Journal of Conservation & Museum Studies
http://www.jcms.ucl.ac.uk
No. 3 November 1997

TESTING CORROSION INHIBITORS FOR THE CONSERVATION OF ARCHAEOLOGICAL COPPER AND COPPER ALLOYS

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Abstract

This is a synopsis of the Ph.D. research undertaken at the Institute of Archaeology, University College London. The aim was to evaluate corrosion inhibitors for use in the conservation of copper and copper alloy archaeological artefacts. The objective of this work was to acquire an insight into the performance of copper corrosion inhibitors, when applied to archaeological copper.

Introduction

Corrosion Inhibitors

The evaluation of inhibitors poses several questions, such as:

- How effective is the inhibitor?
- Does it damage the corrosion products covering the metallic core?
- Does it induce unacceptable colour changes?

It has been common practice to answer these questions by applying corrosion inhibitors to archaeological material. Brunner's study (1993) provides one example. However, the wide variability of archaeological copper and the heterogeneity of the corrosion products do not allow a precise comparison between test results, and the resulting data are more specific to the artefact and its condition. Moreover, it is inappropriate to apply new corrosion inhibitors to archaeological material without preliminary screening. Test procedures based on non-archaeological materials are therefore required.

This research focused on the development of experimental procedures based on coupons of modern copper, and on the reproducibility of results. The test procedures undertaken allowed a direct comparison between corrosion inhibitors, and these results were subsequently evaluated by treating archaeological objects of copper alloy.

Chlorides are known to be a major factor in the deterioration of copper artefacts in the museum environment. The literature lists only one test (Angelucci, *et al.* 1978) for copper corrosion inhibitors in archaeological conservation. Industrial corrosion tests were therefore sought in the American Society for Testing Materials (ASTM), the British Standards Institution (BSI), the Deutsche Industrie Norm (DIN), and the International Standards Organisation (ISO). No test was found entirely suitable for the evaluation of inhibitors on corroded metallic surfaces in conservation, so an appropriate corrosion test had to be developed.

Copper coupons were immersed into cupric chloride solutions to produce cuprous chloride corrosion, the structure of which is similar to the corrosion found directly against the remaining metal of copper artefacts (Figure 1). These coupons in contact with 95% relative humidity at ambient temperature produced paratacamite (Figure 2).

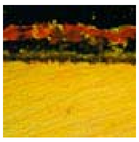

Figure 1: Coupon covered with nantokite and cuprite-50 microns. (30K)

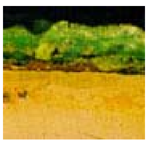

Figure 2: Coupon covered with cuprite and paratacamite-250 microns. (34K)

The nantokite covered coupons were subsequently treated with corrosion inhibitor solutions (Figures 3, 4), and exposed to 95% relative humidity (Figure 5). The effectiveness of the inhibitors was assessed by monitoring the weight change of the coupons after exposure to 95% relative humidity.

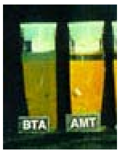

Figure 3: Inhibitor treatment. (24K)

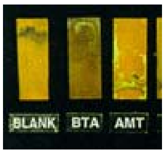

Figure 4: After drying. (30K)

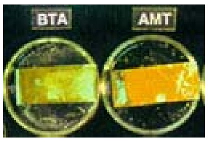

Figure 5: After corrosion at 95% RH. (41K)

In another experiment the colour of the coupons was monitored with a chroma meter. The inhibitor solutions were analysed for the presence of copper removed from the corrosion products, using atomic absorption spectroscopy (AAS).

Two of the corrosion inhibitors chosen were benzotriazole (BTA) and 2-amino-5-mercapto-1,3,4-thiadiazole (AMT). These compounds have previously been applied as corrosion inhibitors in archaeological conservation. A search was conducted for similar compounds that could also be applied in the conservation of copper and copper alloys. According to a list of requirements specific to archaeological conservation:

1. The type of inhibiting action should be based on a complex formation, resulting in a polymeric layer of metal and inhibitor. These types of inhibitors are found to form the most suitable structure of corrosion inhibition. They develop a barrier between the metal and its environment. They should feature a thick and dense polymeric structure to stop further oxidation of the metal.

2. The inhibitor-copper polymer film formed should not be soluble in water or organic solvents, since an object is often cleaned with alcohol or acetone after treatment.

3. The inhibitor should adsorb or chemically bond to the substrate.

4. The effective range of a corrosion inhibitor should be as low as pH 2. The surface of corroded copper has areas such as corrosion pits where very low pH was detected. Cuprous chloride can have a pH 3.5-4 (Scott 1990). It is suggested that the acidity in chloride pits is even lower. So the inhibitor should be effective over the pH range between 2 and 8.

5. The compound should preferably act as an anodic inhibitor. During pitting corrosion the anodic areas in the central area of the pits are actively corroding, while the surrounding surface is cathodic (Jones 1992). The best inhibitors would react in anodic and cathodic areas. Considering the case of an actively corroding copper artefact, the metallic parts act as an anode and the corrosion layers mainly act as a cathode. The inside of corrosion pits are also found to be anodic. Due to the heterogeneity of an alloy and its corrosion products, the boundaries of anodic and cathodic parts in a corroded object are usually not clear or distinct (Lucey 1971).

6. The visual appearance of the patina should not be altered by the application of the inhibitor. As mentioned above, some of the previous treatments applied in conservation caused the disfiguration or discolouration of the outer corrosion layers. Benzotriazole, for example, was found to darken the appearance of the corrosion products, especially in repeated application, as sometimes required. AMT was shown to cause some darkening of metallic copper when applied in industrial methylated spirits at 1% by weight (Faltermeier 1992).

7. The inhibitor should not be hazardous or harmful to the user. In many instances laboratories are not equipped with air extraction systems, or the inhibitor has to be applied immediately post excavation in the field. Benzotriazole is suspected of being carcinogenic (Cronyn 1990).

8. Metallic based inhibitors should be avoided. In many instances they are very powerful inhibitors. Titanates have been used on iron and chromates, and silver-oxide on copper.

According to this, six new inhibitors were tested: 2-aminopyrimidine (AP), 5,6-dimethylbenzimidazole (DB), 2-mercaptobenzimidazole (MBI), 2-mercaptobenzoxazole (MBO), 2-mercaptobenzothiazole (MBT), and 2-mercaptopyrimidine (MP).

Conclusion

None of the compounds were found to be 100% effective. However, AMT and MBT were selected for more extensive performance tests against BTA on archaeological metal artefacts. These tests, and a more detailed account of the procedures described in the present paper, are reported in Faltermeier (1995) and in Faltermeier (forthcoming).

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