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Corrosion inhibitor testing in archaeological conservation

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Metal objects from archaeological contexts often suffer serious damage by corrosion. Various methods for inhibiting corrosion have been developed, but their effects need to be evaluated. Here new research is described on how treatments to inhibit the corrosion of copper and copper-alloy artefacts may be tested.

Corrosion inhibitors are used to arrest corrosion on archaeological metal artefacts and stop them from deteriorating further, so that they can be preserved for future generations. Inhibitors are mainly applied as solutions and these alter the mineralized metal surface. The compounds not only form a chemical bond with the patina, but can also alter the appearance of an object. They can cause colour changes and partial dissolution of the admired patina. This article focuses on the evaluation of inhibitor treatments for copper and copper alloys, and outlines various ways of testing the damage caused by a new conservation treatment. These treatments aim to preserve artefacts with as little change as possible to the surviving archaeological information.

Archaeological copper and copper alloys frequently contain actively corroding areas on their surface (Fig. 1). These corroding parts can destroy archaeological evidence contained in the mineralized surface, by a process known as "cyclic chloride corrosion". To prevent this sort of continuous damage occurring, artefacts are often treated with corrosion inhibitors. However, the inhibitor most frequently used (benzotriazole) is not always successful in preventing chloride corrosion.

The research outlined here had the aim of finding a corrosion-testing procedure by which corrosion inhibitors might be assessed without testing them on archaeological artefacts, because there is a danger that damage might be inflicted on an artefact by action of a new unknown compound. The project also examined colour changes induced by corrosion inhibitors. Many artefacts are highly prized for the colour of their patina, which is known as a noble corrosion surface. The corrosion inhibitors applied react with this surface of the artefact and are adsorbed onto the minerals present. This can cause drastic changes in the appearance of an object. Any new compound chosen as an inhibitor should not alter the appearance of an artefact.

Corrosion of ancient copper and copper alloys

Ancient copper and copper alloys usually have a stratified corrosion layer covering a metallic core. The innermost layer covering the remaining copper is the ruby red cuprous oxide known as cuprite (Cu_2O). It is in turn covered either with a dark green copper carbonate, malachite ($Cu_2(OH)_2CO_3$), or with the less commonly found blue copper carbonate, azurite ($Cu_3(OH)_2(CO_3)_2$). If harmful chlorides are present in the corrosion layers, pale grey waxy cuprous chloride, nantokite (CuCl), will probably cover parts of the remaining metal. Nantokite is unstable when in contact with moist air and will change into basic copper chloride, either green paratacamite ($CuCl_2 3Cu(OH)_2$), bright to dark green atacamite ($Cu_2(OH)_3Cl$), or rarer blue-green botallackite ($Cu_2(OH)_3$-$Cl.H_2O$). Bronzes going through this process are often referred to as suffering from "bronze disease".[1]

Conservators have treated artefacts with corrosion inhibitors, to prevent the conversion of cuprous chloride to basic copper chloride. Only benzotriazole (BTA) has been widely accepted in the stabilization of copper and copper-alloy artefacts. Madsen proposed BTA for archaeological conservation based on a vast amount of research done for industrial purposes.[2] Because of its perceived advantages and satisfactory results, BTA has been the predominant corrosion inhibitor used in the conservation of copper and copper alloys. Since that time Oddy,[3] Sease[4] and others have investigated the properties of BTA, but very little research has been done on other corrosion-inhibiting compounds in conservation. The most recent corrosion inhibitor suggested for copper-corrosion inhibition in conservation is 2-amino–5-mercapto–1,3,4-thiadiazole (AMT).[5] However, AMT has not been accepted generally for use in archaeological conservation, because of the lack of information available on its effects, both in industrial applications and in the field of archaeological conservation.

Generally, conservation research into corrosion prevention aims to compare the effectiveness of different treatments,[6] and it usually uses archaeological samples to compare their effectiveness. However, corrosion testing using archaeological copper and copper alloys has several disadvantages:

- the size and shape of the artefacts are different
- the type and amount of alloying constituents of the original metal are often not known and might influence the corrosion inhibitor treatment
- the type and amount of corrosion products present on and in the surface of the artefact vary greatly
- the porosity of corrosion products may differ
- the inhibitor treatment might damage the patina of the archaeological artefact
- the long-term effects attributable to an inhibitor treatment are not known
- the corrosion inhibitor treatment is probably irreversible.

Bearing these disadvantages in mind, a corrosion-testing procedure was developed by the author using specially prepared copper coupons, covered in copper-chloride corrosion products, for testing corrosion inhibitors for copper and copper-alloy archaeological artefacts

Testing procedure

Virtually (99.9 per cent) pure copper coupons were immersed in 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. These

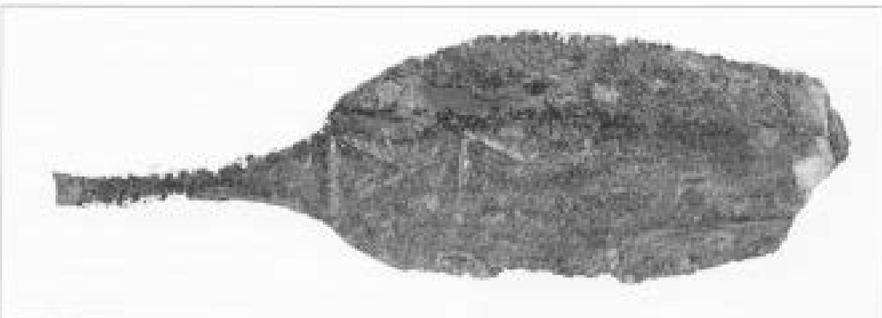

Figure 1 *A copper-alloy arrowhead in the Al Ain Museum, Abu Dhabi, United Arab Emirates, covered in copper corrosion. The tip of the arrowhead is undergoing active copper-chloride corrosion.*

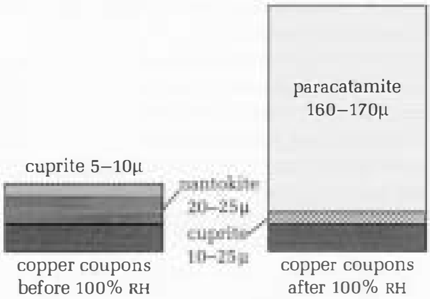

Figure 2 *Copper coupons containing artificial copper-chloride corrosion.*

coupons in contact with 95 per cent relative humidity at ambient temperature produced paratacamite (Fig. 2). This is similar to the reaction that occurs on archaeological artefacts containing chloride corrosion.

The corrosion inhibitors in Table 1 were tested with this new corrosion test.

Table 1 *Corrosion inhibitors.*

Nitrogen based inhibitors	Formula	Abbr.
Benzotriazole	$C_6H_5N_3$	BTA
2-Aminopyrimidine	$C_4H_5N_3$	AP
5,6-Dimethylbenzimidazole	$C_9H_{10}N_2$	DB
Sulphur based inhibitors		
2-Amino-5-mercapto-1,3,4-thiadiazole	$C_2H_3N_3S_2$	AMT
2-Mercaptopyrimidine	$C_4H_4N_2S$	MP
2-Mercaptobenzoxazole	C_7H_5NOS	MBO
2-Mercaptobenzothiazole	$C_7H_5NS_2$	MBT
2-Mercaptobenzimidazole	$C_7H_6N_2S$	MBI

The inhibitor test found that none of the inhibitors was 100 per cent successful in inhibiting the conversion from nantokite to paratacamite. BTA and MBT prevented corrosion best. The other inhibitors were less effective or completely ineffective. All of them induced colour changes on the corroded surface of the coupons, and, to determine the amount of colour changes, further experimental work was undertaken.

Colour changes attributable to corrosion inhibitors

Some archaeological artefacts are covered in very beautiful green and red corrosion products, considered indicative of the ancient pedigree of the artefact. However, the colour changes induced on these surfaces by corrosion-inhibitor treatments have not been accurately assessed qualitatively or quantitatively. Describing slight alterations in colour poses many difficulties when evaluating corrosion surfaces after a conservation treatment. An attempt was made to qualify and quantify colour changes induced by corrosion inhibitors for copper and copper-alloy archaeological artefacts, as precisely as possible.

Every observer perceives colour differently. A major obstacle encountered when comparing colours is the choice of descriptive words. This was found to be largely dependent on the observer's colour perception, and on changes in light source. It is also necessary to take into account the possibility that some people might suffer from a small degree of undetected colour blindness. The drawbacks encountered with a visual assessment of colour changes led to the use of a colour-measuring device (colorimeter), which assigns a numerical value to colour. This avoids individual colour perception, and results in a higher accuracy and reproducibility of colour values. The Minolta Chroma Meter CR-200 expresses colours in precise numerical values and was used for colour matching in the research. The instrument relies on modern optoelectronic technology, and completely discounts the subjective variations of individual observers. This tool was ideal for measuring the small variations in colour observed on copper minerals treated with corrosion inhibitors.

To evaluate the colour changes induced by corrosion-inhibitor treatments, the inhibitors chosen were individually dissolved in ethanol and exposed to cuprite, malachite and nantokite. These are the three main copper-corrosion products found on archaeological copper and copper alloys. This evaluation indicated that all corrosion inhibitors will change the colour of a mineralized surface containing cuprite, malachite and nantokite. Chloride-free copper and copper alloys will not benefit from treatment with these inhibitors. They cause colour changes and therefore should not be used.

If the artefact has to be treated because of active copper-chloride corrosion present in the corrosion surface, a drastic colour change of the nantokite can be expected. For example, BTA causes almost double the amount of colour change in the nantokite than AMT – a colour change that is very apparent to the naked eye.

Conclusion

The testing procedure developed shows that corrosion inhibitors do not have to be tested on archaeological material. The inhibitors can be quantitatively compared using the technique outlined and the best performing inhibitor can be selected for further testing for factors such as colour changes.

The evaluation of colour changes led to the recommendation that copper and copper-alloy archaeological artefacts, with a highly prized mineralized surface, should not be treated with these inhibitors because of the colour changes induced. If the artefact contains chlorides, it should be stored in a desiccated environment and its condition monitored at regular intervals. However, it must also be borne in mind that a corrosion-inhibitor treatment might be of benefit to the long-term stability of an artefact, and the colour changes might be acceptable. This means that the decision to carry out an inhibitor treatment must be made by looking at each object as an individual case.[7]

Notes

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