed. These samples were analysed by X-ray powder diffraction (XRPD) to determine their composition. On a comparative basis the surface sample (Fig. 1a) contained less than one-third of the elemental iron found in the underlying material (Fig. 1b), with corresponding increases in the oxide content of the surface material. In this study, samples taken for XRPD analysis were also analysed by X-ray fluorescence (XRF) in the atomic number range 9-92. No chloride (Cl\(^{-}\)) concentration greater than 0.001% was detected among the trace elements found. It was deduced that corrosion was continuing, as the cracks had developed since the last inspection.

While the most expedient and direct method of cleaning and stabilizing iron artefacts from the sea is to remove mechanically every trace of oxidized material, leaving only metallic iron behind, this can be akin to ‘throwing the baby out with the bath water’ if the outermost layer of corrosion products preserves evidence of manufacture and use, as well as unique markings. The resulting dilemma for the archaeological conservator is to pacify the metallic core while at the same time protecting the stable ‘rind’ of corrosion products, which although derived from the core has become an entirely different material. An additional complication is that this rind prevents any coating applied to the exterior from reaching the still-reactive metallic core and leaves the artefact susceptible to on-going corrosion.

Because the 1534 Plate Fleet artefacts still have their outer corrosion layers intact, the decision was made to re-treat the collection with a corrosion inhibitor and to provide a coating to minimize the penetration of air and moisture. The decision to treat the entire collection with tannic acid was made because it would be relatively simple to accomplish—provided an effective tannic acid/surfactant system and a removable vapour barrier coating could be developed.

**Tannic acid-based corrosion inhibitors**

Tannic acid and its derivatives have been used as corrosion inhibitors for ferrous materials for many years (Knowles & White, 1958; Matamala et al., 1960), although recently some investigators have raised questions about its effectiveness (Morcelli et al., 1992; Ashton, 1993: 20). The chemistry of tannic acid and its derivatives is complex; the material itself varies greatly from one source to another. Generally speaking, ‘tannic acid’ refers to hydrolysable tannins which are essentially galloyl esters of glucose. The hydrolysis of tannic acid yields primarily gallic acid and glucose. Tannic acid’s corrosion inhibiting mechanism has not been determined due to the complexity of the large tannic acid molecule. Some investigators have suggested that anodic polarization of the metal occurs, forming a passive film (Parkins & Pearce, 1966: 649-650; Rosenberg, 1987: 15). Considering the complexity of the system, ‘anodic polarization/film-forming’ is a generality that can be accepted because there are ample data to support the claim that tannic acid is a corrosion inhibitor.
Sixteen percent alcohol is often used to condition and wet these object materials such as shell, bone, and objects made of natural fibers. A mixture of water and glycerin has also been successfully used as a preservative. Some of the most common treatments are those that involve boiling in a solution of 40% glycerin and water. This treatment is known as a "glycerine bath" and is used to preserve organic materials such as wood and paper.

For larger objects, the use of a light flammable means of drying is often necessary. The wax treatment method is another method used to preserve organic materials. In this method, a mixture of wax and a preservative is applied to the object, and the object is then heated to a temperature high enough to melt the wax. This process helps to preserve the object by sealing it from the environment.

Corrosion inhibitors are also used to prevent the oxidation of metal objects. These inhibitors can be applied to the surface of the object by the use of a chemical solution. The solution is applied to the surface of the object, and the object is then placed in a sealed container to allow the inhibitor to penetrate the object.

A new method for the preservation of organic materials involves the use of a vacuum-sealed chamber. This method allows for the removal of air and the introduction of a preservative gas. This method is particularly useful for the preservation of delicate materials such as textiles and paper.

Prior to the use of preservatives, the increase in the concentration of acid in the soil was a major concern. The use of preservatives has helped to mitigate this problem by reducing the concentration of acid in the soil. This has allowed for the preservation of organic materials in a more controlled environment.
Sixteen to eighteen percent aqueous alcohol solutions of tannic acid have been used to coat ferrous artefacts. However tannic acid solutions have poor metal wetting properties, particularly on artefacts such as those in the 1554 Plate Fleet collection which have been coated with microcrystalline wax. Theoretically, the wax can be removed. But in practice, the object must be immersed in a hot volatile solvent (such as Stoddard’s solvent). For small artefacts this could be accomplished safely enough in a well-vented hood with ample protection from sources of ignition. For large artefacts the inhalation and flammability hazards of microcrystalline wax removal are too serious to be contemplated.

Corrosion of the objects indicated that the protective wax coating was no longer fully effective. There was a possibility that they could be treated without removing the microcrystalline wax coating, but this made it imperative to design a tannic-acid inhibitor with good penetration and wetting properties. Although the surface was hydrophobic and poorly wetted by either water or the aqueous/alcohol solution of tannic acid, when tested with an aqueous solution containing a suitable surfactant, the wax-treated artefact surface was sufficiently porous to allow penetration of the tannic acid. Other tests demonstrated that a fresh, thick coat of microcrystalline wax is completely impermeable, even to the surfactant solution.

A new tannic acid coating
Prior to determining if a surfactant could increase the ‘wetting’ of aqueous tannic acid it was necessary to determine what types of surfactant were compatible with concentrated tannic acid solutions. A second mandate was that the surfactant should contain no chloride ion due to the inherent corrosive nature of that molecule. For example, surfactants derived from alkali metal sulphates or sulphonates are compatible with tannic-acid solutions but the presence of chlorides preclude their consideration. The properties of 35 commercial surfactants were reviewed and seven chloride-free materials were selected for testing. The surfactants tested were products of PPG Industries, Specialty Chemicals, Chemicals Group. Although several manufacturers produce similar surfactants these were selected because of the investigators’ familiarity with their product line. The initial compatibility test was to determine which chloride-free surfactants were soluble in 18% aqueous tannic acid. In this simple test, 0.25 g of each surfactant were mixed with 100 gms of aqueous (18%) tannic acid solution and the degree of solubility was observed.

As revealed in Table 1, only one of the tested surfactants, Mazon 40®, was compatible with the tannic acid solution. To ensure that the surfactant incompatibility demonstrated in Table 1 was not a function of tannin-acid concentration, the test procedure was repeated with 8% tannic-acid concentrations. The results were the same. To determine the effectiveness of the Mazon 40® surfactant on the ‘wetting’ properties of aqueous 18% tannic-acid solutions, a series of simple tests was performed by adding known quantities of the surfactant to the tannic acid solution and then placing a 0.2-ml drop of the mixture on a rusted flat iron plate. The spread or coverage of the solution on the surface of the plate is a reliable measure of the effectiveness of the surfactant’s performance. The tannic-acid solution contained 18% tannic acid (technical grade, water soluble), 11% denatured ethanol with the remainder distilled water. To this solution Mazon 40® was added at various concentrations.

The data in Table 2 reveal that the addition of the surfactant to the aqueous tannic acid solution increases the surface coverage and the penetration of the inhibitor into the oxide-metal interface. With
Table 1. Compatibility of various chloride-free surfactants with 18% aqueous solutions of tannic acid

<table>
<thead>
<tr>
<th>Trade name*</th>
<th>Chemical type</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macol NPG®</td>
<td>POE (6) nonyl phenol</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Macol OP-10 PS®</td>
<td>POE octyl phenol ether</td>
<td>Reacts</td>
</tr>
<tr>
<td>Macol OP-30 (70)®</td>
<td>POE (30) octyl phenol</td>
<td>Reacts</td>
</tr>
<tr>
<td>Mazwet 30®</td>
<td>Nonionic surfactant</td>
<td>Reacts</td>
</tr>
<tr>
<td>Mazon LDA®</td>
<td>Lauramine oxide</td>
<td>Reacts</td>
</tr>
<tr>
<td>Mazol 13®</td>
<td>Ampholytic surfactant</td>
<td>Reacts</td>
</tr>
<tr>
<td>Mazon 40®</td>
<td>Caustic coupling agent</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

*PPG Industries, Inc. Specialty Chemicals, Chemicals Group, 3938 Porett Drive, Gurnee, IL 60031.

Table 2. Area of rusty iron plate covered by 0.2 ml of tannic acid solution in square centimetres (cm²)

<table>
<thead>
<tr>
<th>Surfactant concentration (wt %)</th>
<th>0</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test No. 1</td>
<td>3.1</td>
<td>3.8</td>
<td>11.9</td>
<td>12.8</td>
</tr>
<tr>
<td>Test No. 2</td>
<td>2.8</td>
<td>3.6</td>
<td>12.3</td>
<td>14.0</td>
</tr>
<tr>
<td>Test No. 3</td>
<td>3.3</td>
<td>3.7</td>
<td>12.6</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Table 3. Area of rusty iron plate covered by 0.2 ml of tannic acid solution in square centimetres (cm²)

<table>
<thead>
<tr>
<th>18% tannic acid</th>
<th>Fertan®</th>
<th>18% tannic acid w/1.5% surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test No. 1</td>
<td>3.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Test No. 2</td>
<td>2.8</td>
<td>4.1</td>
</tr>
<tr>
<td>Test No. 3</td>
<td>3.3</td>
<td>4.6</td>
</tr>
</tbody>
</table>

heavily-corroded artefacts where a large percentage of the particles are iron oxides, it is necessary to have the corrosion inhibitor in contact with the metal/oxide interface to prevent or impede further corrosion. Therefore, it is essential to have an inhibitor solution that thoroughly penetrates the corrosion products to inhibit and stabilize the corrosion process. A comparison of the 'wetting' properties of tannic acid, tannic acid with surfactant added, and Fertan (a widely-used commercial tannin-based inhibitor/coating), are presented in Table 3.

Artifact treatment

The collection contained objects of various shapes and size ranging from small nails and bolts to wrought-iron, broach-loading cannons 0.15-0.20 m in diameter and up to 2.6 m in length. The initial intention was to paint the tannic acid solution on the artefacts, applying one or more coats as necessary. It quickly became apparent that due to the presence in the collection of many tubular objects (cannons, breech chambers) a better method of application would be to immerse them in the solution. For treatment, they were grouped by size in order to minimize the quantity of solution necessary. Small artefacts were treated simultaneously in small tanks, while large ones were treated individually in larger tanks. The immersion tanks were kept covered to minimize evaporation and oxidation of the solution. The fact that they absorbed a surprising quantity of solution was indicated by an incremental lowering of the solution level each time an artefact was withdrawn.

W. CARLING

A new vapour-impermeable paint as MOP-10, 100, 300 and Christi MOP-30. A combination of OP-30 (PPG Industries: MACOL® Corp.), POE octyl phenol and chloride-free surfactants. These systems have not been studied or similar tests. It is good practice to ensure that any artefacts exposed to water, such as oxyethylene or chlorinated hydrocarbons, are oxygen barrier coated. The immersion of any tannic acid coating and eventually of the water, but it is a barrier coating well known for its protection of tannic acid artefacts from the elements. Who have tried tannic acid artefacts really question the environmental value.

Treatment of artefacts

The treatment consists of:

1. Synthesis of MOP-10, 100, 300, and Christi MOP-30. The difficulty is to prepare sufficient quantities of these materials.

2. Dispersing 720 ml of 18% tannic acid solution and 24 ml of OP-30 and 10 ml of Christi MOP-30. This reaction was carried out in a chemical syrup, at least 5°C, for 2 days. The supernatant from the process was re-used to water converted by the artefact, gently stirring to ensure good contact and distribution.
A new vapour-barrier coating

The new vapour-barrier coating, known as MOP-30, developed at the Corpus Christi Museum, is derived from a combination of the surfactant MACOL OP-30 (PPG Industries) and tannic acid. MACOL OP-30 is an ethoxylated octyl phenol containing thirty ethylene oxide units. The composition of MOP-30 has not been studied, presumably it is an ester or similar condensation product. It is a good coating for artefacts that will not be exposed to the elements because its high ethylene oxide content provides a good oxygen barrier, a good moisture barrier and excellent compatibility with tannate films. Easily removed with alcohol, the coating will not withstand prolonged immersion in water. The effectiveness of any tannic acid treatment is counteracted and eventually negated by exposure to water, but the addition of a vapour-barrier coating can enhance the protection offered by tannic acid. Judging from the literature, those investigators who have denigrated the usefulness of tannic acid as a corrosion inhibitor were really questioning its effectiveness in wet environments.

Treatment procedure and formulae

The treatment procedure is as follows:

1. Synthesize the protective coating (MOP-30) well in advance due to the difficulty of preparing it in large quantities.
2. Dissolve 180 g of tannic acid in 720 ml distilled water. To the resulting solution, slowly add 92 g of MACOL OP-30 with minimum stirring. Let the reaction product, a brown resinous syrup, separate from the solution for at least one hour. Slowly decant the supernate and set aside for further processing. Add a volume of deionized water equal to the resinous mass, stir gently and let sit for one hour. Decant and discard the aqueous supernate.
3. Clean the artefact with a stiff nylon brush to remove dust or loose particles.
4. Immerse the artefact in the tannic acid solution for 25-35 minutes. Tubular objects such as guns or breech chambers should be gently rocked to prevent the formation of air pockets.
5. Allow artefact to air dry for 24-48 hours.

Repeat the previous step at least three times. After discarding the final wash, let the resin dry (by air or under a heat lamp) until it becomes a hard, wax-like substance. This material, dissolved in three parts (by weight) of denatured ethanol, is the protective coating, MOP-30. The first decantation of the reaction mix, which had been retained, is performed after 48 hours. The recovered resin is added to future preparations. A batch with 180 g tannic acid should yield approximately 171 g of MOP-30 product. The MOP-30 is applied to the artefact which has been previously covered with at least two coats of tannic acid, making sure that each coating is dry before applying the next.

(2) Mix the tannic acid-surfactant solution. Solution number 1: To 3080 ml of deionized water add 340 ml of (denatured) ethanol. Mix in 738 g of a commercial grade of completely water soluble tannic acid. Note: tannic acid is very dusty, the weighing and mixing should be performed in a well-ventilated area with the technician wearing a dust mask and eye protection.

Solution number 2: To 380 ml of deionized water add 38 g of PPG Industries Mazon 40°, a thick, viscous alkyl glucoside. The surfactant dissolves slowly with moderate stirring. Combine Solutions number 1 and number 2. Agitate gently, as the mixture has a tendency to create foam.

(3) Clean the artefact with a stiff nylon brush to remove dust or loose particles.

(4) Immerse the artefact in the tannic acid solution for 25-35 minutes. Tubular objects such as guns or breech chambers should be gently rocked to prevent the formation of air pockets.

(5) Allow artefact to air dry for 24-48 hours.
Artefacts destined for display should be given an additional coat consisting of a mixture of 40% powdered graphite and the MOP-30 coating. Best results are obtained when the coating is applied with a small sponge roller, which imparts a soft, dull finish (Fig. 2).

Conclusion

This coating system for the protection of ferrous artefacts not exposed to the elements consists of three components: (a) a tannic acid solution with increased penetration properties (Fig. 3). (b) A clear coating derived from tannic acid that provides good compatibility when applied over a tannic-acid inhibitor coating. Identified as MOP-30, this coating has good vapor-barrier properties. (c) The addition of a graphic pigment into the MOP-30 coating produces a gray matt appearance. Applied over the clear protective coating, this mixture imparts an aesthetically-pleasing finish that can be removed.

The three-component system is durable, and it is recommended for artefacts having a cast or wrought iron core, in contrast to the elements.

Acknowledgments

The authors thank the Metropolitan Museum and the Stux and Dioguardi families.

References


W. CARLIN & D. N. KEITH: CORROSION INHIBITOR-COATING SYSTEM

pleasing finish. Like MOP-30, the coating can be removed in an alcohol bath.

The three-coating system is based on a time-proven inhibitor (tannin). It is reversible, and it penetrates permeable, thin layers of microcrystalline wax. Although the coating system is suitable for ferrous artefacts having a porous structure, such as cast or wrought iron, it is not recommended for artefacts that will be exposed to the elements.

Acknowledgments
The authors would like to thank Rick Stryker, Director of the Corpus Christi Museum and J. Barto Arnold III, Texas State Underwater Archaeologist, for permission to research, develop and apply this treatment to artefacts from the Padre Island 1554 Plate Fleet collection. Special thanks go to Linda Zitting of the Corpus Christi Museum history section, who is undoubtedly more familiar with the 1554 collection than any other person. Messrs Charles Holfield and Michael Feeney obtained the XRPD analysis for us gratis. With regard to the artefacts themselves, we would like to thank Dr. D. L. Hamilton and all the people involved in the treatment of this collection more than 25 years ago. The excellent condition of the hundreds of artefacts is a testament to their skill, inventiveness, and determination.

References
Oluts, Doris, 1974, Texas Legacy from the Gulf. Austin.