The Evaluation of Corrosion Inhibitors for Application to Copper and Copper Alloy Archaeological Artefacts

by

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Abstract

This thesis concerns corrosion inhibiting compounds which slow the deterioration of archaeological copper artefacts. Benzotriazole (BTA) and 2-Amino-5-mercapto-1,3,4-thiadiazole (AMT) have been applied as corrosion inhibitors in archaeological conservation. A search was conducted for similar compounds that could be applied in the conservation of copper and copper alloys. According to a list of requirements specific to archaeological conservation, six new inhibitors were tested. 2-Aminopyrimidine (AP), 5,6-Dimethylbenzimidazole (DB), 2-Mercaptobenzimidazole (MBI), 2-Mercaptobenzoxazole (MBO), 2-Mercaptobenzothiazole (MBT), 2-Mercaptopyrimidine (MP), were tested for potential archaeological conservation applications.

The literature lists only one corrosion test for copper chloride corrosion in archaeological conservation, with intact surface corrosion products. Industrial corrosion tests were checked in American Society for Testing Materials (ASTM), British Standards Institution (BSI), Deutsche Industry Norm (DIN), International Standards Organisation (ISO).

Chlorides are known to be a major factor in ongoing deterioration of copper artefacts in the museum environment. The mechanisms and types of chloride corrosion are discussed, including past and recent literature on the subject. No corrosion test was found entirely suitable for the evaluation of corrosion inhibitors against 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 corrosion found directly against remaining metal of artefacts. These coupons were subsequently treated with corrosion inhibitor solutions, and exposed to elevated relative humidity to assess corrosion inhibition, by monitoring the weight changes during the experiments.

The inhibitor solutions were analysed regarding the depletion of copper in copper corrosion products, using Atomic Absorption Photospectroscopy (AAS). The colour changes of copper corrosion products treated with inhibitor solutions were determined using a chroma meter.

According to these findings AMT, and MBT were selected for more extensive performance tests against BTA on archaeological metal artefacts.

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Chapter 1

Introduction

The aim of this research is to evaluate corrosion inhibitors for the use in the conservation of copper and copper alloy archaeological artefacts. The objective of this work is to acquire an insight into the performance of copper corrosion inhibitors, when applied to archaeological copper material. Since it seems inappropriate to apply new corrosion inhibitors to archaeological material, new testing procedures had to be established. The treatment of archaeological artefacts with unknown compounds poses several problems. These had to be taken into account when assessing corrosion inhibitors, such as:

- How effective is the compound?
- Does the compound damage the corrosion products covering the metallic core?
- Do the new compounds induce unacceptable colour changes?

It is standard practice to answer these questions, by applying corrosion inhibitors to archaeological material. As in the study, for example undertaken by Brunner (1993), into the application of AMT as a copper corrosion inhibitor. The wide variety of archaeological copper and the heterogeneity of the corrosion products, does not allow a precise comparison between test results. The resulting data are more specific to the artefact and its condition. This research focuses on experimental procedure of corrosion testing and the reproducibility of corrosion test results. The corrosion testing procedures undertaken, allow a direct comparison between corrosion inhibitors, and these test results are finally assessed by treating archaeological copper alloy objetcs.

1.1 Copper Corrosion

Even as a copper artefact leaves the foundry, its surface has already started to corrode. Corrosion is due to the interaction between a metal and its environment. This includes various electrochemical reactions, initially leading to an oxide layer on a metallic core. Copper oxides, carbonates and chlorides are the most commonly found compounds on the surface of archaeological copper and copper alloy artefacts. The products resulting from these deterioration processes are similar in composition to minerals found in nature. To a degree, these minerals are usually stable with respect to their environment. Excavated copper artefacts are usually covered by corrosion. The stability of the corrosion products depends on the burial environment of the object. Stable patina (noble patina) are normally found to be resistant to fluctuations in relative humidity. This work is concerned with the features of unstable patina, also called “Vile Patina“ (Gettens, 1970). A list of commonly found copper minerals can be found in the following table.

Mineral name	Formula	Chemical name	Colour	Crystal structure
Oxides/Hydroxides				
Cuprite	Cu_2O	Copper-I-oxide, Cuprous oxide	Ruby red	Cubic
Tenorite	CuO	Copper-II-oxide, Cupric oxide	Black	Monoclinic
Cassiterite	SnO_2	Tin-IV-oxide, Stannic oxide	white	Tetragonal
Carbonates				
Malachite	$Cu_2(OH)_2CO_3$	Copper-II- Hydroxycarbonate, Basic copper carbonate	Green	Monoclinic
Azurite	$Cu_3(OH)_2(CO_3)_2$	Copper-II- Hydroxycarbonate, Basic copper carbonate	Blue	Monoclinic
Chalconatronite	$Na_2Cu(CO_3)_2{\cdot}3H_2O$		Blue-green	Monoclinic
Cerussite	$PbCO_3$	Lead carbonate	white, grey, colourless	**Orthorhombic**
Sulphates				
Brochantite	$Cu_4(SO_4)(OH)_6$	Basic copper sulphate	Green	Monoclinic
Antlerite	$Cu_3(SO_4)(OH)_4$	Hydroxyl copper sulphate	Green	**Orthorhombic**
Connellit	$Cu_{19}(SO_4)Cl_4(OH)_{32}{\cdot}3H_2O$		Light-blue	Hexagonal
Sulphides				
Covelite	CuS	Copper-II-sulphide	Indigo blue	Hexagonal
Chalcocite	Cu_2S	Copper-I-sulphide	Blackish-lead grey	Monoclinic
Chalcopyrit	$CuFeS_2$	Copper iron sulphide	Brass-coloured	Tetragonal
Bornite	Cu_5FeS_4	Copper iron sulphide	Bronze-brown with purplish tarnish	Octahedral
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$	Copper iron antimony sulphide	grey to black	Isometric
Enargite	Cu_3AsS_4	Copper arsenic sulphide	Greyish-black	Orthorhombic
Chlorides				
Atacamite	$Cu_2(OH)_3Cl$	Basic cupric chloride	Bright to dark green	Orthorhombic
Paratacamite	$CuCl_23Cu(OH)_2$	Basic copper chloride	Green	Hexagonal
Botallacit	$Cu_2(OH)_3Cl{\cdot}H_2O$	Basic copper chloride	Blue-green	Monoclinic
Nantokite	$CuCl$	Copper-I-chloride , Cuprous Chloride	Colourless to white or greyish waxy	Isomeric
Cotunnite	$PbCl_2$	Lead chloride		Orthorhombic
Silicates				
Chrysocolla	$CuSiO_3{\cdot}\,2H_2O$	Silicate copper hydrate	Bluish-green	Monoclinic

Table 1. 1 The data was collected from various mineralogical and chemical texts (Dana, 1951).

1.2 Vile Patina

This type of corrosion surface is detrimental to an artefact. The term ″vile patina″ is usually used to describe chloride containing patinas on copper objects. Damage to copper artefacts exposed to environments containing chloride, occurs during burial as well as after excavation, due to the presence of harmful copper chlorides in corroded areas. Before excavation, most of the objects and their corrosion products have reached partial equilibrium with their burial environment. The oxide layers over a metallic core can partially protect it from further corrosion. In the case of a reactive patina, the layers of corrosion products include chlorides. This mineralised layer is usually very fragile. When the object is excavated, the relative humidity changes. In most cases, any protective corrosion layer will be ruptured because it starts to react again with oxygen, moisture and other components in the atmosphere. Under such conditions, the reactive chlorides continue to attack any remaining metal until a further protective layer of corrosion excludes oxygen and water. Post-excavation corrosion can lead to the complete mineralisation of the remaining metal.

1.3 Nantokite

In marine and coastal areas, and in saline soils of desert regions, corrosion products on copper and copper alloys can accumulate chlorides due to their presence in the environment. Chlorides are known to enhance metallic corrosion processes.

Chloride ions migrate through the primary oxide layers and react with copper underneath and are a primary cause of corrosive damage. The copper (I) chloride, *nantokite,* forms on and in the copper surface. It is thought that soluble copper-II-chloride ($CuCl_2$), transforms partially to copper-I-chloride (CuCl) and then to basic copper chlorides ($CuCl_2 \cdot 3Cu(OH)_2$) (Ullrich, 1985, 100). Nantokite (CuCl) and cuprite (Cu_2O) have almost the same molar volume, 23.9cm^3 and 23.653cm^3 respectively (MacLeod, 1987, 1079).

Ullrich (1985, 100) outlined the formation process of copper chloride compounds as follows:

$$2\,CuCl + Cu_2O + O_2 + 3H_2O \leftrightarrow CuCl_2 \cdot 3Cu(OH)_2$$

$$6CuCl + 1\tfrac{1}{2}O_2 + 4H_2O \leftrightarrow CuCl_2 \cdot 3Cu(OH)_2 + H_2O + 2CuCl_2$$

During this reaction some copper may redeposit as secondary cuprite, which does not adhere as well as the primary oxide layer. If a high concentration of chloride is present in corrosion pits, even the strong adherent primary cuprite is lost.

When present, white-grey waxy looking nantokite is easily detected during the mechanical cleaning of copper and copper alloys. When trying to reveal the "original" shape of an object during conservation, nantokite is encountered when pits or blisters of chloride corroded surfaces are cut open. Nantokite can be easily cut since it only has a hardness of 2.5 on the Mohs' scale (Scott, 1990, 195). It usually lies between the metallic core and a layer of secondary cuprite. The surface above the nantokite is mostly covered in warts of malachite and cuprite, and areas of basic copper chlorides. Within the secondary cuprite layer there may also be small amounts of redeposited elemental copper. Nantokite is very unstable if exposed by mechanical cleaning. When the warts on top of the nantokite are ruptured, further transformation of nantokite occurs. Exposed to air with elevated humidity as low as 50% RH, nantokite converts in to cuprite and lumps of green atacamite ($Cu_2(OH)_3Cl$), the basic cupric chloride. This then forms a powdery substance known as paratacamite ($Cu_2(OH)_3Cl$). It is still not exactly clear at which RH values cuprous chloride (nantokite) is stable. Scott (1990,203) found that objects could be stored at an RH between 42% and 46% RH and that this was adequate to prevent further oxidation of nantokite. Above 55% RH, he found that the nantokite becomes very reactive

The process of active change from nantokite to paratacamite is described in the literature as "bronze disease". If all the cuprous chloride is allowed to transform into basic copper chloride, the object is thought to be in a stable chemical state. The structure of such a mineralised object is physicaly very fragile and cannot be handled without losing some material.

Organ (1963) proposed a reaction for bronze disease as follows:

$$\text{(I)} \quad 2CuCl + H_2O \leftrightarrow Cu_2O + 2HCl$$

$$\text{(II)} \quad 2HCl + 2Cu \rightarrow 2CuCl + H_2$$

According to Scott (1990, 196-7) this proposed reaction sequence ignores two facts. Cuprous chloride has a very low solubility, its solubility being only 0.006g per 100ml water at room temperature.

Cuprous chloride does not produce hydrochloric acid and cuprite, when in contact with water. This is not a spontaneous reaction at $25^{o}C$. Scott (1990) indicated that bronze disease does not occur under normal conditions. The reaction sighted above is possible with an additional thermodynamic driving force. The electrical current needed for this form of corrosion, might be given by alloying constituents such as zinc and tin often present in the matrix of copper alloys.

Scott (1990,196 -7) showed that cuprous chloride spread over a piece of brass, in contact with a drop of water, causes gas bubbles to evolve and a layer of cuprous oxide to form. The same procedure was applied to a tin bronze (24% tin) but this was not sufficient to produce cuprite.

When cuprous chloride was placed in contact with copper and water, no formation of cuprite was observed. Scott (1990) found that cuprous chloride could produce a pH of 3.5-4.0. The main reaction products were trihydroxychlorides.

$$4CuCl + O_2 + 4H_2O = 2Cu_2(OH)_3Cl + 2H^+ + 2Cl^-$$

When a copper sheet is placed into a solution of cupric chloride, paratacamite is formed. The first reaction is a thin layer of cuprite which in turn is covered by a thin layer of paratacamite (Scott, 1990, 197). In the following experiments, it was found that cuprous chloride and cuprite are formed during this immersion.

Scott (1990) lists the four essential reactions that might occur on the surface of an archaeological copper artefact containing chlorides.

1) Reaction within a corrosion layer above a pit (depending on the ionic species present).

$$4CuCl + Ca(HCO_3)_2 + O_2 = CuCO_3Cu(OH)_2 + CaCO_3 + 2CuCl_2$$

2) A cathodic electrode reaction on the outer surface of the cuprite:

$$Cu^{2+} + e^- = Cu^+$$

3) An anodic reaction on the inner side of the cuprite covering the pit:

$$Cu^+ - e^- = Cu^{2+}$$

4) The reaction between anodic product and copper within the pit:

$$Cu + Cu^{2+} = 2Cu^+$$

This $2Cu^+$ can react with water to produce cuprite (Scott,1990, 198).

The basic copper chlorides formed are usually stable after a certain thickness, but they do not form a very strong adherent layer. The basic copper chloride layer can rupture through to the lower nantokite and a new attack can occur.

1.4 Atacamite, Paratacamite, and Botallackite

These three basic copper chloride isomers, have the same formula $Cu_2(OH)_3Cl$. They are polymorphs and crystallise in different crystal lattices. Atacamite is orthorhombic, paratacamite is rombohedeal and botallackite is monoclinic (Scott, 1990, 194). Paratacamite is usually considered to be the prevalent phase.

The primary copper chloride CuCl can be very reactive. When moist air is present, it converts copper into basic copper chloride. Most often the atacamite (orthorhombic) is altered into a pale green mass which is more amorphous. In this form it has a different crystal shape (Gettens, 1963a, 90). Paratacamite is a copper (II) hydroxychloride ($\gamma Cu_2(OH)_3Cl$) (MacLeod, 1987, 1080). It is formed when bronze or copper, contaminated with $CuCl_2$, comes in contact with humidity, and a solution with the concentration of approximately 0.1 mol $CuCl_2$ (ca. 1%) is formed. Ullrich (1985) found that a higher or lower concentration of $CuCl_2$ forms atacamite. Botallackite can be formed in a basic environment. The exact pH required to cause its formation is not clear. Botallackite is rare and transforms usually into atacamite or paratacamite. Ullrich (1985, 101) suggests that a transformation of atacamite to paratacamite does not happen under normal conditions. The presence of large amounts of atacamite, and paratacamite in a patina causes further corrosion of the object.

Paratacamite and atacamite can form inhomogenous layered structures (McNeil,1992,362). Feitknecht (1949,1640-46) found that natural occurring atacamite, hydroxychloride-IIδ, is the most stable form. Feitknecht (1949) proposed that naturally occuring atacamite forms only very slowly. However, Scott (1990,201) lists in his article 8 methods of producing paratacamite and atacamite artificially. In conservation, the basic copper chlorides found on copper artefacts have not been used as a sign of authentication, therefore their artificial growth on objects has not been discussed.

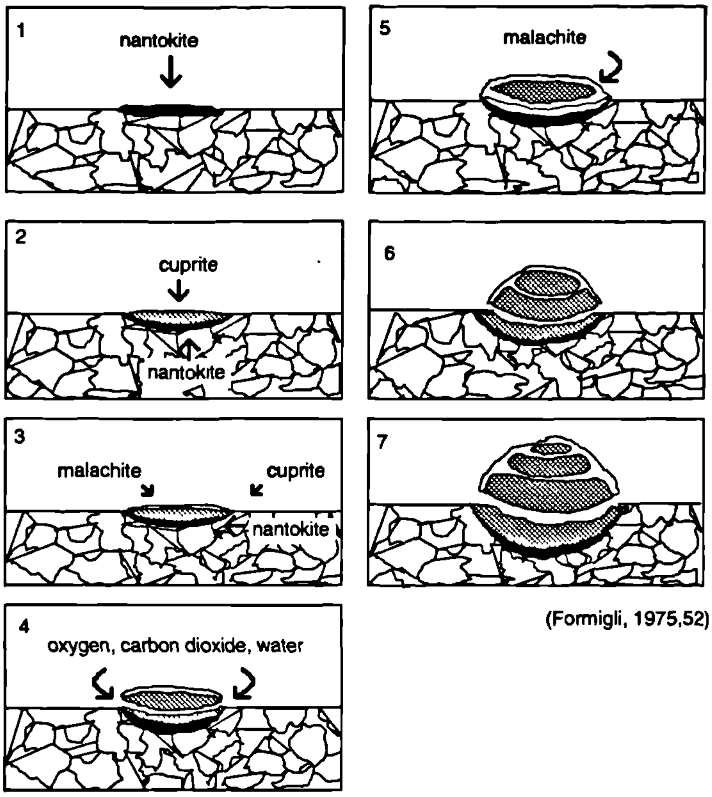
The greenish-blue Botallackite $Cu_2(OH)_3Cl \cdot H_2O$ was first reported by A.H.Church in 1865, but for almost a century no other occurrence of this mineral was mentioned. Gettens (1963a, 90) states that the mineral was also found on the interior of an Egyptian bronze figurine, by Professor Frondel in the Fogg Museum of Art. Botallackite is seldom identified but is probably more common than is thought (Gettens, 1963, 90). Most of the time atacamite and paratacamite are reported. Scott

(1990) found it difficult to synthesize botallackite artificially under ordinary laboratory conditions.

1.5 Wart/ Blister corrosion

This is the most damaging and disfiguring form of chloride related corrosion encountered on copper and copper alloys. The pits formed by chloride corrosion are first covered with a cuprite layer, which in turn is partially converted into malachite. These layers are permeable to oxygen, moisture and carbon dioxide, so the corrosion continues and underneath more cuprite is formed. The increase in corrosion products imposes pressure on the malachite strata above, causing cracks parallel to the corrosion layer, which bends slightly inward. Oxygen, moisture, and carbon dioxide enter and form new malachite, which reacts with parts of the cuprite underneath. This process is cyclic and the blister start to grow towards the centre of the metal (Ullrich, 1985, 102).

The layers bend towards the centre of the metal, due to the larger amounts of more reactive cuprous chloride in the centre. The malachite layers are thicker towards the rim of the blister since there is more oxygen, moisture and carbon dioxide available. In some cases cavities develop at the end of the green layers, and the inside of the wart is empty (Formigli, 1975, 51). The cavities near the edges form due to the lack of malachite growth. In most cases the bottom of the blisters are still covered in cuprous chloride, which is in direct contact with the metal. It was found that the warts did not necessarily need to be removed since the top layer of the warts, the basic copper carbonate contained the original surface. Born (1985, 93) describes decorated objects which had decoration running over the surface of the blister.



(Formigli, 1975,52)

Figure 1. 1 Blister Corrosion

Formigli (1975,52) describes the wart growth in the following steps :

1) Cuprous chloride is formed in the metal surface.
2) Cuprous chloride reacts with moisture and forms a cuprous oxide layer.
3) The cuprous oxide reacts with oxygen, carbon dioxide, and humidity to form a malachite layer.
4) Remaining cuprous chloride underneath keeps reacting with moisture, and more cuprous oxide is formed, which increases pressure towards the layers above. This causes the higher regions to rupture since they have solidified.

5) This way more humidity, oxygen, and carbon dioxide can penetrate in to the cavities, to transform the present cuprite into malachite.
6) More malachite is formed.
7) The wart grows and more layers form until an equilibrium is reached or the metal is consumed .

The basic copper chlorides are the most damaging corrosion products on an object. They rarely reproduce any surface details, and are very susceptible to changes in relative humidity. Their physical instability is another cause of loss of surface details. If an artefact is covered with basic chlorides, touching the affected areas by hand, or the abrasive action of packaging materials can move them or spread them. When these basic copper chlorides are transferred on to stable areas, as for example by contaminated gloves or packaging material, they can cause further breakdown.

1.6 Copper chloride corrosion and Pourbaix diagram

This type of diagram illustrates equilibrium stability regions for potential and pH. The lines are calculated from the Nernst equation. These diagrams show the reaction products when an equilibrium has been reached based on variation in Eh and pH. Pourbaix diagrams give equilibria for most chemical reactions in pure water, in some instances other solution concentrations are specified such as in Figure 1. 2 for chlorides. No predictions on corrosion rates can be made, since the corrosion rate is also dependent on the temperature and other variables in the aqueous solution (Jones, 1992, 49).

Regions in Pourbaix diagrams are generally labelled passive, corrosion and immune. The metal is passive in areas where an oxide is stable. Corrosion is probable in regions of the diagram where the soluble metal ions are stable. The metal is immune in areas of the diagram where only the reduced form of the metal is thermodynamically resistant to corrosion (Jones, 1992, 51)

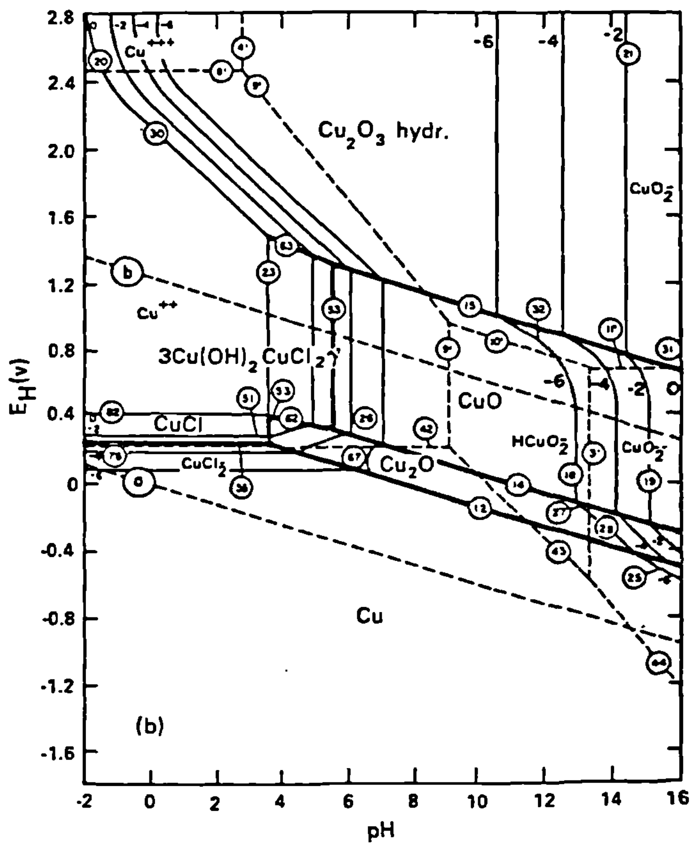


Figure 1. 2 Pourbaix diagram of Copper-Chlorine-Water

Figure 1. 2 shows the system of copper-chlorine-water at 25^0C and a chloride concentration of 10^{-2}g Cl- ion per litre. This is approximately the amount of Cu^- present in a saturated solution of CuCl. The diagram shows that CuCl is not stable at pH7. CuCl hydrolyses as follows: $2CuCl + H_2O \rightarrow Cu_2O + 2H^+ + 2Cl^-$. As previously discussed, the pH at the bottom of a chloride containing pit is thought to be acidic (Scott, 1990, 199). Under equilibrium condition at Eh=270 mV_{ehs} and pH 3.5, Cu, Cu_2O and CuCl are simultaneous stable, this situation is thought to be present at the bottom of a pit (Pourbaix, 1976, 30). At pH3-5, CuCl exposed to more oxidising conditions changes to Paratacamite ($3Cu(OH)_2CuCl_2$) (Scott, 1990, 199).

However, Pourbaix diagrams cannot describe completely the corrosion reactions occurring on an archaeological artefact. The diagram assumes an ideal equilibrium when pure copper, chloride and water is present. Archaeological artefacts generally contain various alloying constituents, which influence corrosion rates. Therefore the diagram is only a guide to the complex corrosion reactions occurring on an artefact.

1.7 Corrosion Inhibitors

To retard corrosion reactions, corrosion inhibitors are widely used in conservation. In the past, BTA has been used most commonly in archaeological conservation of copper and copper alloys. Corrosion inhibitors can be defined as substances added to the surface of a metal retarding the electrochemical process by altering properties of the surface state. Inhibitors are substances that inhibit one or more of the corrosion processes on a metal. This Ph.D. research is concerned with the application of organic inhibitors to copper and copper alloy archaeological artefacts. Corrosion inhibitors in industrial use find the widest application in recirculating systems. All of the organic inhibitors reviewed in this text are possibly toxic a description of health and safety measures taken during the experimental work can be found in appendix 8. Many inhibitors are effective for more than one type of metal, but ranges for pH, temperature and other conditions are often more specific.

Some inhibitors suppress the anodic reaction, other inhibitors suppress the cathodic reaction. Some even suppress both electrochemical reactions. Inhibitor compounds are adsorbed to the surface of the corroded metal. An effective inhibitor has to be chemisorbed, by the means of electrostatic or van der Waals forces reacting rapidly with the electrode. The inhibitor is generally the electron donor and the metal the electron acceptor. The organic inhibitors used in this work are compounds with a polar function. They often have atoms of nitrogen, sulphur and oxygen. The polar functions are thought to be the reaction centres resulting in the chemisorption of the inhibitor on to the metal. The ranking of effectiveness for organic inhibitors is thought to be sulphur > nitrogen > oxygen. The elements on the left have a lower negativity, resulting in an easier polarisability, resulting in a stronger inhibitor-metal bond (Trabanelli, 1970, 149).

Compounds such as Benzotriazol (BTA) have shown to polymerise (Sease, 1978). This polymerisation takes place through several points on the molecule. In the case of BTA, it is the nitrogen containing part. This N-metal polymer should result ideally in a corrosion inhibiting polymer film over the copper substrate.

The corrosion inhibiting inhibitor-metal film has to be adherent to the metal substrate, has to have a low solubility and prevent further dissolution of metal ions. If the complexes are soluble, an increase in corrosion rate is to be expected. The efficiency of a corrosion inhibitor is related to first layers of the chemisorbed inhibitors on to the metal. It is thought that film-forming inhibitors are dangerous inhibitors because of the possibility of localised attack in regions where no inhibitor is present (Trabanelli, 1970, 149-190).

This research is mainly concerned with the selection of appropriate corrosion inhibitors from those inhibitors already in use in industry. These selected inhibitors are then tested according to specific criteria for archaeological conservation. The testing procedures are not only based on corrosion rates, but also damaging effects that might occur on an artefact. Such damages are: the depletion of copper corrosion products found on the surface of an archaeological copper artefact and the discolouration of the artefact due to the corrosion inhibitor.

Industrial inhibitors are generally applied to clean copper substrates, initial copper depletion and surface discolouration are not of great concern. However, the ethical constraints given to modern conservation treatments of archaeological artefacts, do not allow such drawbacks. The main guideline of a new treatment has to be minimal intervention with the archaeological artefact. Minimum intervention is a paramount principle in this research.

Chapter 2

The Choice of New Corrosion Inhibitors for Copper and Copper Alloy Artefacts

2.1 Introduction

Only Benzotriazole (BTA) has been widely accepted in the stabilisation of copper and copper alloy artefacts. Madsen (1967) proposed BTA for archaeological conservation, based on the vast research done for industrial purposes. Due to its perceived advantages and satisfactory results, BTA has been the predominant corrosion inhibitor used in the conservation of copper and copper alloys. This has seemingly lead to the exclusion of research on other compounds for copper in archaeological conservation. Recently another corrosion inhibitor was suggested for copper corrosion inhibition in conservation: 2-amino-5-mercapto-1,3,4-thiadiazole (AMT) (Ganorkar et al., 1988). AMT has been selected since it showed better corrosion inhibition properties than BTA. This compound has not been accepted generally for use in archaeological conservation, due to the lack of information available, both on industrial applications and in the field of archaeological conservation. Another complication was the purchase and supply of this chemical. In the past it was not available in a refined form, and many conservation laboratories are not equipped to perform the required chemical processes. The article written by Ganorkar et al. (1988) is not sufficient for the application of AMT in archaeological conservation. As a third year B.Sc. dissertation I undertook further research in to the application of AMT in the field of conservation (Faltermeier, 1992). However, the experimental results were not conclusive. It was therefore decided to further investigate selection strategies for application of other corrosion inhibitors in archaeological conservation of copper and copper alloy artefacts.

2.2 First Search for New Inhibitors

A literature survey was undertaken in the field of industrial copper corrosion inhibitors. The current chemical and engineering literature was consulted. At an early stage it was expected that no copper corrosion inhibitor would be found which could be clearly identified on the basis of published data alone for its suitability for the conservation of copper objects. All inhibitors were recommended for specific tasks, in an industrial or household environment. Inhibitors are usually tested on uncorroded metallic copper and copper alloys, used in modern installations. Inhibitors were applied to metallic, polished and, in many cases, oxide free copper surfaces. No study published dealt with samples comparable to the heterogeneous corrosion layers found on archaeological artefacts from burial environments. In no case was a ternary alloy such as copper-tin-lead tested, one of the various copper alloys found in archaeological sites. These findings made it obvious that published test results given in the industrial literature were of value only for preliminary selection for use in archaeological conservation. The published data gave an indication of what to expect in further trials in conservation. A re-evaluation of published literature from a conservation point of view was necessary to identify new inhibitors specifically related to objectives in archaeological conservation.

There are several industry based comparative studies in the area of copper corrosion inhibitors such as Musiani et al. (1987), Lewis (1982), Horner et al. (1982,1985), and others. Many publications cover corrosion protection in water flow systems such as boilers, radiators, chemical containers and sea water systems. Industrial inhibitors are all subject to much harsher conditions than those to which an archaeological artefact would be exposed. Such industrial environments have little direct relevance to conditions an archaeological artefact would generally experience in a storage area, or a show-case.

To identify potentially suitable inhibitors for conservation, a new list of known industrial inhibitors was prepared. The Chemical Abstracts were consulted, to find articles published on this subject between 1972 and 1992. The subject index in Chemical Abstracts was screened for key words such as *inhibitors*, *corrosion inhibition*, and *copper*. To narrow the lengthy search, only copper corrosion inhibitors in aqueous chloride and hydrochloric acid media were further pursued. The same type of search was conducted using the Science Citation Index, on CD-ROM. Only the years 1986-1993 were available in the computer search on CD-ROM. The computerised search on laser disk had the advantage that not only articles with specific key words in the title would be detected. The computer would also refer to articles with similar subject matter. This enabled a more in-depth search of a range of related subjects, in a relatively short time.

This type of literature search produced a vast number of references to some 82 corrosion inhibitors, all related to copper in the above specified environments. It was apparent that some of the articles covered the same inhibitors. From this preliminary list (see appendix 1), a closer review of the publications was undertaken. Some of the references referred to Japanese patents or company reports, or for example, to Czechoslovakian conferences. In such cases it was not practicable to proceed beyond reading the abstracts.

The studies consulted were screened for specific features such as applications and types of compound potentially suitable for archaeological metallic objects. To be appropriate as a copper corrosion inhibitor for conservation, the compound should satisfy various requirements arising from the object, the environment and the conservator. These requirements include the following:

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, 208). 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, 36).

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, 229).

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. The later is frequently used as a treatment for bronze disease in conservation. The metallic traces left in the corrosion products and on the surface may interfere with the analytical results of trace element studies.

9. The solubility of the compound in water or alcohol is another important factor. The solvent in which it is applied should be inexpensive, non-toxic, and not hazardous. It would be ideal to be able to control the viscosity of the inhibitor formulation in order to influence penetration and spread of solutions.

10. The inhibitor should be readily available in a pure form through chemical suppliers. However it is apparent that in many cases inhibitors are produced on a trial basis. Many conservation laboratories do not have the facilities to refine mixtures of compounds.

11. The price of the inhibitor is a relative measure, but should still be economical for large scale applications. Some inhibitors are active in the low concentration of 10^{-3}M.

The industrial literature search identified three main types of inhibitors, which were found to be very effective in the inhibition of copper corrosion in industry and which had not yet been tested in archaeological conservation. These inhibitors contain sulphur, nitrogen or a combination of both. Corrosion Inhibition efficiency was found to be as follows: sulphur containing > nitrogen containing > oxygen containing (Thierry and Leygraf, 1985, 1013)

2.3 Copper Corrosion Inhibitors Chosen for Further Testing:

The literature cited covered a wide range of inhibitors. The research into these publications aimed at finding inhibitors suitable for museum environments. The following inconsistencies with conservation aims were encountered:

- Industrial tests were performed on reagent grade copper or alloys rarely comparable to those expected to occure in an archaeological context.
- Archaeological artefacts are covered in oxide layers, the metal surfaces used in industrial experiments are free of contamination. The surfaces were cleaned since oxides would have interfered with test results.

- In many cases the pH range of inhibitor solutions was not indicated or the application was in a very narrow pH range. Frequently the pH was buffered to allow the evaluation in near neutral solutions. In the case of archaeological copper and copper alloys, the pH range over which the inhibitor is effective should be as low as 2 since it is thought that chloride corrosion pits develop at a pH between 3.5-4p (Scott,1990)
- Only in a few instances, was it mentioned if an inhibitor formed an anodic, cathodic or both types of corrosion protection.

Inhibitors obviously not complying with the requirements, listed above for archaeological metals were not considered.

Some of the comparative industrial studies, such as Horner (1981, 1982) cover a wide range of inhibitors, and try to determine the suitability of compounds in a given environment. L.Horner, University of Mainz, Germany, recently published six articles concerning copper corrosion and inhibitors. In publications between 1981 and 1982 in "Zeitschrift für Naturforschung" and "Werkstoffe und Korrosion", he considered 595 possible inhibitors for copper in sodium chloride solutions at pH4 at room temperature. The results showed that 2-amino pyrimidine (AP) had the highest inhibiting efficiency. It forms a three dimensional structured AP-Metal film on the surface.

In later trials he reported (1985) that 2-mercaptopyrimidine (MP) is an even better inhibitor than AP under some circumstances. He determined the total corrosion time of copper in the solution inhibited with 2-aminopyrimidine to be >2000 hours and 2-mercaptopyrimidine (MP) to be >800 hours. 2-mercaptopyrimidine had higher inhibiting efficiency on copper grains, whereas 2-aminopyrimidine was more protective on copper plates. The better protection of copper grains may suggest a higher effectiveness of MP on more porous structures of corroded copper artefacts. A later study of AP and BTA showed that under the same conditions 10^{-2} M AP protects copper grains for >840 hours, 10^{-3}M AP 400 hours. 10^{-2} M BTA protects the grains for only 150 hours and 10^{-3}M BTA for as little as 90 hours. Horner et al. (1981) clearly states that AP is a much more effective inhibitor than BTA . Already at pH 4, AP and MP are shown to have better inhibiting efficiency than BTA, and with falling pH their effectiveness increases. The data published for 2-aminopyrimidine and 2-mercaptopyrimidine were encouragement for further evaluation for archaeological conservation applications.

The industrial studies by Trabanelli (1974), reported that 2-mercaptobenzoxazole (MBO), 2-mercaptobenzimidazole (MBI) and 2-mercaptobenzothiazole (MBT), had inhibition efficiency similar to BTA at near neutral pH. Like BTA they interact with the copper to form a film of inhibitor-copper complex. Musiani et al. (1987) found that not only were they similarly effective in near neutral solution, but also superior in inhibiting corrosion at a pH as low as 2. The polymeric complexes formed by BTA deteriorated when exposed for a longer period to pH 2 and the film started to fail (Musiani, 1987, 194). Hence these inhibitors may be suitable for conservation since they cover a wider pH range.

The only other nitrogen based copper corrosion inhibitor shown to be suitable enough for copper corrosion inhibition in conservation is 5,6 dimethylbenzimidazole

(DB). This compound developed a higher inhibiting efficiency than 2-methylbenzimidazole and benzimidazol and was almost as effective as 2-mercaptobezimdazole (Patel, 1974). Lewis (1982) showed that DB is similar in effect to BTA in a 3% NaCl solution. It was better than 2-methylbenzimidazole, benzimidazole, and indazole. Benzimidazole, indole and indazole molecules are similar to BTA, and do not contain sulphur. They are film forming, relatively insoluble in water, but soluble in many organic reagents.

Other nitrogen based inhibitors had unacceptable features which would be disadvantagous for archaeological conservation. Benzimidazole had the draw back that it forms its bonds to only every other copper atom, which leaves the unbonded copper subject to attack. Indole copper complexes are soluble in water, and tarnish copper. The complexes of indazole are soluble in organic solvents, and it has a much lower inhibiting effect than DB (Fang et al., 1986, 486-487).

Compared to all copper corrosion inhibitors found in the literature 5,6-dimethylbenzimidazole (DB) seems a suitable nitrogen-copper complex forming inhibitor, with the possibility to be suitable for conservation purposes. The author proposes that purely nitrogen complex forming inhibitors might be more suitable for conservation on the basis that in the industrial literature it was reported that some of the sulphur containing compounds cause a darkening of the polished copper surface during the complex formation. In the conservation of archaeological copper objects, it is seldom encountered that a copper or copper alloy artefacts has a metallic surface: normally it is covered with different types of corrosion products. It is however possible that the copper ions from the corrosion products might form colour influencing surface films.

Some objects have been stripped of their corrosion products and in such cases, where a corrosion inhibitor is desired, the industrial literature serves as a better guide.

As a result of this literature survey of industrial research, in addition to BTA and AMT, six additional compounds have now been found to have effective corrosion inhibiting properties together with other properties, suggesting that they may be suitable for the application to archaeological copper and copper alloy artefacts. These copper corrosion inhibitors are thought to be potentially more effective than BTA or AMT for application in archaeological conservation. These six industrial inhibitors will be further investigated to determine the conditions under which they may be more suitable for conservation of copper and copper alloy artefacts than BTA or AMT.

Nitrogen based inhibitors	*Formula*	*Short*
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

Table 2. 1 Selected Corrosion Inhibitors

Chapter 3

Eight Possible Copper Corrosion Inhibitors for Conservation

The following chapter presents eight corrosion inhibitors selected according to the criteria outlined in the previous chapter. Most of the observations represented in this section are related to chemical factors. Little is available on the physical properties of various inhibitor films. The industrial tests results cited were used as a guideline to predict the behaviour of archaeological copper and copper alloys. It was difficult to compare the corrosion inhibition results (listed in percent) from different corrosion tests, because various inhibitors perform differently in different testing environments. This is the fundamental problem, which inhibitors work "best" for archaeological copper artefacts. Information and data relevant for each inhibitor were collected and listed according to its relevance to conservation. Emphasis was placed on chemical hazards to conservators, and the mechanisms of complex formation with copper species, as found in the literature.

3.1 Benzotriazole (BTA)

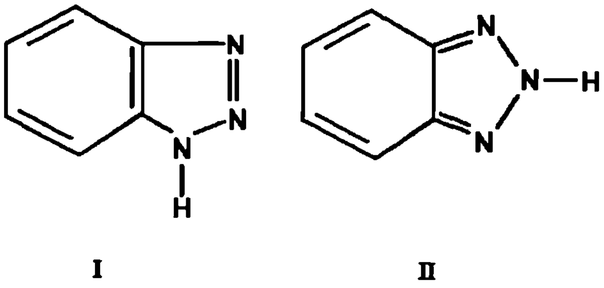


Figure 3. 1 Tautomeric Forms of BTA

The chemical formula for Benzotriazole (BTA) is $C_6H_5N_3$. BTA is known under the following synonyms: BTA, 1,2-aminozophenylene, azimidobenzene, aziminobenzene, benzene azimide, benzisotriazole, 1,2,3-benzotriazole, cobratec #99, 2,3-diazaindole, NCI-CO3521, 1,2,3-triazaindene, U-6233. BTA is a crystalline, yellowish almost odourless substance. It has a molecular weight of 119.13 g/mol, a melting point between 94-97°C and a boiling point of 203-205°C. Its solubility in water at 20°C is 20 g/l, and it is also soluble in some organic solvents such as alcohol and acetone (Schuchardt Safety data sheet 1993). It has a pH 5-6 in water at 20°C. At temperatures greater than 160°C there is a risk of explosion during distillation (Schuchardt, 1991, safety data sheet). BTA has come to represent an industrial standard, against which the performance of other inhibitors can be compared.

3.1.1 Chemical Hazards

BTA is certainly harmful if swallowed. It may be harmful when inhaled, or absorbed through the skin. It is known that it causes eye and skin irritation and that it is irritating to mucous membranes and the upper respiratory tract, but still BTA has not been thoroughly investigated. In fire conditions it emits toxic fumes of carbon monoxide, carbon dioxide and nitrogen oxides. Precautions have to be taken when BTA is handled and stored. Chemical safety goggles, chemical resistant gloves, and a respirator should be worn. A mechanical exhaust is also required (Aldrich, 1993, safety data sheet).

3.1.2 Corrosion Inhibition

Benzotriazole has for some time been known to enhance the corrosion resistance of copper and copper alloys. Madsen (1967) first recommended its use for archaeological conservation. Aqueous, near-neutral BTA solutions with cuprous and cupric salts produce yellow to green precipitates of BTA-Cu complexes. They are virtually insoluble in water, and many organic solvents. These complexes are also thermally stable up to about 250°C. These properties are probably associated with the triazole ring. Cotton (1967) found that the N-H group forms insoluble complexes with at least one of the other nitrogen atoms. The complex film formed over treated objects is extremely thin and amorphous. The stoichiometry of BTA to copper is 1:1 (Cotton, 1967, 1-3). Bo-Shung Fang mentions the stoichiometry of 2:1 Cu:BTA by vapour deposition on oxidised copper (Fang, 1986, 485).

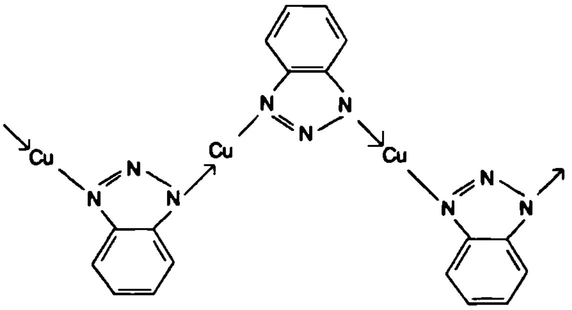


Figure 3. 2 Cuprous Benzotriazole Polymeric Chain. This Diagram is Presented as Presented by Cotton (1967).

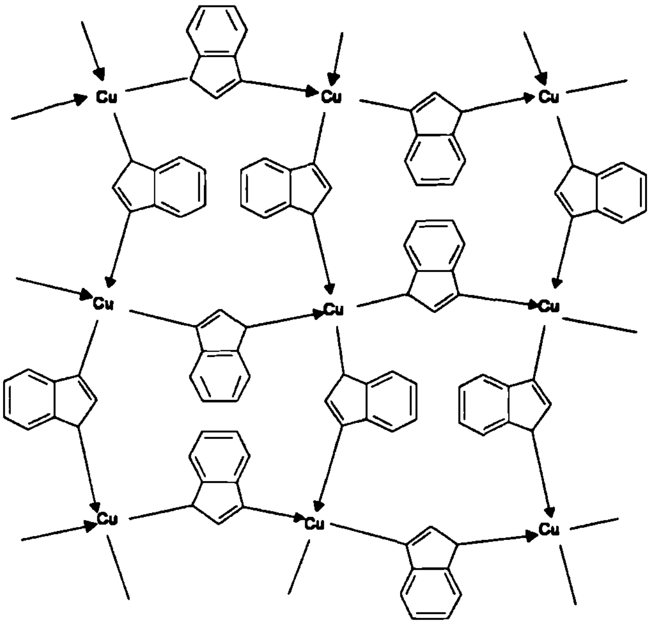


Figure 3. 3 BTA-CuII Polymer (Sease, 1978)

The copper is bonded to the amino-nitrogen on one side of the molecule, and attached to the electron pair on an unsaturated nitrogen ring on the other (Brusic et al., 1991, 2257).

Metallic copper reacts faster with azoles than oxidised copper surfaces. The conclusion reached is that the reaction order is Cu(0) > Cu_2O > CuO. An oxide covered copper surface immersed in BTA showed the following reaction:

$2BTA + Cu_2O \rightarrow 2Cu^+BTA^- + H_2O$ (Xue, 1991, 763)

Xue (1991, 763) proposed the following reaction for BTA with copper in air:

$$2BTA + Cu(O) + \frac{1}{2}O_2 \rightarrow 2Cu^{+}BTA^{-} + H_2O$$

Brusic (1991) found that copper in the Cu-BTA complex is Cu^{+}. The copper nitrogen bond can be formed on an oxidised and an oxide-free copper surface. The BTA polymeric film on oxidised copper, provides a better barrier for the copper ions and hinders them from travelling into solution, in contrast to a BTA film on an oxide free surface (Brusic et al., 1991, 2253). This is an advantage in the conservation of archaeological copper and copper alloy artefacts. The film thickness alters between 5-40Å in the pH range of 3 to 12. It was found that in pH 2 the thickness can reach up to 250Å. Fang mentions film thickness of 50-60Å for evaporated films and 40-140Å for films formed in solutions. Films of a thickness of up to 5000Å are possible. The thick films are of multiple layers of Cu, Cu_2O, Cu(I)BTA 4-5Å thick (Fang et al., 1986, 485).

The BTA film reacts mainly as a retardent for the dissolution of copper, and secondarily as a coating to stop oxygen reduction on the metal surface (Brusic et al., 1991, 2253). BTA acts as a cathodic inhibitor at low concentration ($<10^{-3}$ M) and when added in high concentration ($>10^{-3}$M) it acts as an anodic corrosion inhibitor. Hence, either stopping hydrogen evolution at the cathodic sites, or oxygen absorption on the anodic reactive sites. At a concentration of 7.5×10^{-3} M, Mayanna and Setty (1975, 636) found BTA inhibits corrosion to a maximum extent, during the dissolution of single crystals of copper in 0.1N sulphuric acid.

If a copper surface consists of Cu_2O, and is treated with an aqueous solution of BTA, Cu(I)-BTA, and Cu(II)-BTA complexes form. If the substrate consist of

CuO, the Cu(I) compound forms first, which in turn is oxidised to Cu(II)-BTA (McCrory-Joy and Rosamilia, 1982, 105). At pH 3 the anodic dissolution of copper is higher than at pH 6, so that the BTA present in the solution is more likely to react with the copper ions in solution. At a near neutral pH, Cu_2O and CuO are much less soluble and so the copper-BTA film is much more stable (McCrory-Joy and Rosamilia, 1982,117).

At pH 7 the film grows slowest on oxides and the resulting film thickness is thin. However this type of film has the most polymerised structure, and thereby provides the best corrosion protection. At pH 2 the film grows rapidly and a thick film formation occurs. The structure of these films are least polymerised, and their structure offers less protection for the copper underneath. Films grown at pH 3 act as cathodic inhibitors of the hydrogen evolution process, but they do not inhibit the oxygen reduction process. The failure to inhibit the oxygen reduction suggests that the film is at least somewhat permeable to oxygen. The entering oxygen could cause further copper oxidation at the Cu/Cu-BTA interface (Brusic et al., 1991, 2257). The film grown at pH 2 is thicker but more permeable to oxygen, resulting in a lower protection rate than films grown at a neutral pH (Brusic et al., 1991, 2258).

Brusics et al. (1991) study is confirmed by Musianis et al. (1987, 188) earlier findings. To adjust the pH of the treatment solution, they buffered with hydrochloric acid or KOH. The inhibitors tested were Benzotriazole (BTA), 2-mercaptobenzothiazole (MBT), 2-mercaptobenzimidazole (MBI) and 2-mercaptobenzoxazole (MBO). The treatment 1M KCl solution had a neutral and an acidic pH (pH 2). The copper was in the form of a disc with an area of 0.03-0.32 cm^2.

BTA in mM	*pH*	*Time/h*	*protection efficiency in %*
1	7	1	95
1	2	1	60
1	7	3	97
1	2	3	21
10	7	1	98
10	2	1	70

Table 3. 1 Corrosion Inhibition of BTA at Different pH and Different Concentrations (Musiani et al., 1987).

The table above clearly identifies the low protection rate of BTA at pH2. At a 1 hour exposure at pH 2 BTA corrodes 60%. At an exposure to the solution for 3 hours, the effectiveness drops to 21%. This might explain why the corrosion pits (pH 3.5-4 (Scott, 1990, 197)) on objects heavily infested with copper chlorides are not inhibited after several days of immersion in BTA. The present author has even observed the corrosion of artefacts after several days in the same inhibitor solution. This leads to the conclusion that objects should not be left for an excessive time in BTA solutions.

Ishida and Johnson (1986, 61) used Fourier transform infrared reflection-absorption spectra for BTA coated copper plates. This has shown that water interferes with BTA on a copper surface at 80°C (100% RH, 24 hours). BTA degraded partially in this extreme environment.

Xue (1991, 146) measured the effectiveness of BTA and 2-mercaptobenzimidazole films on copper with cyclic voltammetry. Copper was pre-treated with BTA or 2-mercaptobenzimidazole (MBI), and exposed to 10% HCl or 15% NaOH. The BTA polymer layer on the copper surface disappeared completely after 1 hour. The film formed by MBI was still present and protected the metal effectively after 24 hours.

Several copper corrosion inhibitors were compared by Prajapati et al. (1976, 723). He found that BTA and 2-mercaptobenzoxazole gave almost 100% protection for copper and brass in a solution of 1 N ammonium chloride for 2 days, when compared to a blank (see Table 3.6).

Corrosion tests undertaken by Lewis (1982) used copper plates in 3% NaCl (20°C, for 187 hours). The copper plates (coupons) were inhibited by various copper corrosion inhibitors. This test indicated that the inhibition efficiencies were in the order: BTA> 5.6-dimethylbenzimidazole > 2-methylbenzimidazole > benzimidazole > indazole.

Test solution	*20 mM/l inhibitor*	*corrosion loss of Cu ions in solution in ppm*	*inhibition efficiency in %*
3% Na Cl		76.0	0
3% Na Cl	BTA	1.0	98.68
3% Na Cl	5.6-dimethylbenzimidazole	2.5	96.71
3% Na Cl	2-methylbenzimidazole	5.0	93.42
3% Na Cl	Benzimidazole	6.0	92.11
3% Na Cl	Indazole	6.5	91.45

Table 3. 2 Comparative Study (Lewis, 1982, 61)

The studies undertaken and the data given lead to the conclusion that BTA is a good inhibitor on oxidised surfaces. In archaeological conservation almost all copper surfaces are oxidised, suggesting that BTA is an ideal inhibitor. However, some conservation treatments with BTA have shown that artefacts containing large amounts of chlorides are often not protected by BTA. Publications cited indicate why BTA might have failed.

1. At pH2 BTA forms thick, not very well polymerised films (Brusic et al., 1991). Scott (1990) found that cuprous chloride can cause a pH 3.5-4. This might be

further decreased when a solution of BTA is applied. BTA is known to have a pH of 5-6 in water (Aldrich Safety data sheet 1993). The BTA-copper polymer film formed is thick and porous, and allows oxygen to enter, leading to further corrosion.

2. It is also not clear if the application of BTA in Industrial Methylated Spirits, water, methanol, or ethanol causes a change in pH, leading to a change in the polymer structure. Different solvents might also change corrosion rates in BTA solutions, and penetrate differently into the corrosion layers.

3. The BTA-copper polymer film might also be susceptible to UV. Polymers are known to have poor ageing properties when exposed to high levels of UV radiation. Generally the UV output of lighting in showcases is not monitored for metal artefacts.

The above mentioned points strongly suggest that objects treated in the past with BTA, should be carefully monitored during and after an exhibition period. The porous BTA-Cu film covering chloride pits, could further break up and allow humidity to enter, causing an increase in acidity and further enhancing the breakdown of the protective inhibitor layers. The so damaged film could allow the formation of anodic and large cathodic areas, again causing further corrosion of an object. In the future, a treatment is needed which will protect against chloride containing areas, evacuating them or rendering them inactive since they seem to be the main source of degradation.

3.2 2-Amino-5-Mercapto-1,3,4-Thiadiazole (AMT)

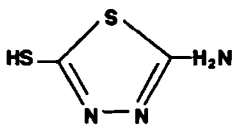


Figure 3. 4 AMT Molecule

The chemical formula is $C_2H_3N_3S_2$. It is also known under the synonyms of: AMT, 5-amino-2-mercapto-1,3,4-thiadiazole, 2-amino-1,3,4-thiadiazole-5-thiol, 5-amino-1,3,4-thiadiazole-2-thiol, 2-amino-delta(2)-1,3,4-thiadiazoline-5-thione, 5-amino-1,3,4-thiadiazoline-2-thione, 5-amino-1,3,4-thiadiazole-2(3H)-thione, 2-mercapto-5-amino-1,3,4-thiadiazole, 1,3,4-thiadiazole-2(3H)-thione, 5-amino- (9CI), 2-thiol-5-amino-1,3,4-thiadiazole. AMT is a white-yellowish crystalline powder. Its weight is 133.19 g/mol. It has a very low solubility in water, at 20°C only 2g/l. Its pH in water at 20°C is 3.9. Thermal decomposition is higher than 245°C (Schuchardt & Co., 1991, safety data sheet).

3.2.1 Chemical Hazards

AMT may be harmful by inhalation, ingestion, or skin absorption. It is known that it causes eye and skin irritationand that the compound is also irritating to mucous membranes and upper respiratory tract. All chemical, physical and toxicological properties have not been thoroughly investigated. Though it emits toxic fumes, of carbon monoxide, carbon dioxide, nitrogen oxides, and sulphur oxides under fire conditions. When handled and stored, chemical safety goggles, respirator, and chemical resistant gloves should be worn. The compound should only be applied under a mechanical exhaust system. The dust should not be inhaled, and contact with eyes, skin and clothing should be avoided (Aldrich, 1993, safety data sheet).

3.2.2 Corrosion Inhibition

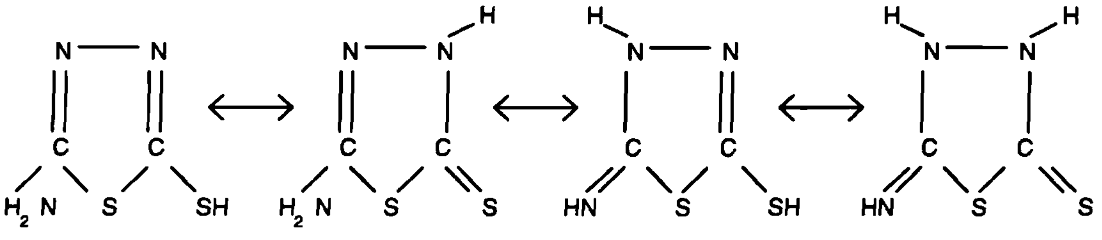
Ganorkar et al. (1988) was the first to publish AMT as a new corrosion inhibitor for the conservation of copper and copper alloy artefacts. AMT seems to be the only compound since the introduction of benzotriazole, proposed to prevent further corrosion of copper and copper alloy artefacts. Reportedly, AMT reacts without interfering with the objects appearance and morphology. Ganorkar et al. claim that the compound dissolves the copper chloride present on the surface; complexing the water insoluble chlorides into solution. This fact would indicate AMT would be a better, more effective inhibitor than BTA, since the latter has shown to only cover the surface of the corroding area without actually passivating the chloride minerals underneath the protective Cu-BTA polymer film. If the BTA film is ruptured, the chlorides can be activated again to continue the corrosion cycle. The paper published by Ganorkar et al. has caused grave concerns for many conservators, since the treatment suggested has ethical drawbacks, specifically the use of nitric acid to adjust the pH.

> *"The cleaned coins were then immersed in 150 ml of 0.01M aqueous solution of the AMT compound. In order to speed up the reaction a few drops of nitric acid (1:1) were added and the solution was heated up to about 60°C It was observed that a pale yellowish-green crudy precipitate was formed on the diseased areas of the coins."* (Ganorkar et al, 1988, 98)

The addition of nitric acid should be avoided, since it might contribute to further damage to the patina. It could cause severe corrosion of perfectly well preserved areas.

Ganorkar et al. (1988, 99) undertook infrared studies to investigate the bonding between AMT and the copper surface. He found that the S-H bond in the compound was absent in the coating material. This suggests a deprotonisation of the S-H group. The sulphur subsequently bonds to the metal ion. Further to this, he found a metal-nitrogen bond which he attributed to the participation of the NH_2 group in AMT.

Gajendragad and Agrawala (1975) found that AMT can exist in four tautomeric forms:



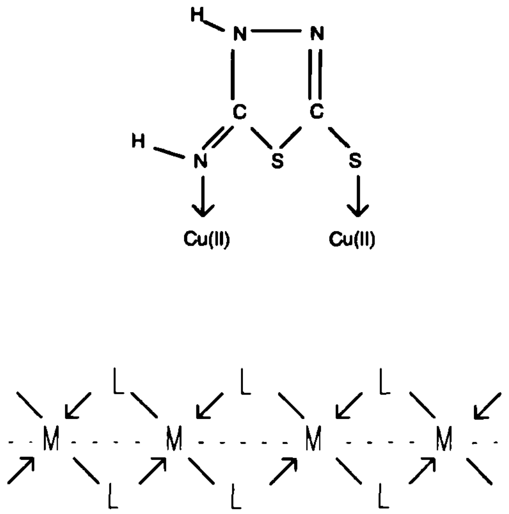
1 2 3 4

Figure 3. 5 Tautomeric Forms of AMT (Gajendragad and Agrawala, 1975, 1331)

Pandit Rao et al. (1987, 38) stated that AMT forms a completely insoluble and polymeric complex with copper. In a test he found that a thin yellow coloured complex layer develops over the copper surface, when it is immersed for 6 hours into a 0.01M solution of AMT. The pH of the solution varied in his tests from alkaline to acidic. The specimens immersed into the solutions which contained AMT had a weight increase, which is probably due to the complex formation. He also found that the inhibiting efficiency of AMT in nitric acid, acetic acid, ammonium chloride, sodium chloride and ammonium hydroxide was 100%. This however does not indicate how AMT will behave on an archaeological copper artefact, it only suggests a good performance in conservation.

Copper sheets treated with AMT in nitric acid were washed with water and dried. The sheets were then exposed for about one month to variable temperatures, humidity, gases and tap water. The sheets were shown to be completely resistant to atmospheric corrosion. If they were placed in a 3% sodium chloride solution, they developed stains on the surface after the course of 4 days (Pandit Rao et al., 1987, 39). The reaction with sodium chloride might give an indication as to its behaviour under extreme saline conditions. This is not necessarily comparable to conservation environments, but could indicate a lack of protection in highly concentrated chloride areas.

The complex formation and infra red bands of AMT with several metals such as Zn(II), Cd(II), Pb(II), Cu(I), Ag(I) and Tl(I) were studied by Gajendragad and Agrawala (1975). They found that the (S-H) band in AMT is absent in the spectra of the complex. It is presumed that the S-H undergoes ionisation, and the sulphur bonds to the metal. Also the N atom of the imino group is considered to bond to the metal (Gajendragad and Agrawala, 1975, 1332). The complex formation is with sulphur rather than with nitrogen. Cu(I) probably forms a linear bond through the sulphur atom and a weak bond through the imino nitrogen. Since most of the Zn(II), Cd(II), Pd(0), Pt(0) and Pb(II) complexes have a tetrahedral geometry, the same geometry is suggested for the copper complex. Gajendragad and Agrawala (1975, 1028-29) proposed the following bonding and polymeric structure: for Cu(II):



M = Cu(II), L = structure above

Figure 3. 6 AMT- Metal Bond

The AMT-Cu complex is insoluble in water and other organic solvents, which refers to its polymeric nature (Gajendragad and Agrawala, 1975, 1333). Domagalina and Przyborowski (1965, 413) reported that the stability constant for copper, lead, silver, nickel and zinc were as follows:

$$Cu > Pb \geq Ag > Ni \geq Zn$$

AMT may be dissolved in several suitable organic or inorganic solvents, but preferably in an aqueous or alcoholic medium. This is preferable for conservation purposes, because of health, safety, and financial considerations. The pH of the solution should be above 5, but preferably at about 8. At a lower pH the metal film is attacked (US Pat. No. 4,357,396).

E. Sander (1991) in the Staatliche Akademie der Bildenden Künste Stuttgart, Institute für Technologie der Malerei, undertook in the course of teaching, an unpublished investigation in to the reaction of AMT and copper, and copper corrosion products. She acquired corrosion samples of archaeological bronze objects, which were visually investigated. The minerals present were probably malachite and atacamite/paratacamite. Each corrosion sample was placed into a watch glass and a solution of AMT (0.01 mole in H_2O, straight from the Merck-Schuchardt supplier canister Nr.814266) was added, and heated to 60°C. After a short time the "chloride" corrosion products transformed in to a light-green deposit. The "carbonate" corrosion products did not change in appearance. The chloride containing samples were then filled with AMT until they were completely dissolved. The samples were then allowed to dry. In the chloride containing watch glass a light yellow-green to dark green powdery deposit was observed. In the watch glass containing the carbonate corrosion products, two kinds of crystals were visible after re-crystallisation, a white needle like crystal and the visually unaltered carbonate corrosion products. The needle like crystals were compared with a third sample, a re-crystallised solution of pure AMT. The pure sample again showed the same white needle like crystals, which were slightly larger than the one from the carbonate sample. The size difference is probably due to the difference in evaporation time. The same needles are mentioned by Gajendragad and Agrawala (1975, 1331), when they actually synthesised AMT. Sander performed the test mentioned above also with BTA (3% in Ethanol), and none of the corrosion products were altered.

Sander (1991) also undertook corrosion inhibition tests, since she wanted to compare the effectiveness of AMT and BTA. In these tests a number of copper strips were treated after the standard BTA treatment (3% in ethanol, at room temperature for 24 hours). Another batch was treated with AMT after the Ganorkar et al. treatment (0.01 mol AMT in water at 60°C for 1 hour). After one day some of the treated copper strips were exposed to a corrosive atmosphere of Na_2S dissolved in water, and HCl. Using this method H_2S and HCl vapour was produced. Sander did not measure this vapour accurately. After 20 hours the untreated copper strips were black, the AMT treated samples were entirely black and the BTA treated samples were only a little stained. After the following three days even the BTA samples were black. The rest of the samples were exposed to laboratory conditions. After one year, the untreated samples and the BTA treated strip were unchanged and the AMT treated copper strips were a little darker and stained. Sander found that after treatment with AMT, the samples seemed to be darker. The samples treated with BTA were slightly mat and had a green appearance, and the BTA treated surface had not changed since. Sander indicated that AMT is not a very good corrosion inhibitor for copper. She suggested that this suspicion had to be consolidated using better, and long-term tests.

Sander's (1991) tests concerning the dissolution of the copper corrosion products, have clearly shown that AMT has a complexing effect with copper chlorides and could dissolve them into the AMT inhibited solution. The test should be refined on the basis that each known copper corrosion product on an archaeological copper artefact is tested. The corrosion products used should be in a refined form, most of which can be supplied by chemical manufacturers such as Merck and Aldrich. The results obtained by pure minerals could give clearer indication about morphological changes.

Sander and Ganorkar et al. have been the only people to test AMT. Both made the observation that AMT complexes cuprous chloride in to solution. The darkening of AMT treated copper coupons had to be expected, since sulphur compounds are known to tarnish metallic copper. These findings indicate the necessity of colorimetric tests of corrosion inhibitors. One important aspect of the resulting complex that is formed, which is not cited in the literature is the thickness of the AMT-Cu polymer films.

3.3 2-Aminopyrimidine (AP)

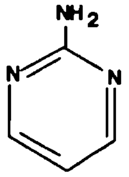


Figure 3. 7 AP Molecule

Aminopyrimidine (AP) is $C_4H_5N_3$. The chemical structure is shown above. Other synonyms under which the compound is known are AP, 2-Pyrimidineamine, and 2-Phyridilamine.

3.3.1 Chemical Hazards

AP may be harmful by inhalation, ingestion, or skin absorption. It can also cause skin and eye irritation. The toxicological properties of this compound have not been thoroughly investigated. AP emits toxic fumes under fire conditions; carbon monoxide, carbon dioxide and nitrogen oxides. When used, chemical safety goggles, rubber gloves, respirators, suitable protective clothing and a mechanical exhaust is required. AP has to be stored in a cool dry place. AP has a melting point of 125°C to 127°C, and takes the form of a light-yellow powder (Aldrich, 1993, Safety Data Sheet).

3.3.2 Corrosion Inhibition

This inhibitor was discovered to be the most powerful nitrogen containing inhibitor, of 592 inhibitors tested by Horner and Pliefke (1981-85). All inhibitors tested were in a standard solution of 2.5% NaCl, buffered with acetate buffer (0.55M Eisessig + 0.1M sodium acetate), at pH4, and 22°C under oxygen. AP was tested against BTA, the most widely used inhibitor for the prevention of copper corrosion. Horner and Pliefke (1985) found that AP is much more effective in its inhibiting action. Copper powder or sheets treated with AP in the standard solution mentioned above, formed a yellow-green complex film on the surface of the copper (Horner and Pliefke, 1981, 989). The AP-copper complex is soluble in nitric acid and hydrochloric acid, both attack the copper substrate at the same time. The complex layer analysed showed to be 30-32% copper and 15-18% chloride. When cuprous chloride and AP is mixed in acetate buffer, a complex precipitate forms (Cu · AP · Cl), which contains the same molar volume.

The molecular size of the [Cu x AP x Cl] complex has not been studied yet, since it is insoluble in organic solvents. [Cu^+ x AP x Cl]-complex is in a ratio 1:1:1 (Horner and Pliefke, 1981a, 995). It is thought that the complex consists of Cu^+ and 2% Cu^{2+}. The complex formation was determined using infrared spectroscopy. Cu^+ is thought to co-ordinate with the amino group as well as a N-atom from the ring. In a chlorine media, the bridging is done via the chlorine atom. There is a possibility that a hydrogen bridging is involved in the three dimensional structure of the polymeric film (Horner and Pliefke,1981a, 996).

To resolve the thickness of the film formed, neutron activation was applied, and ^{64}Cu with a half-life of 12.8 hours was produced. An activated copper sheet was placed into the standard NaCl corrosion solution, it was found that approximately 10 monolayers of copper go into solution (1 monolayer is 1.5×10^{16} atoms or 2.43×10^{-8} M). If AP is present in the solution, only 1-2 monolayers go into solution and subsequently further corrosion is almost halted. In the non inhibited solution, a fast increase was detected. After 19 hours the uninhibited solution had approximately 900 times more copper ions in solution than the sample with 12.6 mM AP. The same test was applied with BTA. In both cases where the inhibitor was applied a protective layer formed over the metal. (Horner and Pliefke, 1981a, 992).

It was established that the ratio Cu^+ and Cu^{2+} has a strong influence on the effectiveness of the polymeric layer formed. If there is an excess of Cu^{2+} in a 12.6 M AP inhibited NaCl, and pH 4 buffered solution, there is still a copper-AP complex film forming over the surface. This film is not dense enough to protect the metal underneath from further attack. If the concentration of inhibitor was increased by five times, the full corrosion inhibiting protection was restored after 7 hours. Horner and Pliefke found that during this period 70-80 monolayers of copper went into solution (Horner and Pliefke, 1981, 992-993). An increase of 10^{-2} M AP in a solution of copper powder resulted in the decrease of oxygen consumption, and an immediate inhibition occurred.

Between 1981-1985 Horner and Pliefke conducted tests to determine the effectiveness of AP. Their research showed a dramatic inhibition efficiency in NaCl, pH4 buffered solution. They immersed 0.5 g of copper powder into the standard NaCl solution. If the solution was inhibited by 10^{-3} M AP, the total corrosion time was 400 hours. If instead the solution was inhibited by 10^{-3} M BTA, the total corrosion time was 90 hours. A copper sheet immersed in a NaCl standard solution and inhibited with 10^{-2} M AP, did not corrode for 18 months (Horner and Pliefke, 1982a, 189-190).

Horner and Pliefke stated that the formation of the complex BTA film over the metal is faster than in the case of AP. However, AP builds a thinner film which gives better protection even at a low thickness. The film growth with AP takes longer but the film has a less porous structure than the BTA film. The tests concluded that the AP-copper complex film gives full protection with a thickness of 119 monolayers (178.5 x 10^{16} atoms) (Horner and Pliefke, 1982a, 191-3).

Horner and Pliefke's (1985) comparative study of AP and BTA showed the following:

0.5g copper dust in:	*total corrosion time:*
10^{-2} M BTA	20 hours
10^{-2} M AP	4-5 hours
$5 \cdot 10^{-2}$ M BTA	100-150 hours
$5 \cdot 10^{-2}$ M AP	500 hours

Table 3. 3 Comparative Study of AP and BTA.

AP loses its effectiveness with an increase of copper surface area. Nevertheless AP has shown to be more effective in small concentrations, and on larger copper surface areas such as copper grains and copper sheet than BTA (Horner and Pliefke, 1985, 547).

Horner and Pliefke 's research into the properties of 2-aminopyrimidine, led them to the search for an even more powerful inhibitor. They concluded that pyrimidine derivates are the most suitable inhibitors for copper corrosion inhibition in sodium chloride solutions. In a test series they conducted in 1982, they compared 570 inhibitors, under standard conditions (0.5g copper, 120ml NaCl, pH4 acetate buffer, at 22°C). The most outstanding inhibitors were again both pyrimidine derivatives, 2-aminopyrimidine (AP) and 2-mercaptopyrimidine (MP). The copper in chloride solution inhibited with AP, had a total corrosion time of >2000 hours and MP >800 hours. The article does not state what form the copper samples took. These findings indicate that 2-Mercaptopyrimidine should also be tested for its suitability in the conservation of copper artefacts. The addition of a mercapto group in MP, could increase the inhibition efficiency on the corroded copper and copper alloy artefacts.

3.4 5,6-Dimethylbenzimidazole (DB)

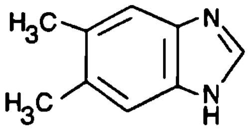


Figure 3. 8 DB Molecule

Dimethylbenzimidazole has a chemical formula of $C_9H_{10}N_2$. Its molecular structure is shown above. It is a white crystalline powder and has a melting point of 203-205°C (Schuchardt, 1991, safety data sheet).

3.4.1 Chemical Hazards

The compound may be harmful by inhalation, ingestion, or skin absorption. It can cause irritation. The toxicological properties of DB have not been thoroughly investigated. By thermal decomposition it emits toxic fumes of carbon monoxide, carbon dioxide, and nitrogen oxides. During handling and storage, respirator, chemical resistant gloves, safety goggles, and protective clothing should be worn. For application, a mechanical exhaust is required.

3.4.2 Corrosion Inhibition

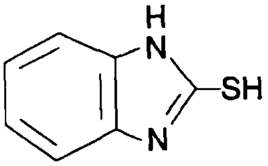
Only two articles were found which cover basic research into the corrosion inhibition of this compound. Patel (1974) applied DB in a 0.2M sodium hydroxide solution, to protect the corrosion of brass. He compared its inhibition efficiency with known inhibitors such as benzimidazole, 2-methylbenzimidazole and 2-benzimidazolethiol (MBI). The latter was also chosen in the search for a possible corrosion inhibitor for copper artefacts. MBI is found to be a better inhibitor than DB. DB is thought to be as good as 2-methylbenzymidazole and benzimidazole (Patel, 1974, 91).

Lewis (1982) treated copper plates (99.5% purity) in 3% sodium chloride solution for 187 hours at 20°C. The solutions were inhibited with benzotriazole and DB. The corrosion protection of BTA was 98.68% when compared with a blank, and the protection of DB was 96.71%. DB has like all the other inhibitors, a film forming tendency. The film on the metal surface, is well-adherent and compact. Patel found that copper ions form brown-red, dark-blue, brown-black and yellow precipitates with

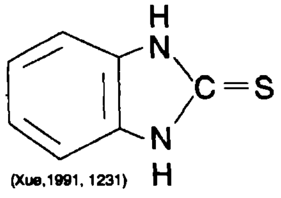
DB. This could indicate a possible surface discoloration of a treated object, depending on free copper ions present (Patel, 1974, 91).

There is very little information available on this inhibitor. DB was not tested at low pH, so the active pH range for effective corrosion inhibition is unknown. The fact that its inhibiting efficiency is slightly less than BTA, in 3% sodium chloride solution, does not give any indication as to its behaviour at lower pH, where BTA has clearly shown to fail. DB is also one of the few inhibitor compounds not to contain sulphur. It should be able to compete in effectiveness with compounds such as MBI. These findings, as well as missing data, are reasons to further investigation into this compound's properties. There was no information published on the inhibitor film thickness, or other physical or mechanical properties of DB.

3.5 2-Mercaptobenzimidazole (MBI)



(Aldrich, 1993, safety data sheet)



(Xue,1991, 1231)

Figure 3. 9 MBI Molecule

The compound has the formula $C_7H_6N_2S$. MBI is known under several synonyms, Antigene MB, MBI, Antioxidant MB (Czech.), AOMB, ASM MB, Benzimidazolinthion (Czech.), Benzimidazole-2-thiol, 2-Benzimidazolethiol, Mercaptobenzimidazole, 2-Mercaptobenzoimidzole, Mercaptobenzoimidazole, O-Phenylthiourea. It is a white-powder, with a melting point of 301-305°C (Schuchardt, 1991, safety data sheet).

3.5.1 Chemical Hazards

The compound may be harmful by inhalation, ingestion, or skin absorption. It can cause eye and skin irritation. The toxicological properties of this chemical have not been thoroughly investigated. Under fire conditions it emits toxic fumes of carbon monoxide, carbon dioxide, nitrogen oxides and sulphur oxides. Precautions have to be taken when handling and storing MBI. Respirator ought to be worn. Chemical resistant gloves, safety goggles and protective clothing are needed. It is recommendet that it be used only in a chemical fume hood. Prolonged and repeated exposure should be avoided. The compound has to be stored in a cool and dry place with the appropriate labelling (Aldrich , safety data sheet, 1993).

3.5.2 Corrosion Inhibition

MBI reacts as a cathodic inhibitor in salt solutions (Patel, 1972, 156). It was found that MBI forms a chemisorbed monolayered film on metallic copper. Like BTA, it not only reacts with metallic copper, but also forms a chemisorbed layer onto copper oxide surfaces, resulting in a co-ordination film. This would render it useful on archaeological artefacts, which are covered by oxide layers.

MBI has a strong N-H...S intermolecular hydrogen bonding in its solid state (Xue et al., 1991a, 140). Xue tested a 2% solution of MBI and copper powder, mixture which was agitated for two days. The copper powder formed a complex with MBI and change in to a yellow solid.

The reaction with metallic copper under nitrogen atmosphere, shows a C=S and a CSN-H bond in a Surface Enhanced Raman Scattering spectra. When MBI is applied onto copper in air, the C=S bond disappears and the spectra for CSN-H bond is reduced. This suggests the opening of the C=S double bond, and the deprotonation of parts of the imino groups. The chemisorption of MBI on metallic copper results in a new bonds, a Cu-N or Cu-S bond. Using the same tests and applying infra red spectra, the disappearance of C=S bonds and a decrease in N-H intensity was observed. There was also a change in the nitrogen bonding energy in the complex of MBI with copper (Xue et al., 1991b, 1230).

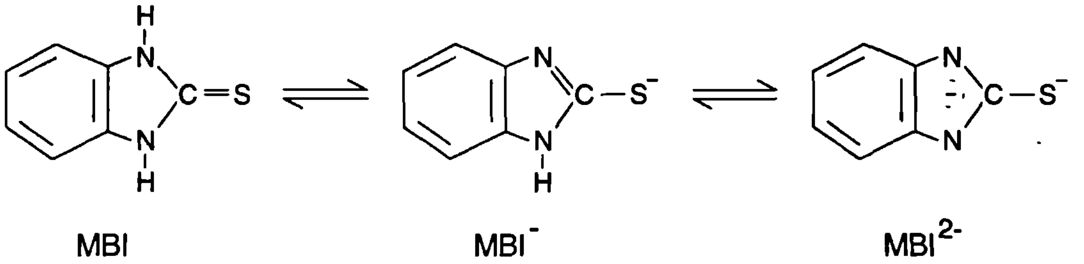


Figure 3. 10 Bonding of the MBI Molecule (Xue et al., 1991a, 142)

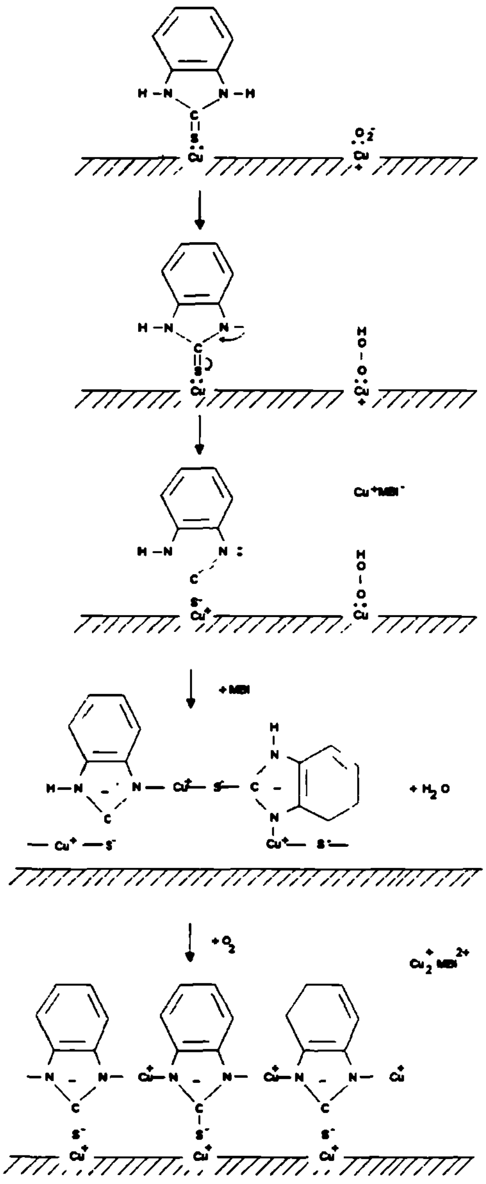
The reaction products of MBI and copper oxide analysed under infrared spectra showed a strong N-H absorption band, so little deprotonation takes place during the complex formation. The same MBI and copper oxides show a vibration of the C=S band, which is absent in the spectra of the MBI and copper metal product. So Xue concluded that MBI reacts better with the copper metal, cleaving the C=S bond, and that most of the pyrrole hydrogen atoms are lost. MBI has two nitrogen atoms which are called pyrrole nitrogen. The imino groups are deprotonated in the complex formation, resulting in a MBI^- and MBI^{2-} anion, which are also aromatic (Xue et al., 1991a, 142).

In the presence of air, MBI is deprotonated and the copper oxidised to Cu_2^+-MBI^{2-} or Cu^+-MBI^-. The reaction products of MBI with copper powder were analysed by Xue and they constituted C=35.5, N=11.92, H=2.02, Cu=36.9%. This indicates that the reaction is a mixture of the complexes of Cu_2^+-MBI^{2-} and Cu^+-MBI^-. The benzene and the heterocyclic ring is not lost, it remains in the product. The MBI anion forms a complex with Cu^+ (Xue et al., 1991a, 144).

In neutral solution it is suggested that MBI forms a ligand through sulphur. It is thought that the first reaction step of MBI with copper is MBI+Cu(0). MBI has three ligation sites involved in the formation of a copper-MBI complex, sulphur and 2 deprotonated imino groups. The deprotonated imino groups resulted in the formation of an MBI anion, which is aromatic. It has a negative charge which is distributed over several atoms. Both the sulphur and the nitrogen atom bond to the cuprous cations. The cuprous cations in turn can co-ordinate with two ligands. This results finally in a polymeric structure on the surface of copper. Since every Cu^{2+}-MBI^{2-} contains three ligation sites, the resulting film is compact and bounds strongly to the copper matrix. These three sites allow the complex to bind to the metal substrate (Xue et al., 1991a, 144).

Xue et al. (1991) found that MBI reacts in several different solvents. It also forms complexes with silver. A minute quantity of water was detected after the complex formation of silver with MBI. So Xue et al. proposed the reaction below (in Figure 3. 11)

In the comparative study by Xue et al. (1991), they treated copper samples with MBI and BTA and immersed them into 10% hydrochloric acid or 15% sodium hydroxide. They found that after one hour of immersion time the BTA-copper complex film disappeared completely. The sample which was treated with MBI, was still protected from etching after 24 hours. MBI treated copper samples exposed to the ammonia and alkali containing etching agent, at 60°C for 5 minutes, did not corrode (Xue et al., 1991a, 146).



(Xue, 1991, 1231)

Figure 3. 11 MBI-Copper Polymer Formation

Patel (1972) tested MBI treated copper sheets in a 3% sodium chloride solution. The sheets were rolled and annealed to 550°C. The inhibitor was applied in ethanol and the samples were exposed for 15 days at 30±2°C. The highest concentration of MBI (0.02%) inhibitor protected the copper sheet 99% from corrosion. He found that on the surface of the copper sheets a brown film formed, which could not be easily removed in a 5% solution of sulphuric acid (Patel, 1972, 156). The brown copper-MBI complex film formed, could indicate a possible discoloration of a reacted copper alloy artefact, which should be born in mind when applying this compound in conservation.

Patel (1974) found that MBI gives a 98% inhibition efficiency at $1.33 \cdot 10^{-3}$M concentration, when compared to a blank specimen. In this research he compared several compounds, one of which was DB, and he found that MBI is a better corrosion inhibitor on copper in alkaline solutions of sodium hydroxide (Patel, 1974, 92).

Trabanelli (1973) compared the efficiency of BTA, MBI, MBO and MBT. These copper corrosion inhibitors were tested in 0.1N sodium chloride solution, at a concentration of 10^{-3}M inhibitor, at a temperature of 25°C. MBT had to be applied in a saturated solution since it is not very soluble. After 10 days the MBO inhibited copper tags were seen to have areas of localised attack. He found that all inhibitors diminish the rate of corrosion at the anode and cathode.

The inhibition efficiency is as follows:

BTA 99% > MBT 98% > MBI 97% > MBO 88%

A similar comparative test undertaken by Prajapaty et al. (1976), showed a somewhat different order of efficiency. They also tested MBT, MBI, BTA, and MBO, but they changed the environment and test samples. They used a 250ml solution of 1N ammonium chloride as a corrodend, and as test pieces they used copper and brass tags. They found that with a maximum of 200ppm of inhibitor added into the solution, a maximum corrosion inhibition could be achieved.

Inhibition efficiency for
copper: BTA = MBO 100% > MBI 83% > MBT 75%

brass: BTA = MBO 100% > MBI 97% > MBT 84%

(Prajapati et al.,1976, 723)

Thierry and Leygraf (1985) also compared BTA and MBI as corrosion inhibitors on copper. The corrosive environment in this case was 0.1M and 0.01M sodium chloride solution in distilled water. The inhibitor was added in a concentration of 5mM.

Inhibitor	*0.01M Sodium Chloride*	*0.1M Sodium Chloride*
BTA	90% inhibition	69% inhibition
MBI	99% inhibition	83% inhibition

Table 3. 4 Comparative Study of BTA and MBI (Thierry and Leygraf, 1985, 1013)

Chadwick and Hashmi (1979) conducted a similar test in 0-0.5M sodium chloride. They buffered the pH from 2-7. They discovered that the thickness of the complex film formed varied with the treatment conditions in which the specimens were placed. An exact film thickness was not given. The surface film was proposed to consist of Cu(I)-MBI species, and the stoichiometry for MBI was $Cu(I)_2(MBI)$. When they analysed the film with X-ray photo-electron spectroscopy, no chlorides were present in the film. This is in contrast to other inhibitors which form Cu(I) complexes via nitrogen, with the elimination of H(-N) atoms. By Infrared studies they found that MBI and MBT exist in tautomeric rather than a mercapto form, and that the hydrogen is eliminated during the compound formation with metal ions.

The Cu^{-}MBI complex film was studied by X-ray photo-electron spectroscopy (XPS) (Chadwick and Hashmi, 1979). The film exposed to air for 48 hours and 5 days showed a progressive oxidation. It is suggested that top Cu-MBI layers are oxidised from Cu(I) to Cu(II). The sulphur atom in the upper regions of the surface are also oxidised when exposed to air, despite the fact that the crystalline inhibitor is stable when exposed to air. The oxidation of Cu(I) to Cu(II) is almost complete after the course of five days. The oxidation of the complex film formed has an important effect on the stability of the polymer layer. The oxidised Cu(II) and the sulphur can be removed by washing. Which results in the exposure of a fresh layer of unoxidised Cu-MBI to air. This new surface reacts in a similar way to the removed layer. This elimination of the surface layer, concludes ultimately in the breakdown of corrosion inhibition, and the inhibitor has to be reapplied (Chadwick and Hashmi, 1979, 654).

Chadwick and Hashmi (1979) did not state how long it took for the complete removal of the MBI-copper complex, since they only analysed the uppermost regions of the polymer film. The research undertaken by others, did show that MBI is a very effective inhibitor. The oxidation of the top layers of the inhibiting complex film were only studied by Chadwick and Hashmi, and I suggest that the same reaction could take place with other sulphur containing organic inhibitors, since it was found that many of the sulphur containing films break down in an etching solution where no inhibitor is added continuously, to allow the repair of the film. In conservation the oxidation of the top layer of an inhibitor-copper complex film seems not to be of major importance, since the object is not continuously exposed to washing. It has to be tested to find out what amount of washing actually removes the complex film completely. It should be born in mind that the removal of the surface layer by prolonged washing, could have the advantage of reversibility of the treatment, which is another aspect of great importance in conservation.

3.6 2-Mercaptobenzoxazole (MBO)

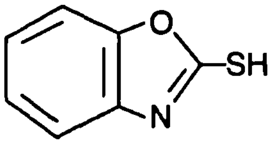


Figure 3. 12 MBO Molecule

This compound has the formula C_7H_5NOS. It is also known under synonyms such as MBO, Benzoxazol-2-thiole and 2-Benzoxazolethiol. It is available in the form of a fine-crystalline powder, which is a beige-brownish colour, and is almost odourless. MBO has a weight of 151.19 g/mol. In the 1991 safety data sheet supplied by Schuchardt, MBO has a melting point between 189-192°C. Aldrich safety data sheet from 1993 indicates a melting point between 193-194°C. The product has a pH5 in 5g/l water at 20°C. Thermal decomposition sets in >250°C (Schuchardt, 1991, safety data sheet).

3.6.1 Chemical Hazards

The compound may be harmful when inhaled, ingested or absorbed through the skin. MBO may also cause eye and skin irritation. The chemical, physical, and toxicological properties have not been thoroughly investigated. Under fire conditions MBO emits toxic fumes of carbon monoxide, carbon dioxide, nitrogen oxides and sulphur oxides. When handling and storing the compound precautions have to be taken. Chemical safety goggles, rubber gloves and respirator should be worn. MBO should be only used under a mechanical exhaust system. It has to be stored in a dry cool place (Aldrich, 1993, safety data sheet).

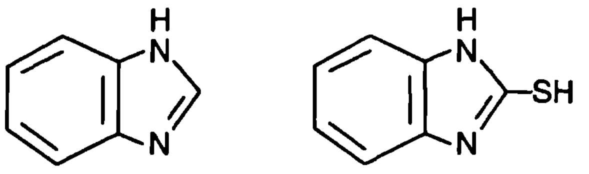
3.6.2 Corrosion Inhibition

Trabanelli (1973) compared several copper corrosion inhibitors such as benzimidazole, 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, benzotriazole, sulphathiazole and 2-mercaptobenzoxazole. He applied these inhibitors in an aggressive media of 0.1N NaCl. The inhibitors were in a concentration of 10^{-3}M. The copper used was in the form of 0.3mm thick sheets (99.9% Cu, 0.001%Bi, 0.01%Pb, 0.013-0.05% P). Trabanelli (1973) reports that copper in sodium chloride solutions inhibited with mercaptobenzoxazole and sulphathiazole had, after 10 days, a slight localised attack. Only sulphathiazole became less efficient during this period. After 10 days; despite the localised attack of the metal surface treated with MBO, the inhibitive action of this compound was still high. Anodic and cathodic areas were inhibited in the sodium chloride solution. The corrosion inhibition in percent was calculated by comparison with a blank specimen.

Solutions of 0.1N NaCl, and 10-3M inhibitor	*corrosion inhibition of 99.9% Cu*
benzotriazole	*99%*
2-mercaptobenzimidazole	*97%*
2-mercaptobenzothiazole	*98%*
2-mercaptobenzoxazole	*88%*
benzimidazole	*92%*
sulphathiazole	*94% (Trabanelli, 1973, 604).*

Table 3. 5 Comparative Study of Various Inhibitors.

In the case of 2-mercaptobenzothiazole, 2-mercaptobenzimidazole and 2-mercaptobenzoxazole, the presence of a sulphur or nitrogen atom in the molecule lead to a higher inhibiting efficiency, compared to inhibitors with solely oxygen atoms present. The presence of an -SH group, appears to promote the inhibiting action, when comparing benzimidazole and 2-mercaptobenzimidazole. This might be due to the direct interaction of the SH-group with copper (Trabanelli, 1973, 604).



benzimidazole 2-mercaptobenzimidazoel

Figure 3. 13 Comparison of Benzimidazole and 2-Mercaptobenzimidazole.

Prajapati et al. (1976, 723) found that 2-mercaptobenzoxazole is very effective as a corrosion inhibitor for copper. 2-mercaptobenzoxazole and benzotriazole gave 100% inhibition efficiency in a 1N solution of ammonium chloride on copper and brass. 2-mercaptobenzothiazole, 2-mercaptobenzimidazole, benzimidazole and indole all gave approximately 10% less corrosion protection. As in other mercapto compounds the ionic species form insoluble complex salts with metal (copper) ions (see Table 3. 6).

Loss in weight for copper and brass (63/67) in a 1N ammonium chloride solution

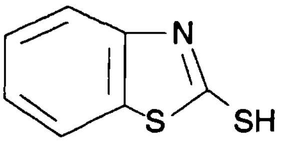
200 ppm inhibitor	*copper*	*brass (63/67)*
benzotriazole	*~100%*	*100%*
2-mercaptobenzoxazole	*100%*	*100%*
2-mercaptobenzothiazole	*75%*	*84%*
2-mercaptobenzimidazole	*83%*	*97%*
Indole	*94%*	*87%*
benzimidazole	*94%*	*92%*

Table 3. 6 Comparative Study of BTA, MBO, MBT, MBI, Indole, and Benzimidazole (Prajapati , 1976, 723).

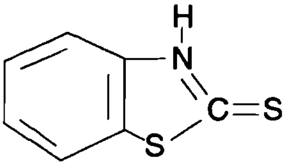
Musiani et al. (1987) studied the corrosion of copper in 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, 2-mercaptobenzimidazole and benzotriazole in neutral and acidic (pH 2) in 1M KCl solutions for 1-3 hours. MBO was active over a wider range of pH than BTA. After 1 hour MBO gave a 94% corrosion inhibition at pH 7, and 97% at pH 2, where as the corrosion inhibition values of BTA after one hour were, 95% at pH 7 and 60% at pH 2. This shows clearly the superiority of MBO in a chloride containing solution (see Table 3. 8) (Musiani et al., 1987, 191).

The work by Trabanelli (1973), Prajapati et al. (1976) and Musiani et al. (1987) show the effectiveness of 2-mercaptobenzoxazole in comparison to other copper corrosion inhibitors. The studies show clearly its good performance in different environments. Although they give an indication of possible performance, these conditions are only partially comparable with situations encountered in the conservation of copper and copper alloy artefacts. The fact that 2-mercaptobenzoxazole has a high effectiveness over a wide pH range, and its higher effectiveness than benzotriazole at low pH range might render it more suitable for applications in conservation. Of concern are the findings by Trapanelli (1973) that MBO did not prevent attack in localised areas on the copper, while immersed for 10 days in a diluted sodium chloride solution. In archaeological conservation the prolonged suspension of a copper object in a chloride containing environment is not relevant. Nevertheless, the chloride pits in an archaeological copper object might in part represent these sort of circumstances. The thickness of the inhibitor films has not been discussed in the literature cited.

3.7 2-Mercaptobenzothiazole (MBT)



(Aldrich, 1993, safety data sheet)



(Chadwick, 1979, 650)

Figure 3. 14 Tautomeric Forms of MBT.

This compound has the formula $C_7H_5NS_2$. It is known under the following synonyms: MBT, Benzothiazole-2-thiole, 2(3H)-Benzothiazolethione, 2-Benzothiazolyl Mercaptan, Captax, Kaptax (Czech), MBT, Mercaptobenzothiazole, 2-Mercaptobenzothiazole, 2-Merkaptobenzothiazol (Polish), 2-Merlkapto-benzthiazole (Czech.), NCl-C56519, Pennac MBT Powder, Rokon, Rotax, Sulfadene, USAF GY-3, USAF XR-29 and Vulkacit Mercapto. The compound has the appearance of a dull-yellow powder, with a melting point of 177-181°C (Aldrich, 1993, safety data sheet). Musiani et al. (1987, 191) found that the concentration of MBT in potassium chloride solution could be increased above 0.001M (Schuchardt, 1991, safety data sheet).

3.7.1 Chemical Hazards

MBT is harmful when swallowed, inhaled, or absorbed through the skin. It may cause allergic respiratory and skin reactions. Exposure can cause nausea, headache and vomiting, and may also be a possible carcinogen. The toxicological properties have not been thoroughly investigated. Under fire conditions it can emit toxic fumes of carbon monoxide, carbon dioxide, sulphur oxides and nitrogen oxides.

Precautions have to be taken when handling MBT: Chemical safety goggles, rubber gloves, respirators and protective clothing should be worn. Like BTA, the compound has to be used in a chemical fume hood, because the dust should not be inhaled. Repeated exposure should be avoided. MBT has to be stored in a cool dry place (Aldrich, 1993, safety data sheet).

3.7.2 Corrosion Inhibition

2-merkaptobenzothiazole is like 2-mercaptobenzimidazole, a very effective corrosion inhibitor for copper. Several studies on its complex formation with copper in different environments have been made. MBT is only slightly soluble in aqueous solution, but at the same time it increases its inhibiting efficiency when the concentration is increased. This was tested by Prajapaty et al. (1976). They treated copper and brass plates in a 1N ammonium chloride solution. Inhibitor treated specimens were compared with blank specimens, to calculate the percentage of inhibition. They found that MBT is slightly less effective than MBI and BTA. At 200 ppm concentration, MBT and MBI were effective.

1N Ammonium Chloride solution:	*Copper inhibited*	*Brass (63/37) inhibited*
2-Mercaptobenzothiazole (MBT)	*75%*	*84%*
2-Mercaptobenzimidazole (MBI)	*83%*	*97%*
Benzotriazole (BTA)	*~100%*	*100%*

Table 3. 7 Comparative Study of MBT, MBI, and BTA.

The ionic species of MBT form complexes with copper ions. Like other mercapto compounds, the complexes formed react to from a protective coating on the copper surface. The composition of the copper-MBT complex film in a chloride solution is likely to be cuprous oxide/chloride. At a concentration of 2.5ppm the complex film formed is thinner, but more protective. The exact thickness was not given. An increase in concentration results in the thickening of the polymer film (Ravi et al., 1986, 337).

Copper plates treated under varying conditions with MBT, indicated a variation in the thickness of the complex film. The surface film consisted of a Cu-MBT compound, with the copper in this complex being in the Cu(I) state. This does not depend on the copper species present on the surface before immersion into the treatment solution. The stoichiometry of MBT with copper is Cu(MBT). Like MBI, the surface does not contain chloride when the copper-MBT complex is formed in a chloride solution. This exclusion of chlorides during the process of polymer formation is in contrast to the proposition by Ravi et al. (1986) above.

The complex of copper-MBT is expected to form with Cu(I). In this formation, the primary bonding is through the nitrogen atom, with the elimination of the H(-N) atoms. The resulting complex is Cu(I)MBT. Like MBI, it is suggested that the surface film is prone to oxidation. The sulphur oxidises, and Cu(I) oxidises to Cu(II). These oxidised surface areas can be washed of as explained in the case of MBI

(Chadwick and Hashmi, 1979, 654). These findings suggest an unstable polymer film is formed. How fast this oxidation occurs is not known.

It has been suggested that 2-Mercaptobenzothiazole is the most effective copper corrosion inhibitor from a set of mercapto compounds, according to SERS measurements (surface enhanced raman spectroscopy) (Musiani et al., 1987, 188). Musiani et al. added KOH to distilled water to facilitate the dissolution of MBT and MBI. To adjust the pH of the treatment solution, they buffered with hydrochloric acid or KOH. The inhibitors tested were benzotriazole (BTA), 2-mercaptobenzothiazole (MBT), 2-mercaptobenzimidazole (MBI) and 2-mercaptobenzoxazole (MBO). The treatment 1M KCl solution had a neutral and an acidic pH (pH 2). The copper was in the form of a disc, which had an area of 0.03-0.32 cm^2.

Inhibitor	*mM*	*pH*	*Time/h*	*protection efficiency in %*
BTA	1	7	1	95
BTA	1	2	1	60
BTA	1	7	3	97
BTA	1	2	3	21
BTA	10	7	1	98
BTA	10	2	1	70
MBT	1	7	1	95
MBT	1	2	1	98
MBT	1	7	3	96
MBT	1	2	3	97
MBT	0.1	2	1	90
MBI	1	7	1	95
MBI	1	2	1	97
MBO	1	7	1	94
MBO	1	2	1	97

Table 3. 8 Comparative Study of BTA, MBT, MBI, and MBO.

This study indicates that the effectiveness in percent, varies with the pH of the inhibitor solution. BTA decreases in effectiveness in acidic environments while MBT and MBO increase in effectiveness, in acidic environments. This suggests that mercapto compounds are more effective in acidic solutions, such as those present in the conservation of chloride containing copper and copper alloys.

In neutral pH MBT protects the copper in potassium chloride solution to ~95%. At pH2 MBT is much more effective than BTA. After 1 hour MBT protects the copper more effectively than BTA. If the exposure time is increased to 3 hours the effectiveness of MBT stays about the same. Whereby the effectiveness of BTA decreases rapidly to only about 1/5 of the effectiveness of MBT. This decrease can be overcome partially by raising the concentration of BTA by 10 times. With 10mM at pH2 at an exposure time of 1 hour, BTA is still ~18% less effective (Musiani et al., 1987, 191). It would be interesting to know if the 70% effectiveness of BTA after 1 hour, deteriorates as drastically by prolonged exposure to the corrosive solution, as it does at lower concentrations.

Musiani et al. (1987, 201) found that MBT formed a stronger bond to copper and silver over the entire pH range between 2-7 than BTA. The difference in adsorption strength increased with the drop in pH. With increasing the acidity of the KCl solution, there were no chlorides bonded into the copper-MBT complex film.

3.8 2-Mercaptopyrimidine (MP)

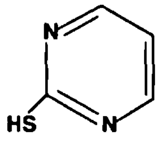


Figure 3. 15 MP Molecule

Mercaptopyrimidine has the formula $C_4H_4N_2S$. It is also known under the name MP and 2-Pyrimidinethiol. MP has a melting point of 230°C, an atomic mass of 112.15 and it appears as a yellow powder (Schuchardt, 1991, safety data sheet).

3.8.1 Chemical Hazards

MP may be harmful by inhalation, ingestion or skin absorption and can cause eye and skin irritation. The compound has not been thoroughly investigated with regards to health and safety. It produces hazardous combustion products, and under fire conditions it emits toxic fumes; carbon monoxide, carbon dioxide, nitrogen oxides and sulphur oxides. Precaution should be taken when handling the product: Chemical safety goggles, chemical-resistant gloves and a respirator should be worn. Prolonged or repeated exposure to MP should be avoided. It should be used under a mechanical exhaust system (Aldrich, 1993, Safety Data Sheet).

3.8.2 Corrosion Inhibition

After reading Horner and Pliefke 's (1982) test results, in which they concluded that MP protects some forms of copper better than AP, it was decided also to assess this compound for conservation. The structure of MP is similar to the structure of AP. MP, like AP, forms a complex film with copper ions, to protect the underlying copper surface. In the presence of oxygen it was found that the protective film forms faster (Horner and Pliefke, 1982, 456). It forms a complex with Cu(I)-Cl, which is difficult to dissolve in organic solvents.

If the Cu^{2+}: MP ratio is 1:1, the inhibition efficiency in a corrosive solution of NaCl is 500 hours. Should the Cu^{2+}concentration be $5 \cdot 10^{-2}$ which is five times more than MP(10^{-2}M), the protection lasts only for three hours. MP is a better inhibitor than AP in hydrochloric acid and sulphuric acid. In tests it showed that MP is better at inhibiting the corrosion of larger surface areas in comparison with AP and BTA.

The effectiveness of MP at inhibiting corrosion in hydrochloric acid, suggests its effectiveness in protecting the highly acidic chloride pits on an archaeological copper artefact.

0.5g copper dust were totally corroded after	130 hours in MP
"	5 hours in AP

Table 3. 9 Copper Dust Inhibited with MP and AP.

If the copper is in sheet form (3.885g) and corroded under standard conditions (NaCl, pH4) for 130 hours, the order is different (Horner and Pliefke, 1982, 455):

10^{-2} M MP	*32mg copper are missing*
10^{-2} M AP	*4mg "*
10^{-2} M BTA	*1465mg "*

Table 3. 10 Copper Sheet Corroded and Inhibited with MP, AP, BTA.

MP and AP are protective at pH4. This suggests that both pyrimidine derivatives are better in protecting copper corrosion in a lower pH range than BTA. It is not stated how they behave at a pH lower than 4. Since it is known that the efficiency of BTA rapidly decreases with a drop in pH, it is suggested that AP and MP are better inhibitors for conservation purposes.

3.9 Conclusion

The literature cited has where ever possible, been selected according to comparative studies. Most of the testing procedures included BTA as a standard. BTA as the most widely used corrosion inhibitor, showed clear deficiencies, one of the main ones being the low protection it gives to copper in an acidic environment.

The formation of thick loosely polymerised films at low pH, does not protect from further corrosion. Most of the inhibitors selected clearly prove their effectiveness in lower pH, when compared with BTA. This leads to the assumption that their performance in the conservation of chloride containing copper artefacts should be better than BTA.

In most cases the literature does not cite the film thickness and the physical properties of polymer films formed. The film thickness and its structure are important in the performance of an inhibitor film. The literature suggests that thin, densely polymerised films are the most protective (Brusic et al., 1991). There is also little data available on the effectiveness of an inhibitor over a specific pH range, as discussed earlier, the effectiveness of an inhibitor at low pH is of vital importance when it comes to the performance of an inhibitor film in the prevention of chloride corrosion on copper.

The table below lists the properties of the inhibitors selected for further testing.

Properties	***BTA***	***AMT***	***AP***	***DB***	***MBI***	***MBO***	***MBT***	***MP***
water soluble	✓	*low*	*O*	*O*	*O*	*O*	*low*	*O*
alcohol soluble	✓	✓	✓	✓	✓	✓	✓	✓
pH in water	*5-6*	*O*	*O*	*O*	*O*	*5*	*O*	*O*
harmful	✓	✓	✓	✓	✓	✓	✓	✓
complexes with Cu(I)	✓	✓	✓	*O*	✓	*O*	✓	✓
complexes with Cu(II)	✓	✓	✓	*O*	✓	*O*	*O*	✓
anodic inhibitor	✓	✓	✓	*O*	✓	*O*	*O*	✓
cathodic inhibitor	✓	*O*	*O*	*O*	*O*	✓	*O*	*O*
polymer film forming	✓	*O*	*O*	*O*	*O*	✓	*O*	*O*
effective at low pH	✓	✓	✓	✓	✓	✓	✓	✓
tested inchloride media	✓	✓	✓	✓	✓	✓	✓	✓

Table 3. 11 Properties of selected corrosion inhibitors ✓= reported, O= unspecified in the literature.

The experimental work, discussed in this chapter, is based on different corrosion testing procedures. These tests generally have little relevance to archaeological conservation. It is also difficult to compare different experiments, since different tests are based on varying parameters. For the presented work here, the conclusions drawn, are mainly based on the percentage of corrosion inhibition, when compared to a blank specimen. Trabanelli (1970) suggests the following formula for the calculation of the effectiveness of an inhibitor in percentage.

$$\text{P.I.} = \frac{\text{uninhibited corr. rate} - \text{inhibited corr. rate}}{\text{uninhibited corr. rate}} \times 100$$

The testing procedures applied in the literature sighted, cannot be used for archaeological conservation, since they are not suitable for corroded artefacts. The following work will be based on the selection of appropriate corrosion testing procedures.

Chapter 4

Corrosion Testing and Evaluation

4.1 Introduction

A major problem of comparative studies of corrosion inhibitors in archaeological conservation is the variability of the condition of metal artefacts, and its corrosion products. The aim of quantitative corrosion testing is to determine the effectiveness of a compound or a procedure in preventing metal corrosion. In the present case, the goal is to apply suitable, meaningful schemes with which to test corrosion inhibitors for copper and copper alloy archaeological artefacts.

Corrosion tests need to be standardised to be reproducible, and allow meaningful comparison between specimens. Only at the final stage of evaluating inhibitors, is it useful to test them on ancient artefacts. Trials with artefacts were used to asses the validity of the data recovered from the corrosion inhibitor tests conducted on uniformly precorroded copper coupons.

Corrosion tests in archaeological conservation need to determine the effectiveness of an inhibitor without its being directly applied to an artefact. This need arises both from the need to protect the artefacts from the possibly damaging effects of untested treatments and because artefacts are too varied in their corrosion state and constitutions to provide wholly reliable direct comparison between different treatments. Inhibitors should be effective in inhibiting corrosion in museum environments which may vary considerably. Fluctuating RH is specially problematic with chloride containing copper and copper alloys. Since chloride containing corrosion products are known to cause the most damaging type of corrosion, destroying further archaeological evidence. Even at an RH of 55% Scott (1990) found that nantokite becomes very reactive.

As previously discussed in chapter 2, the selection criteria for conservation limit the range of protective inhibitors that are potentially useful in the present context. The inhibiting compound used should cause minimal intervention with the morphology of the specimen and its corrosion products. The objective is to limit chemical alteration in and on the surface of an artefact. Alterations in the corrosion can lead to the irreversible loss of information such as that preserved in mineralised organic remains. During burial the copper salts limit microbiological degradation so the organic cell structure can remain (Roberts, 1989). The preservation of such mineralised organic remains is of upmost importance.

The following selection of corrosion testing procedures for corrosion inhibitors for archaeological copper artefacts were made, according to two main criteria; a) maximum effectiveness, b) minimum intervention, and are based on the requirements listed below.

1. determination of the effectiveness of the inhibitors at high RH
2. estimated long term performance of a coated specimen
3. accelerated simulation of cycles of RH levels found in museum environments
4. physical characteristics of inhibitor film failures
5. evaluation of the chemical deterioration of patina
6. visual changes of surface appearance

1. Determination of Effectiveness of the Inhibitors at high RH

Testing has to determine the effectiveness of the selected corrosion inhibitors. The effectiveness is evaluated on a qualitative and quantitative basis by visual and gravimetric assessment. After the evaluation, the more effective inhibitors can be selected for further testing or analysis.

2. Estimated Long Term Performance of a Coated Specimen

Corrosion tests are often designed to determine the threshold of a corrosive environment above which a protective surface film will fail. Short term, extreme environments are applied to evaluate the long term performance of an inhibitor under less extreme environments. However, an inhibitor might perform differently in an accelerated corrosion test than in a service environment. Changes in environmental factors and time, might change the range of effectiveness of corrosion inhibitors. Accelerated short-term tests in which corrosion factors are intensified are used for quality control of protective coatings. This type of accelerated short-term test should always be compared to a service environment (Wranglen, 1985, 220)

3. Accelerated Simulation of Cycles of RH Levels Found in Museum Environments

The chosen testing procedure should simulate an environment similar to one found in a museum. Museums are known to suffer from air pollution, but evaluating inhibitors to SO_2 levels is beyond the scope of the present research project. Testing procedures for copper chloride containing artefacts are mainly concerned with temperature and RH levels that are recorded in a museum environment. In tropical regions, as in south east Asia for example, extreme RH levels require better inhibitors than might be needed in Europe. This project evaluates several inhibitors against BTA for this function.

4. Physical Characteristics of Inhibitor Film Failures

Corrosion inhibitors may react differently in different areas on a metallic substrate. They can form complex films in anodic or cathodic areas of the surface, or both (Trabanelli, 1970, 147). Such processes may lead to areas of weakness, causing the film to result in new corrosion spots, possibly further accelerating corrosion. It has been stated that film-forming inhibitors might be dangerous in that they might promote localised attack in areas not covered with inhibitor film (Trabanelli, 1970, 190). The examination and evaluation of pitting is outlined in industrial testing procedures (ASTM G 46-76).

5. Evaluation of Chemical Deterioration of a Corrosion Surface

It is most unlikely that during the process of painting or metallic coating, any metal from the substrate of the specimen would be lost. In the case of corrosion inhibitors however, a small amount of copper as ions go into solution to allow the formation of an inhibitor-copper complex film. For example, at pH2 BTA forms thick polymer films comprising of many layers of Cu-BTA complex (Brusic et al., 1991, 2253). Ganorkar et al. (1988) observed that nantokite was complexed into the inhibitor solution, during the treatment with AMT. This could suggest preferential etching of the surface of an archaeological artefact.

6. Visual Changes of Surface Appearance

Industrial testing is also concerned to a degree with the physical appearance of a surface finish (ASTM D 1654-68). In the case of archaeological copper artefacts, their appearance is an important factor. Corrosion testing should emphasise more the evaluation of the surface appearance of the treated surface, and so slight changes have to be quantified. Colorimeters have been used for several years in industry to evaluate colour changes.

4.2 Choice of Corrosion Testing Procedure

To establish the effectiveness of inhibitors, testing procedures had to be selected depending on the stated selection criteria. In reviewing conservation and industrial literature, several standard tests seemed applicable. None of these tests however was specifically appropriate for the qualitative testing of corrosion inhibitors on corroded artefacts. Only one test of this type appears to have been published: that by Angelucci et al.(1978), in which they evaluated inhibitors on precorroded copper coupons, with a view to the conservation of ancient artefacts. Unfortunately, this test was found to be inprecise in its published presentation.

There are many standard testing procedures for metal coatings used in industry. In the present case of evaluating inhibitors, initially only recognised standard testing procedures were considered. Standards in general use are: British Standards Institution (BSI), Deutsche Industrie Norm (DIN), International Standards Organisation (ISO) and American Standards for Testing and Materials (ASTM).

The BSI and ASTM standards seem the most wide-ranging tests for the evaluation of coatings on metal. The ASTM standards are the most specific in their description of testing procedures. No industrial testing procedure for corrosion inhibitor testing for corroded surfaces was found. Though a range of tests evaluate organic coatings such as paint, or plated metal coatings (see appendix 2). Standards listed are not specifically designed for inhibitors, but can be used or adapted for specific needs. The emphasis of the present endeavour is the standardisation of testing procedures for archaeological conservation. The point is to advance standardised testing methods, presenting conservators with more straightforward criteria for the evaluation of corrosion inhibiting materials.

Most industrial surface finishes for modern metals such as paint, metallic coatings and corrosion inhibitors have several similar features:

-corrosion protection

-formation of a continuous surface film

-no chemical or metallurgical changes to the core metal

-susceptibility to deterioration (ageing, failure and corrosion) .

These are the same specifications needed for corrosion inhibitors in archaeological conservation. The aim of coatings may be decorative as well as being physically and/or chemically protective. This generally requires a surface film with few defects. Defects generally arise from mechanical damage and ageing of coatings, or faulty application conditions.

The industrial corrosion test standards have two main aspects:

- artificially degrading a protective surface coating (accelerated ageing tests)
- assessment of corrosion damage resulting from testing

From many standard tests available, two types are suitable for testing the efficiency of corrosion inhibitors for copper and copper alloys in conservation: porosity tests and humidity tests.

Frequently salt spray tests are used in industry to evaluate coatings. These tests rinse some of the corrosion products from the surface of the specimen and for this reason, as well as others, are not considered suitable for the present purpose (BS 3900, 1986).

Porosity tests are found more suitable for conservation since they aim to detect points of film failure. The task is to indicate the completeness of surface coverage by a coating. Porosity tests generally aim to identify any hole, crack or discontinuity in a surface film. These are destructive tests and cannot be applied to archaeological artefacts. Pores or voids detected during a porosity test, indicate only the probability of failure of a surface film. Porosity tests are accelerated corrosion tests, and a harsh approach to the testing of materials (ASTM B 380, 1985).

Cyclic humidity tests such as ASTM G60-86 were developed to observe the behaviour of steel under corrosion test conditions. Cyclic humidity tests require a chamber with humidity and temperature control. By exposing specimens treated with corrosion inhibitors to cycles in humidity, their longterm performance is evaluated. This is similar in some respect to exposing BTA-inhibited artefacts to an elevated RH to test for chloride activity.

An important part of corrosion testing is the use of suitable specimens. In this case the aim is to use specimens which will respond in a manner similar to that of typical archaeological specimens. It is not always appropriate to use archaeological copper or copper alloy artefacts themselves because inhomogenity and other variations in copper and copper alloy objects, and corrosion surfaces, are difficult to assess, except by using large numbers of artefacts. Artefacts have differences in metallurgical structures and composition, as well as variations in type and rate of corrosion. To minimise such variations in corrosion testing behaviour, the samples to be tested should be more uniform. The development and choice of samples with an artificially produced corrosion surface, similar to that of copper and copper alloy archaeological artefacts, represents the initial phase of the experimental work.

4.3 General Specimen Requirements

To improve reproducibility, and to be able to compare corrosion tests, a uniformity of the specimen was needed. A list of requirements is given in British Standard (BS 6917 : 1987). This BSI standard was adapted for conservation. The adapted form of the relevant features is given in table 4.1.

The metal test coupons need to:

1. be treated in a similar manner
2. have similar shape and dimensions
3. have a thickness of at least 0.5 mm (so they are not deformed during the test)
4. have the surface area as large as possible and not less than 25 cm^2;
5. have similar surface finish
6. have an even surface with no visible defects such as scratches, crack or pits
7. the marking of the specimen should not interfere with the corrosion process, and be legible after the test
8. at least three specimens should be treated in the same manner
9. an untreated specimen should be stored under conditions which prevent corrosion
10. the specimens have to be examined prior to testing
11. if the specimens have been stored before testing, they have to be checked aigain prior to testing
12. colour, tarnishing, spots, visible corrosion, defects should be recorded prior to testing
13. three untreated specimens have to be added to the test environment

Table 4. 1 Specimen requirements (adapted from BS 6917:1987)

Point 13 in table 4.1 was an addition to BSI standard requirements. The use of at least three untreated blank specimens in the corrosion tests is not usually recognised. These blank specimens are pre-treated in the same manner as the samples treated with corrosion inhibitors. They are added to enable the comparison of corrosion behaviour of uninhibited samples with inhibited specimens. The suggested procedure allows gravimetric, optical, crystallographic, metallographic, and other analytical comparisons. These procedures are suggested for the investigation of the behaviour of inhibitors, and their interaction with metal and corrosion products.

The recording of any irregularities in visual appearance of the test specimens (Point 12 in Table 4. 1), can be recorded using a 5 x 5mm wire frame on an acetate film. The squares are numbered from the top left, and are an aid in pinpointing the same defects after the corrosion testing. Additionally any increased failure of the inhibitor film due to pits, scratches, or dark spots can be documented (BS 6917:1987).

4.4 The Simulation of Copper Chloride Corrosion on Copper Coupons

4.4.1 Introduction

Corrosion inhibitors had to be tested for their effectiveness in inhibiting further corrosion on archaeological copper artefacts already covered with chloride containing corrosion. A procedure had to be established to simulate and standardise this chloride corrosion on copper samples, to be able to compare and repeat the testing procedure.

Accelerated corrosion tests used in industrial standards are primarily based on porosity and relative humidity accelerated ageing tests.

The selection of appropriate corrosion tests was followed by experimental work in the laboratory. The aim of the initial experiments was to develop a testing procedure simulating chloride corrosion that was structurally similar to the one found on chloride pitted archaeological copper surfaces. This was then proposed as a new standard for corrosion testing in archaeological conservation. Succeeding tests were selected in regard to accelerated corrosion tests, to evaluate the coherence and the durability of the copper-inhibitor films formed on the surface at high RH.

4.4.2 Specimen Requirements for Testing Inhibitors to be used on Archaeological Copper Artefacts

The choice of appropriate specimens to produce relevant corrosion testing data was complex. Appropriate specimens are the most important part of corrosion testing. They have a direct influence on the data obtained. The specimens were designed based on the factors listed in table 4.1. The corrosion tests might not accurately simulate naturally occurring corrosion processes on a corroded object, be it in a burial or museums environment, but they can when carefully evaluated give an insight in to what might occur on the surface of an archaeological specimen. Archaeological copper and copper alloy objects usually have complex mixed phase constitutions, and to actually reproduce a specimen with an ideal, layered corrosion structure is not possible.

Copper and copper alloy objects vary greatly in composition. They can be divided into many groups:

copper-arsenic	copper-gold (tumbaga, shakudo)	copper-tin-arsenic
copper-antimony	copper-zinc-lead (bidri)	copper-nickel (cupronickel)
copper-zinc (brass)	copper-zinc-tin (latten)	
copper-silver (shibuchi)	copper-cuprous oxide	(after Scott 1991)

Table 4. 2 List of Copper Alloys

The proportions of alloying components and metalographic phases vary, and the minor element concentrations have wide ranges. Since objects vary in composition, several questions are relevant:

1. Without very detailed study of each artefact, it is not known to what extent the variation of alloying constituents enhance or limit galvanic corrosion processes.
2. How do alloying or minor elements, such as tin, interact in corrosion processes and the final corrosion products?
3. How do elemental changes in a metallic surface and in corrosion products affect the formation of polymer corrosion inhibitor films?
4. Do different elements or metallurgic structures produce significant local variations in anodic and cathodic areas? How uniform is the polymer film formed? To what extent do they cause porosity in the inhibitor film?
5. How is each inhibitor classified? Does it inhibit the anode or cathode reactions, or both?

Answering all these questions is not within the planned framework of this work. To minimise the independent parameters in corrosion testing procedures, it would be possible to use either unalloyed copper specimens or bronze specimens of known phase constitution. "Pure" copper specimens eliminate obvious galvanic effects due to the presence of other constituents present in the matrix, and variations due to complex corrosion products formed on the surface. In an accelerated corrosion test the differences in corrosion rate of elemental copper and copper alloys in contact with a corrosion inhibitor could be studied. Bronze specimens, for example, could give a first indication of any galvanic cell reactions of alloying constituents, and their effects on corrosion inhibiting film formation. A copper-tin alloy could be chosen, since it is frequently encountered in archaeological contexts. The data should help investigate differences in the protection of pure copper and tin-bronze. The copper test coupons chosen for the following experiments were rolled copper. These should be relatively uniform. Annealed or cast coupons were not used in the tests.

Corrosion tests provide observable qualitative and quantitative data on inhibitor reactions under different atmospheric environments. It is suggested that the main causes of failure of corrosion inhibitors on archaeological copper and copper alloy artefacts are inconsistent inhibitor films and defects in the polymer film, due to copper chloride corrosion products present in and on the surface of a copper containing artefact. The major factors known to stimulate chloride corrosion are oxygen, humidity and chloride ions. By producing an artificially corroded copper or copper alloy surface, archaeological specimens might be simulated. Nevertheless it is not possible to precisely simulate layered structures and corrosion processes found in nature. The complexity of elements present, the crystallography and the hygroscopicity of corrosion products cannot be duplicated easily. The type and structure and corrosion rate are governed by the surrounding environment and exposure time.

4.5 Artificial Simulated Copper Chloride Corrosion on Copper Coupons

4.5.1 Introduction

As discussed in the previous section, a procedure had to be developed to simulate mineralised surfaces commonly encountered on corroded archaeological copper artefacts. Test specimens are required to contain a reproducible copper chloride containing surface. These precorroded test coupons are the basis for assessing the selected copper corrosion inhibitors. The procedure discussed in this chapter is proposed as a standard corrosion test for the evaluation of corrosion inhibitors, or other protective coatings on copper chloride containing copper substrates in archaeological conservation.

"Bronze disease" or chloride pitting corrosion through the surfaces of copper and copper alloy archaeological metal objects is a common feature of continued, severe deterioration of archaeological copper and copper alloy artefacts. In the following experiments, the attempt was made to simulate a mineralised pitted chloride containing corroded copper surface. As discussed earlier, archaeological metal is covered in uneven corrosion, whereas artificially produced even chloride corrosion on a copper substrate produces more suitable test specimens, resulting in a higher reproducibility of test results. The procedure proposed results in accelerated chloride corrosion on copper test coupons. Accelerating corrosion tests result in a decrease of testing time, but also in an increased unreliability of test results (Wranglen, 1985, 222). It is acknowledged that uniform production of such a complex corrosion surface is very difficult. The five main minerals commonly encountered on archaeological copper are copper, cuprous chloride, cuprous oxide, basic copper carbonate and basic copper chloride. In the following experiments, it was not possible to produce suitable basic copper carbonate, malachite, on the corroded test coupons

4.5.2 Angelucci et al. Test

Section 4.4 discusses the selection of a testing procedure suitable for the testing of copper corrosion inhibitors for use in archaeological conservation. Angelucci et al. (1978) proposed a testing procedure based on the 'Corrodkote Test' (ASTM B380-85) to introduce chlorides to clean copper sheets, and to produce pitted copper chloride corrosion. According to the publication they were able to produce and identify cuprite, nantokite and paratacamite on the treated copper specimens (Angelucci et al., 1978, 149). This process did not produce the basic copper carbonate (malachite). The discussion is not entirely clear, but it was probably not formed, due to the lack of long term exposure to a carbon dioxide rich environment. Malachite [$Cu_2(OH)_2CO_3$] forms by the reaction of copper and its alloys with carbonates in the surrounding environment. The carbon dioxide can be present in the atmosphere, due to deteriorating lime soil, or ground water rich in carbonates. Ulrich (1985) proposed the following reaction for the formation of basic copper carbonate..

$$3Cu^{2+} + 2OH^{-} + 2CO_3^{2-} \Rightarrow 2CuCO_3 \cdot Cu(OH)_2$$ (Ulrich, 1985, 98)

The procedure used by Angelucci et al. (1978) is cited as follows:

Copper coupons (20 x 50 x 1 mm, 99.8%) to be tested are:

1. *sanded with CIA Carcut c. P600 grade sandpaper;*

2. *degreased in petroleum ether (Merck, boiling point 60- 80°C) at 60°C;*
3. *placed in contact with corrosive paste for 96 hours in a wet chamber, the samples being uniformly steeped (thickness of paste 1-2mm) and rotated vertically 180° every 24 hours at both 50°C and room temperature;*
4. *brushed in running water for 1 minute with a soft brush, and immersed in distilled water for 30 minutes;*
5. *dried with filter paper;*
6. *placed in a wet chamber for 200 hours, samples turned vertically 180° every 24 hours and tapped on edge to eliminate loose corrosion products;*
7. *studied with binocular microscope;*
8. *brushed under running water;*
9. *macrophotographed and observed under binocular microscope;*
10. *placed in a wet chamber; for 48 hours at room temperature to ensure an active corrosion;*
11. *macrophotographed and observed under binocular microscope;* (Angelucci et al., 148, 1978)

After this treatment of copper coupons the specimens should be ready for inhibitor testing. This treatment of copper sheets seemed to be ideal in producing corrosion and subsequently test the performance of corrosion inhibitors. The procedure was repeated in the laboratory of the Institute of Archaeology. However, the procedure was thought not to be very precise in detail, leading to a very low reproducibility.

The Angelucci et al. (1978) procedure had several drawbacks which lead to a low reproducibility of the test results. The following points had to be altered to ensure a higher reproducibility.

1. It is proposed that sanding can cause variations in surface topography, resulting in different corrosion rates. ASTM G1-90 (1990) "Standard practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens" suggests abrading with abrasive slurry or abrasive paper. Angelucci et al. however do not take the size of the specimen into account. It could be suggested that sanding of small sized specimens, as in the present case, leads to uneven surface topography, resulting in uneven corrosion rates. This problem is further elaborated in section 4.6.2.
2. Step 3 is not very clear in its approach. Angelucci et al. do not state the exact RH in the wet chamber. In a previous similar experiment they exposed specimens at an RH between 90-95% in the wet chamber. They also suggested that there was no "perceptible difference between results obtained at room temperature and at 50^0C" (Angelucci et al., 1978, 149). The corrosion rate would be expected to be accelerated at a higher temperature.
3. Removing corrosion products under running water (step 4) is suggested as being highly uncontrollable as well.
4. The drying of the specimen using filterpaper (step 5) could also result in a loss of corrosion products.
5. Tapping the specimens to remove loose corrosion products (step 6) could result in varying amounts of corrosion being left on the coupon, and should be avoided.
6. Brushing under running water (step 8). This removes further corrosion and results in changes of corrosion rate.

7. Macrophotography (step 9, 11); the photographic record does not reveal sufficient corrosion information on the specimens, since the depth of the pits, and the colour and types of corrosion products are not accurately recorded. The data are qualitatively and quantitatively imprecise, since the record is governed by the quality of the photographic print. Angelucci et al. also do not state how they record the data revealed from observing the coupons through a binocular microscope (step 7,9,11)

Angelucci et al.(1978), base the evaluation of corrosion inhibitors on optical observations. There is no gravimetrical quantification possible due to the use of a paste, rinsing methods and other means of removing corrosion products. A comparison of different corroded specimens is problematic, other than by optical assessment. This renders the corrosion test susceptible to subjective evaluation.

During the investigation into this procedure, major changes were undertaken to improve standardisation of the procedure to increase the reproducibility of the data recovered. The new corrosion testing procedure for copper and copper alloys was wherever possible based on known testing standards such as BSI, ASTM, DIN and ISO. The standardised procedure should hopefully improve the reproducibility of the visual appearance and the resulting quantitative data. The standardisation also allows others to reproduce the corroded coupons, and compare results.

The following is a presentation of further investigation and recommended improvements for the preparation of standard test coupons for corroded copper and copper alloys.

4.6 Copper Coupon Preparation

For the following experiments, 99.9% pure copper sheets were used. The sheet as provided was rolled to a thickness of 1 mm. A BSI standard proposes a sample size not smaller than 25cm^2 (BS 6917:1987), but this sample size was considered too large. Samples of this size could not be accommodated in the humidity chambers available during the first part of this research.

The material was cut on a guillotine to the size of 20 x 50 x 1mm. This is the coupon size Angelucci et al. (1978) used, and it also reflects the surface area of many objects handled in a conservation laboratory, such as coins, bracelets, arrowheads etc. This sample size also enabled the treatment of a greater number of coupons in one experiment, this helped assessing the reproducibility of experimental results.

Steps used for the preparation of the copper coupons must be monitored carefully to minimise variations in the corrosion of the surface. Industrial corrosion tests are known to have a very low rate of reproducibility, due to complexity of preparation and corrosion performance. Each step of the surface preparation had to be chosen and observed carefully as slight changes could affect the resulting corrosion data. Establishing reasons for changes in corrosion rates are very difficult after corrosion has occurred, since so many complex interacting factors have to be taken into consideration.

4.6.1 Cutting of the Coupons

The coupons were cut with a guillotine in the engineering department of UCL (University College London). This form of sample preparation is not ideal because it induces slight deformation of the metalographic structure. ASTM G1-90(p36) states that shearing causes cold working, and that it may fracture the edges. The ASTM standard suggests the machining of the specimens used for a corrosion test, such as stamping out, or drilling out the specimens. This type of sample preparation was not possible. The induced stress of cutting with a guillotine, should slightly alter the corrosion rate at the edges, due to the stress caused in the metal grains at the cutting edge. Considering that all the samples were the same size, and were treated similarly, it was assumed that effects of corrosion would be uniform. It also should be born in mind that the $CuCl_2$ corrosion paste is very aggressive in its corrosive action. The effect of work hardening could have been minimised by cutting with a jeweller's saw, this was not feasible because of the large number of coupons needed in the following experiments.

4.6.2 Cleaning of the Surface

The choice of the appropriate procedure to remove contamination from oxides and other surface films deposited on the surface of the copper coupons is important. During the storage of the rolled copper sheets, the metal surface acquired some copper corrosion. This might have been partially prevented by a surface coating of a corrosion inhibiting material, such as an oil or varnish. There might also be dirt and dust from manufacture, storage and handling. Any material other than copper deposited on the surface, or in the surface of the copper specimens may affect the corrosion rate. These discrepancies had to be removed to attain better reproducibility in the experiments.

Two options were further evaluated to clean the surface of corrosion; both having advantages and disadvantages:

1. Sanding with 600 grade sand paper (Angelucci et al., 1978). This is usually specified in corrosion testing.
2. Abrasive cleaning with glass beads. This is not usually used in the standard procedures.

4.6.2.1 600 Grade Sandpaper

This surface treatment is common practice in the ASTM standard GI:90, (ASTM, 1990, 36). All faces and edges should be abraded to remove barbs and any contamination on the surface. The sanding of large numbers of small specimens is very labour intensive, and also likely to vary in its degree of application to different specimens. It was difficult to clean the surface in an even manner. The following factors are known to cause deviations in the rate of corrosion of different specimens in the same corrosive environment;

- differences in pressure when sanded manually
- variations in time spent in each area
- sandpaper used might be abraded unevenly in use

The pressure applied in part governs the depth of the grooves penetrating the surface. The depth of the grooves increases the surface area and may affect surface microenvironments which in turn may slightly affect the rate of corrosion. The time spent on an area causes the diminishing of the thickness of the copper coupons.

Sanding exposes grains in lower undeformed regions of the surface of the copper coupons. A rolled copper sheet is partially work hardened. The outer grains are elongated due to the pressure of rolling. The closer to the core of the sheet the less deformation is caused by rolling the metal, so a decreased stress is acquired. Sanding the surface with a 600 grade sandpaper can remove a large number of surface grains. The surface is roughened and the groves penetrate into deeper regions of the material, exposing less stressed grains. The corrosion rate decreases with diminished strain on a grain, due to a smaller number of dislocations in the crystal structure of the grain. A great advantage of sanding the surface in this manner is the assurance that no unnecessary work hardening is introduced and the surface is effectively cleaned. This method of surface preparation is adapted from standard methods for the preparation of metallographic specimens.

4.6.2.2 Air Abrading with Glass Beads

The other form of preparation evaluated to clean the surface uses spherical, solid glass beads. Glass beads with a mean size of 47 micron were used. Using glass beads to remove oxide and dirt layers has the advantage of being fast. It is judged a more even way of cleaning. It has to be born in mind that the stream of the glass beads may vary in velocity. The centre of the stream is more effective than the outer regions of the circumference, due to the changes in air pressure, density of beads and the impact angle of the stream. The further away from the centre of the impact area, the wider and softer the abrasion. A consistent distance from the coupons has to be maintained to ensure even cleaning of the surface. The bead size range is 44-50 micron. About 6% of the volume can be over that size range. Of the total volume 7%

is a non abrasive lubricant, such as corn-starch. Other additives are used to lower the hygroscopicity and promote even flow (Croxton and Garry Ltd., 1993, personal communication). A 4 mm sized abrasion nozzle was used in the abrading process. Metallic abrasive powder should not be used, because if not thoroughly removed after abrading, it further promotes galvanic cell reactions during corrosion, and can lead to uneven pitting corrosion. It has been suggested that the use of an abrasive might cause surface hardening due to the impact of the glass beads on the surface. This was checked in metallographic section, although the surface profile shows impact areas of the glass beads, the apparent surface microstructure is unaltered.

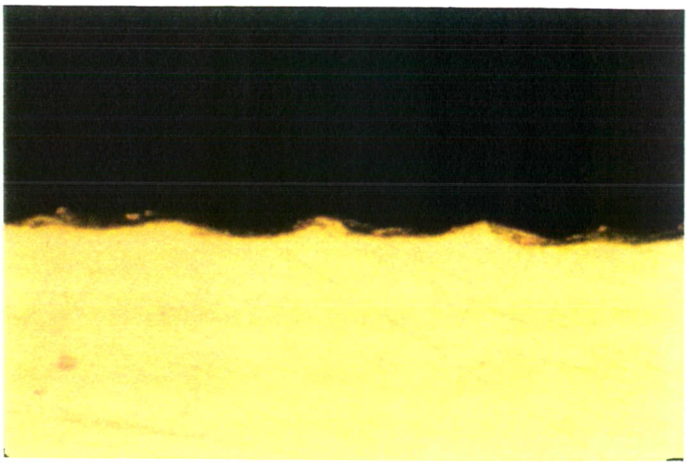


Figure 4. 1 Crossection of air abraded copper coupon —— 20μ

4.6.2.3 Degreasing of the Surface

Both the sanded and the air-abraded surfaces must be degreased. A 2 minute immersion in an ultrasonic tank containing a separate 50 ml acetone bath was chosen to remove any glass beads and other greasy matter which might have accumulated. ASTM GI (1990) states that ultrasonic cleaning with organic solvent is beneficial for the purpose of cleaning corrosion specimens. In this case acetone was selected, as it was readily available in the laboratory in reagent grade form. It has to be mentioned that the time of exposure to an ultrasonic bath, and the amount of water in the ultrasonic basin, as well as the amount of acetone solution used should always be consistently maintained. Changes in these parameters might cause differences in pickling of the surface. The ultrasonic waves might change in strength, with the amount of water used in the basin. The smaller the amount of liquid used in the ultrasonic basin the stronger the vibration, resulting also in an increase in temperature of the solution.

The ultrasonic cleaning was followed by 2 minutes hot air drying on a metallographic specimen dryer (50 °C). This was later substituted by 5 minutes drying under an infrared light, at 30 cm distance (50 °C). With the small metallographic drier only three coupons could be dried. An IR-lamp allowed the drying of up to 12 specimens at a time. Nevertheless it was found that the coupons positioned closer to the centre of the light dried slightly faster. Rapid drying of the acetone was necessary so that the surface would not attract further water or dust. The contamination of the surface of the coupons should be avoided to minimise variation in corrosion conditions between specimens.

The cleaned surface should be used for corrosion testing immediately. Delay would have allowed corrosion to occur under uncontrolled conditions. To prevent contamination, the coupons were handled with gloves or plastic tweezers.

4.7 Evaluation of Cupric Chloride Paste and Cupric Chloride Solution for Corrosion Testing Procedures

The experiments undertaken aimed to produce uniform pitted copper chloride corrosion on the surface of a copper coupon. This type of corrosion was the harsh foundation on which the new inhibitors were to be tested. The simulation of an archaeological copper surface containing chloride corrosion was the aim of this process. Malachite (basic copper carbonate) could not be readily reproduced. The $CuCl_2$ paste treatment suggested by Angelucci et al. (1978), and a variation of this treatment was applied to the prepared copper coupons. Before each experiment, the surface of the coupons were cleaned.

Two treatments to cause chloride pitting corrosion were tested:

1. 60g $CuCl_2$ and 20 ml distilled water, to form cupric chloride paste (Angelucci et al., 1978, 147);
2. The immersion into a 1 M solution of $CuCl_2$ and deionised water;

The treatment by Angelucci et al. was thought to result in low reproducibility as discussed in section 4.5.2. A 1M solution of cupric chloride is suggested as an alternative treatment to increase reproducibility of the data.

4.7.1 Cupric Chloride Paste

Introduction

The procedure suggested by Angelucci et al. (1978) was altered to improve material characterisation and observed reproducibility of products.

The paste (60g $CuCl_2$/ 20ml distilled water) Angelucci et al. (1978) applied was calculated to be equivalent to 22.3 M of cupric chloride in distilled water. When preparing the paste by adding 20 ml of deionised water to 60 g $CuCl_2$, it was found that it did not result in a paste as described in the publication. It rather consisted of lumps of cupric chloride. After several trials, adding water up to a ratio of 50 g $CuCl_2$ to 50 ml deionised water resulted in a spreadable paste. Angelucci et al. (1978) might have used cupric chloride dihydrate ($CuCl_22H_2O$), which (although not specified) resulted in a paste of the published ratio.

The distilled water was replaced with deionised water at pH 7. Distilled water is sometimes contaminated with foreign matter when the distillation coil is not cleaned properly. It is also known that the pH varies greatly, and has the tendency to be slightly acidic (Institute of Archaeology source is known to vary from neutral to acidic).

Rinsing under running water and brushing are very inaccurate ways to remove unwanted unreacted cupric chloride paste. The amount of chlorides removed by the running water, from in the surface corrosion layer varies considerably.

Angelucci et al. (1978) stated that: "*there appeared no perceptible difference between results obtained at room temperature and at 50°C.*" To check this experimental result, the experiments were also conducted at 50°C. An increase in temperature should result in a slight increase in electrochemical corrosion rates.

Experimental Procedure

Applying the paste evenly on both sides in a thickness of 1-2 mm was difficult and not very successful. Variations in the $CuCl_2$ thickness caused different amounts of oxygen and electrolyte to cover the surface. This induced varying corrosion in different areas. The specimens were placed for 96 hours in 90-95% RH at room temperature, and turned 180° every 24 hours to promote even corrosion.

After the 96 hours exposure, the coupons had to be rinsed under running water. This type of cleaning was not found suitable. The rinsing of the surface caused uncontrolled removal of chlorides on the surface and in pits. The pressure of the running water, and the brushing of the corroded surface could not be reproduced precisely. Differences in chloride removal changes further chloride corrosion in later stages of the experiment.

The specimens were placed three times, for 20 minutes, into 100 ml of deionised water. During the first two immersions the deionised water turned slightly green due to suspended $CuCl_2$ paste. After the third immersion the water did not change colour. The immersion into deionised water was observed to increase the reproducibility of the experiment. Nevertheless, the immersion did not change two important factors of inaccuracy. First; the amount of cupric chloride paste removed from the surface of the coupons was variable and difficult to control. The amount of paste initially applied to the surface varied greatly between coupons. Second; the amount of cupric chloride paste adhering to the surface after immersion into deionised water could not be accurately monitored.

Experimental Conclusion

The main concern in the Angelucci et al. procedure was the gravimetrical aspect. Weighing the specimens treated with cupric chloride paste cannot indicate weight changes due to corrosion, they might be due to either differences in corrosion rates or adhering cupric chloride. Angelucci et al. completely neglected the gravimetrical aspects of the corrosion test proposed. Their observations were all based on subjective parameters, such as optical assessment and photographic recording. The Angelucci test does not allow statistical evaluation of the test results, and statistical comparison of corrosion rates between experiments. The proposed changes, discussed further in the following section, such as the use of 1M cupric chloride solution, allow gravimetrical comparison between specimens and experiments.

4.7.2 Cupric Chloride Paste Versus Cupric Chloride Solution

Introduction

As a comparable procedure to the one described by Angelucci et al. (1978), 1M $CuCl_2$ in solution was proposed since it should cause the formation of cuprite and nantokite. The use of $CuCl_2$ in a water solution rather than a paste had three advantages:

1. Only a small amount of cupric chloride is needed in comparison to excessive treatment with a paste.
2. There is no problem of adherent cupric chloride paste.
3. The corrosion is expected to be more evenly distributed, since all the areas are evenly exposed to $CuCl_2$.

Some unquantified factors affecting the corrosion rates, and in turn reproducibility are:

- The concentration of $CuCl_2$ needed in the solution to function as a corrosion inducing factor is not known.
- the exposure time to the solution has to be established.

The experimental procedure was proposed as follows:

1. Copper coupons were cleaned (sanded or air-abraded)
2. Each sample was totally immersed in 25 ml, 1M solution of cupric chloride in a 25ml beaker, and covered to slow evaporation.
3. The immersed specimens in contact with cupric chloride were exposed 96 hours to ambient temperature, or 50°C in an oven.
4. The coupons were checked every 24 hours and turned over.
5. After 96 hours all coupons were removed from solution.
6. Deionised water was used to rinse the surface.
7. 200 hours exposure to 95% RH in a humidity chamber at ambient temperature.
8. Rinsing in deionised water.

9. Placed in to 95% RH at ambient temperature for 48 hours to ensure active corrosion.

Two temperatures were applied in step 3, to assess the difference in corrosion rate. It was thought that the higher temperature would increases the corrosion rate.

Experimental Procedure

The two cupric chloride treatments ($CuCl_2$ paste and $CuCl_2$ solution), were assessed at room temperature (15-25°C) and at 50°C, to monitor corrosion rates. The coupons were either sanded with 600 grade sandpaper or air-abraded, to remove surface contamination. Both types of surface cleaning were applied to contrast the uniformity in corrosion. The coupons were degreased in an ultrasonic bath of reagent grade acetone for 2 minutes. Each variation in treatment was carried out on three coupons (a,b,c) to observe variations in corrosion rate. The samples were prepared and exposed as follows:

Sample	sanded	air-abraded	$CuCl_2$ paste	$CuCl_2$ solution	room temperature	50^{o}C
1a,b,c	✓		✓		✓	
2a,b,c		✓	✓		✓	
3a,b,c	✓		✓			✓
4a,b,c		✓	✓			✓
5a,b,c	✓			✓	✓	
6a,b,c		✓		✓	✓	
7a,b,c	✓			✓		✓
8a,b,c		✓		✓		✓

Table 4. 3 Coupons Treated with $CuCl_2$

Experimental Observations of Coupons Covered with $CuCl_2$ Paste (1-4a,b,c)

These coupons were coated with the $CuCl_2$ paste. The exposure to 95% RH, should have produced cuprous oxide, cuprous chloride and basic copper chloride (paratacamite). The exposure to an RH of 95% produced several problems and did not necessarily produce active pitting corrosion at the end of the procedure, as described by Angelucci et al. (1978).

Angelucci et al. (1978, 147) applied a paste with a composition of 60g cupric chloride and 20 ml of distilled water. The $CuCl_2$ purchased from Aldrich, was mixed with deionised water. The mixture did not result in a smooth paste but in a lumpy mixture. In 1 ml steps deionised water was added until the mixture was in a pasty form. It was found that 50g of $CuCl_2$ had to be diluted with 50 ml of deionised water to produce a suitable paste. Angelucci's procedure was cross-checked repeatedly but never resulted in a paste when using anhydrous $CuCl_2$. The reason for the lack of water in Angelucci's mixture could be that the cupric chloride used was in a hydrated from ($CuCl_22H_2O$). This was checked later.

Samples 1-4a,b,c were placed on watch glasses so air and humidity were able to reach all areas fairly evenly, except at points of contact. Samples 1-2a,b,c were exposed to ambient temperature which fluctuated during the experiment, between 17-24°C at 95% RH, as proposed by Angelucci. During the experiment it was observed that coupons which were treated with the paste and exposed to 95% RH, at ambient temperature, behaved differently to the experiment described by Angelucci et al. (1978). After 24 hours exposure, the paste deliquesced and formed a dark green solution in the bottom of the watch glass. This solution picked up more moisture as observed by the increase in volume of the solution, during the experiment. The paste was to a large extent dissolved, and removed from the surface. During almost all the

$CuCl_2$ corrosion period, the lower parts of the coupons were immersed in the cupric chloride solution.

Relative humidity was monitored by using a hair-hygrometer with an accuracy of ±5%. This was calibrated by wrapping it in a wet towel for 5 minutes and adjusting it to 100% RH. Later this was cross-checked with a hand-held digital thermohygrometer with reported accuracy of ±1-2%. There was a deviation of about ±5% between the two hygrometers.

Samples 3+4a,b,c were placed in an oven at 50°C. Due to lack of equipment, it was not possible to produce 95% RH/50°C during the first part of the experimental work. After 24 hours it was found that the oven produced 65% RH, 50°C at the centre of the oven. The RH was measured with a hair hygrometer, which might not be accurate at a higher temperature. The lower quarter of the chamber had condensation on the glass door and an RH of 80%. The condensation indicated that there was a higher RH, and possibly a drop in temperature from the top to the bottom of the chamber, due to an inefficient circulation of the atmosphere. For the rest of the experiment the coupons were placed into the lower quarter of the chamber at 80% RH, and the temperature was adjusted to 50°C. The lower RH of 65% at the beginning of the test gave an indication that this RH might prevent the deliquescence of the $CuCl_2$ paste. It is not known how the higher temperature interferes with the deliquescence of the paste.

After 96 hours exposure to the paste all samples were removed from the chamber. To remove excess cupric chloride paste, the coupons 1-4 were placed 3 times for 20 minutes in 100 ml deionised water in a 500 ml beaker. The solutions were lightly stirred every 10 minutes for 5 seconds to enhance the dissolution of the soluble corrosion products. Coupons 3-4 had to be lightly brushed with a soft brush during the second immersion, to remove the loose corrosion products as suggested by Angelucci et al. (1978). It was thought that they might interfere with the corrosion rate in later stages of the experiment. It was found that brushing and stirring caused uncontrolled, variable removal of corrosion products. Three times rinsing was found to be sufficient, because no visible particles of the corrosion products were suspended in the wash solution. After the removal of the specimens, it was found that some of the corrosion layers on coupons 3-4, had fallen off and had exposed a red cuprite surface.

Measuring the chloride contents of the wash solutions was found impractical considering variations in the amount of chlorides in the paste applied to the surface of each specimen to initiate corrosion. Rinsing every coupon until a certain chloride deficiency of the wash solution was detected was not found suitable since this causes the disintegration of the corrosion layers, and causes subsequent changes in their corrosion rate.

After rinsing, coupon sets 1 and 2 had a cuprite corrosion surface, due to the previous immersion into the deliquesced $CuCl_2$ in the watch glass. Samples 3-4 exposed a much more uneven pitted surface at a 25x magnification under the binocular microscope. This surface was interpreted visually to resemble the nantokite layer in a corrosion pit in a corroded archaeological surface. As mentioned before, parts of the corrosion layer fell off, and exposed an uneven cuprite surface underneath. This loss of the corrosion layer introduced a factor of inconsistency in the weight and corrosion of the samples. The accuracy of assessing inhibitors by a gravimetrical evaluation was inappropriate for meaningful comparison. Weight changes are suitable for industrial studies, but not for simulated archaeological corroded samples, due to breakaway corrosion. A larger number of replications should diminish the factor of inaccuracy. If a corrosion inhibitor was to be tested on such a precorroded coupon, a large number of corroded coupons would have to be treated with the inhibitor and exposed to an elevated RH to produce useful data.

Coupons 1-4 were than exposed for 200 hours to 95% RH, at ambient temperature (20-25°C) in a humidity chamber. This should increase the pitting corrosion of the surface.

Observed Changes during 200 hours at 95% RH were as follows:

Specimen 1-2: After 24 hours the specimens had a very thin skin of paratacamite corrosion. This was confirmed with X-ray powder diffraction at a later date. The light green paratacamite corrosion layer on the specimens, could be removed by tapping the specimens on to a hard surface, as suggested by Angelucci et al. (1978, 148). Some of the paratacamite corrosion was still adhering to the surface. Repeated 24 hour exposure to 95%RH at room temperature did not result in further corrosion. Continuing exposure to 95% relative humidity did not result in further chloride corrosion.

Specimens 3-4 were not very actively corroding after 24 hours at 95% RH, and did not appear to have changed very much in appearence. Tapping of coupons did not remove any corrosion products. Repeated 24 hour exposure to 95%RH at room temperature resulted in localised active corrosion. At the end of the 200 hours at 95% RH there was small localised active corrosion.

The coupons were removed from the humidity chamber and rinsed by immersion 3 times for 20 minutes in 100 ml of deionised water. The first rinsing was followed by slight brushing of the surface, to remove the loose corrosion products. During the immersion not all of the light green paratacamite was removed. This rendered the evaluation of newly formed chloride corrosion difficult. The coupons were then weighed. However, two factors made the gravimetric evaluations of the corrosion rate unsatisfactory.

1. There was some remaining paratacamite on specimens 1-2. This could not be removed by tapping and rinsing and this interfered with the gravimetrical assessment.
2. The tapping of samples 3-4 removed the corrosion products unevenly.

According to Angelucci et al. (1978), the coupons should be dried and exposed for 48 hours to 95% RH and ambient temperature to confirm active corrosion.

This procedure was followed, but specimens 1-2 showed no signs of any new light green paratacamite corrosion. Samples 3-4 resembled a corrosion surface described by Angelucci et al.. Since remaining light green corrosion products (paratacamite) were not removed by the previous rinsing cycles, new and old paratacamite corrosion could not be readily differentiated after the 48 hours corrosion check. Old green corrosion deposits interfered with gravimetrical assessments.

To assess active pitting corrosion, sample 3a was cleaned partially with a glass bristle brush. This is a technique sometimes used to clean copper surfaces in a conservation treatment. During this process, paratacamite visible on the surface was removed. The cleaned area was then separated from the uncleaned by a black marker line. After 48 hours at 95%RH ambient temperature the cleaned areas had light green corrosion, and some corrosion even appeared on the black line of the marker.

The treatment of a coupon with $CuCl_2$ paste, at 95% RH and ambient temperature, did not produce active chloride pitting corrosion. The cupric chloride paste deliquesced at 95%RH, and the surface of these coupons was similar to that of coupons completely immersed in a cupric chloride solution. Coupons covered in cupric chloride paste and exposed to 50°C at 65-80%RH, resulted in a chloride pitted corrosion surface, with small areas of localized active chloride corrosion similar to those found on archaeological artefacts. This confirms Angelucci et al.'s findings that a treatment of copper coupons with cupric chloride paste results in active chloride corrosion, in order to simulate samples for corrosion inhibitor testing in archaeological conservation.

Experimental Observations of Coupons Immersed in $CuCl_2$ (Coupons 5-8)

Each cleaned copper coupon was placed into a petri dish filled with 25 ml of 1M solution of cupric chloride in deionised water. The petri dishes were covered to slow evaporation. Samples 5,6 were kept at ambient temperature and 7-8 were placed into the oven at 50°C.

After immersion into the cupric chloride solution, the surface of coupons 5-8 darkened in colour immediately.

After 24 hours in the cupric chloride solution, coupons exposed to 50°C had more material in suspension in the solution than the specimens exposed to ambient temperature. This might indicate increased corrosion. Four days in the cupric chloride solution resulted in an even corrosion layer. There was no apparent pitting corrosion.

After rinsing the coupons as explained above, they were placed for 200 hours into the humidity chamber at 95% RH at ambient temperature. After 24 hours all coupons were covered in paratacamite. As suggested in Angelucci's treatment, the coupons were tapped and most of the paratacamite removed from the surface. However, repeated exposure to 95%RH did not result in further paratacamite corrosion.

The samples were rinsed as stated above, followed by the corrosion control exposure for 48 hours. However, this again did not produce reoccurring chloride corrosion.

This treatment did not produce pitting corrosion typical of archaeological material. The formation of a thin skin of nantokite suggested that the corrosion was much more uniform than the corrosion layers formed by the $CuCl_2$ paste. This treatment was used in the following experiments. To evaluate this procedure, a new batch of coupons had to be treated in the same manner, and an average corrosion rate had to be established and the type, thickness, and structure of the corrosion had to be determined.

Discussion of $CuCl_2$ Treatments

These preliminary experiments to determine the suitability of cupric chloride to induce corrosion highlighted many problems:

- Angelucci et al. (1978) treatment results could not adequately be reproduced.
- The sanding or air-abrading of the coupons prior to the corrosion had to be assessed.
- The experimental procedure had to be modified.
- The $CuCl_2$ paste did not result in a uniformly pitted corrosion surface.
- The deliquescence of the paste had to be further investigated.
- The amount of nantokite corrosion of 1M solution of $CuCl_2$ had to be established and its reproducibility.
- Analysis of all corrosion products had to be undertaken.

This experiment resulted in further investigation into the deliquesence of cupric chloride paste, to confirm Angelucci et al.'s observations. However, the application of a solution of cupric chloride seemed to be a better approach since it resulted in an even corroded surface. In the following experiment a standardisation of this procedure was the objective, to improve the reproducibility of corrosion data.

4.8 Further Investigation into Surface Preparation of Samples Treated with 1M $CuCl_2$ Solution

4.8.1 Introduction

The following experiment was designed to evaluate the surface preparation of abraded and sanded coupons. Six coupons were treated simultaneously to permit comparison, and to give an insight into reproducibility and variations. The following experiment was undertaken to standardise the procedure. Ambient temperature was chosen to minimise variations in temperature. Exposure to 50°C was found difficult to replicate in the available oven.

4.8.2 Experimental Procedure

For the experimental procedure the following steps were adopted.

Experimental Procedure:

1. 6 coupons were sanded with 600 grade sandpaper
2. 6 coupons were air-abraded with glass beads (47 micron)
3. degreased for 2 minutes in a 100 ml ultrasonic acetone bath
4. 5 minutes drying under infrared lamp (50°C)
5. weight determination (±0.01mg)
6. 96 hours immersion in 25 ml of 1M solution of $CuCl_2$ in deionised water, at ambient temperature
7. 3 rinses, each 20 minutes in 100ml of deionised water
8. dried in acetone and exposed for 24 hours to 105°C
9. weight (±0.01mg)

4.8.3 Experimental Observations

The 1 M solution was stirred for 5 minutes at 50°C on a hot plate to ensure that all the $CuCl_2$ was dissolved. 25ml of the solution was poured into 30 ml cylindrical glass flasks. The seperate flasks allowed each coupon to be treated on its own. Only the edges of the coupons came in contact with the glass, allowing the two main surfaces of the coupons to be covered with the solution. This would help preferential corrosion.

After immersion in the solution, the surfaces of all the coupons darkened in colour. After 24 hours a thin "skin" of deposit formed on the surface of the solution. After 96 hours the coupons were removed from the solution and rinsed 3 times in 100 ml of deionised water for 20 minutes, to remove excess cupric chloride and water soluble matter. After rinsing they were dried for 24 hours at 105°C, then weighed.

	Coupon	Cleaned	After $CuCl_2$ solution	Weight change	Mean weight change
Air-abraded	1a	9.02733	9.15666	0.12933	
	1b	8.95324	9.08783	0.13459	
	1c	8.76927	8.90033	0.13106	
	1d	8.8362	8.95727	0.12107	
	1e	8.78993	8.91738	0.12745	
	1f	8.78767	8.91414	0.12647	0.12833
Sanded	2a	9.06024	9.18649	0.12625	
	2b	8.81416	8.93838	0.12422	
	2c	8.56613	8.6737	0.10757	
	2d	8.86667	8.97848	0.11181	
	2e	8.84346	8.95503	0.11157	
	2f	8.80164	8.90508	0.10344	0.11414

Table 4. 4 Weight Changes in grams of Coupons treated with $CuCl_2$

The air-abraded coupons corroded most in the cupric chloride solution with a slightly larger increase in weight (Table 4. 4). However, there are no meaningful differences in the weight change data, so air-abrasion was judged a suitable replacement for sanding.

In using cuppric chloride solution as a corrosion initiator in this experimental work, the following preparation procedure for cleaning the copper coupons was adopted. This was based on the results of the previous experiment.

- Air-abrading of the coupons with 47 micron glass beads, to create a clean surface finish.
- Degreasing of the surface for 2 minutes in 100 ml of acetone in an ultrasonic bath, to remove surface contamination introduced while handling the coupons.
- Drying for 5 minutes under an infrared lamp at 50°C, to decrease surface corrosion.

4.8.4 Analysis of Copper Chloride Corrosion Products on Cupric Chloride Treated Coupons

To check the compositions and the structure of the corrosion layers present on the coupons, X-ray powder diffraction, optical microscopy and electron probe microanalysis were undertaken.

Some of the corrosion of an air-abraded coupon was removed for X-ray powder diffraction analysis, to confirm the presence of nantokite, paratacamite and cuprite. One sample was taken after corrosion in the 1M solution of $CuCl_2$, and drying for 24 hours at 105°C. Another sample was taken from the same specimen after the surface was exposed for 24 hours to 95% relative humidity.

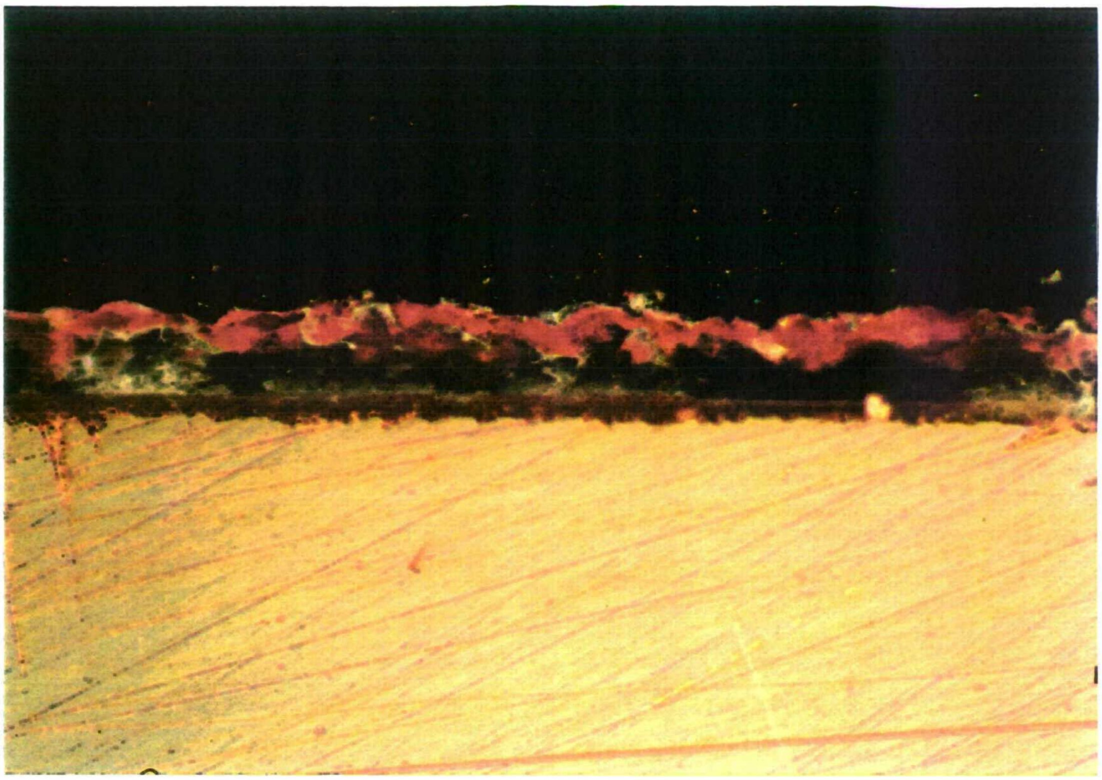


Figure 4. 2 Photomicrograph of nantokite, and cuprite layer on copper coupons.

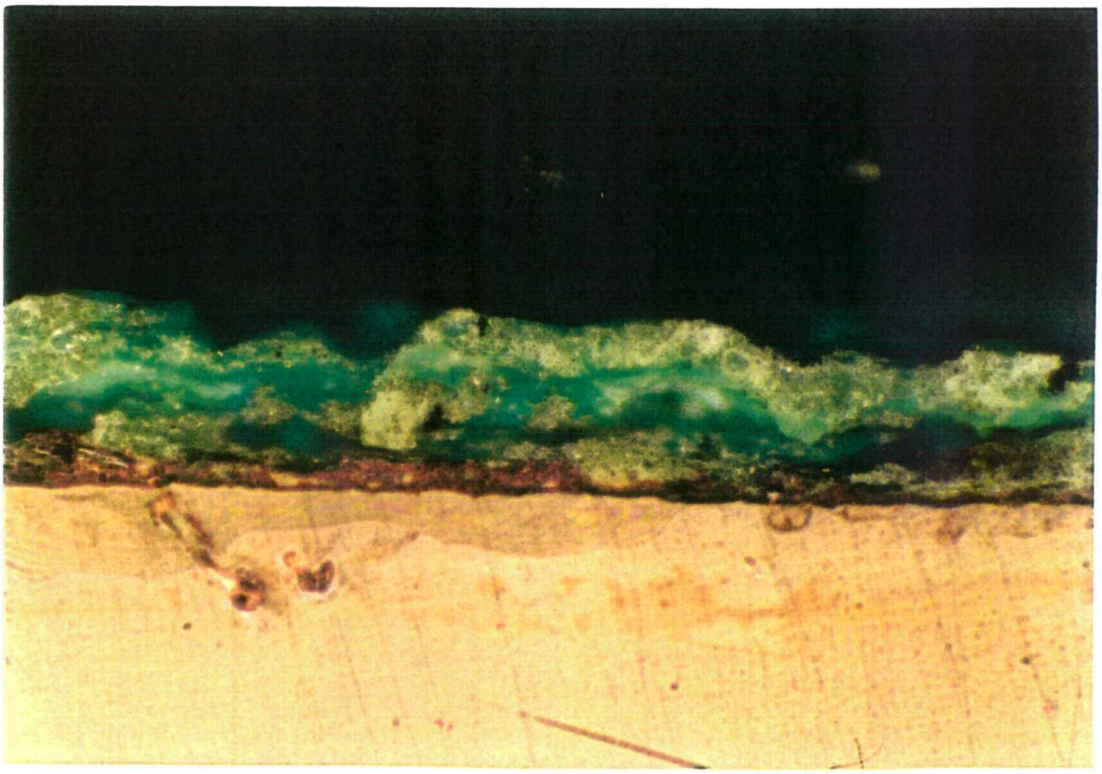


Figure 4. 3 Photomicrograph of Paratacamite corrosion on copper coupons.

The XRD analysis was done on a Siemens X-ray diffractometer D5000 in the department of Chemistry, UCL.

The sample taken after the cupric chloride corrosion clearly shows the presence of nantokite (see Appendix 3.1). The sample taken after the exposure of the nantokite to 95% RH was clearly identified as paratacamite (see Appendix 3.2).

A metallographic sample was taken to investigate the corrosion layers, and the elemental composition of the corrosion present before and after the exposure of the nantokite layer to 95% RH.

The corroded specimen was mounted under vacuum in Buehler Epo-Kwick (epoxy resin) The mounted sample could not be polished in the usual way since moisture uptake had to be avoided. Water would have caused changes to the nantokite. The samples were polished with diamond paste on a cloth-covered polishing wheel. To avoid the loss of nantokite, a hydrocarbon oil was used (CASTROL ILOCUT 430), a polishing fluid for lithic thin sectioning. Rinsing between polishing was done with the same fluid.

The photomicrograph (Figure 4.2) taken of the metallographic section of the nantokite covered coupon shows a layer 20-25 micrometres thick of nantokite on top of the copper substrate. This was covered by a 5-10 micrometere layer of red cuprite, which was of reasonably even thickness.

The photomicrograph of the coupon covered in paratacamite (Figure 4. 3) showed a 10-25 micron layer of what seemed to be cuprite on top of the copper substrate, and a 160-175 micron layer of paratacamite.

The XRD analysis previously undertaken did not detect the cuprite visible in section in the nantokite or the paratacamite samples. This could be due to a smaller crystal size of the cuprite, the inhomogenity of the material, or a smaller amount of cuprite present in the layers. To confirm the presence of cuprite electron probe microanalysis was undertaken.

The mounted metallurgical sections, used for the optical microscopy work, were carbon coated for analysis. Both specimens were analysed for copper, chloride, and oxygen. The line scan taken on the nantokite specimen (Appendix 3.3) clearly suggests the cuprite layer. The cuprite was detected between 26-37 microns on the line scan. It was indicated by an increase of oxygen and copper present and a decrease in chloride. The following 18 micron nantokite layer showed an increase in chlorides, it was observed that the closer one came to the copper substrate, the higher the chloride count. The line spectra might suggest a thin cuprite layer between nantoktie and copper substrate.

The microprobe work undertaken on the paratacamite specimen, did not identify any material other than paratacamite. The cuprite layer seen on the photo micrograph (Figure 4.3, appendix 3.4) could not be detected.

Air-abrading the surface of copper coupons prior to immersion into the corroding cupric chloride solution was found to form a uniform corrosion structure. It was decided, on the bases of time savings, analytical examination and gravimetric measurements, that this type of sample preparation would be used for further studies.

4.8.5 Deliquescence of $CuCl_2$ Paste

As previously established, the cupric chloride paste gained in weight when exposed to 95% RH in a humidity chamber at ambient temperature. To confirm the deliquescence of $CuCl_2$, 5g of anhydrous $CuCl_2$ was placed in a Petri dish and exposed for 4 days to 95% ± 5 RH at ambient temperature. The red $CuCl_2$ powder immediately deliquesced and turned green. After the 4 day experiment, the powder formed a dark green solution and had picked up 10.1g of water from the surrounding environment. This indicated that the 95% RH stated in the Angeluccci et al. (1978) article needed to be lowered, to stop the dissolution of the paste.

To estimate the RH threshold at which $CuCl_2$ was in a saturated solution and did not attract more water, the following procedure was undertaken. (The value could not be readily found in the literature). Deionised water was warmed to 50°C, and $CuCl_2$ was added while stirring. On cooling some of the salt crystallised. This was a visible check that the solution was saturated. The cooled solution was then placed in a sealed polyethylene box at ambient temperature. After 24 hours, the RH inside the box was measured. This was accomplished by inserting an RH probe through a small hole in the box. The RH was 65% ±2%, using the digital hygrometer.

A 65% RH suggests, that any pure $CuCl_2$ paste would pick up moisture as soon as it was placed into a relative humidity above 65%. This saturation point might be different when the paste was in contact with copper coupons, or the temperature was changed.

4.9 Cupric Chloride Paste in Covered Petri Dishes

4.9.1 Introduction

The deliquescence of cupric chloride was found to produce a corrosion surface similar in appearance to that found on coupons immersed in cupric chloride solutions. It was now known that the relative humidity at ambient temperature should be lower than 65%. Angelucci et al. (1978) placed the coupons exposed to 50°C into a "petri capsule". When a Petri dish is covered, the cupric chloride probably produces a relative humidity of 65%. The previous experiment has shown that a saturated solution of cuprous chloride produces such an RH. The paste should not readily pick up more moisture when covered, so the coupons should be exposed to the same relative humidity during the whole corrosion process. The covering of the coupons at 50°C in Angelucci et al.'s experiment, apparently resulted in a suitable micro-environment. So the assumption was made that coupons covered with the paste, and than placed into Petri dishes, and covered at ambient temperature, should result as well in a suitable RH stopping the deliquescence of the paste.

4.9.2 Experimental Procedure:

Twelve copper coupons were abraded, degreased, dried, and weighed as described previously. They were then covered into a paste composed of 30g of $CuCl_2$ and 30 ml of deionised water. All coupons were placed into Petri dishes and covered. Six coupons were placed in an oven at 50°C, and six were exposed to ambient temperature.

4.9.3 Experimental Observations

Over 24 hours, the specimens at 50°C did partially dry. The paste on the specimens at ambient temperature deliquesced partially, similar to samples exposed to 95% RH at ambient temperature.

Only a few changes were detected visually between 24-96 hours. The samples at 50°C were all variably covered with corrosion and paste. Some seem to have corroded more than others. This might have been due to a poor seal between the glass lid of the Petri dish and the dish itself and resulting in evaporation of moisture. The coupons at ambient temperature were all partially under solution. The surface in contact with the Petri dish (bottom side), had different corrosion areas. There were two blackened centres surrounded by green cupric chloride on all samples.

It is assumed that the black areas represented anodic parts of the corrosion process and the surrounding green areas were cathodic. This suggests that the environment in which the specimens were corroded had to be maintained uniformly throughout the corrosion experiment. Slight changes in the procedure, such as the thickness of the cupric chloride paste, temperature or relative humidity, could cause significant changes in the corrosion rate and corrosion product distribution on the coupons. In such a case, the obtained corrosion data could not be directly compared.

The specimens were then removed from the solution and rinsed 3 times in 100 ml deionised water. This revealed the corroded surfaces. The specimens in contact with the solution were more evenly corroded than the specimens at 50°C. The coupons exposed to 50°C had the most severe corrosion. This was estimated by appearance alone. Some of the corrosion layers on the 50°C specimens fell off during the rinsing process, rendering the gravimetric evaluation inappropriate. All coupons were dried under infrared lamp, to allow assessment of the corrosion surfaces. It was found that not even the coupons corroded at 50°C were pitted enough for the inhibitor assessment. Nevertheless, the samples were exposed for 200 hours to 95% RH at ambient temperature.

After the 200 hours the previous findings that the corrosion was insufficient were confirmed, so the experiment was halted. It was concluded that the relative humidity produced through the cupric chloride paste during the four day exposure, did not result in sufficient pitting corrosion.

4.10 Cupric Chloride Paste Mixed with Kaolin

4.10.1 Introduction

The deliquescence of cupric chloride paste did not allow the formation of a structure of copper corrosion products similar to archaeological artefacts. The cupric chloride paste experiment, which Angelucci et al. (1978) applied to stimulate corrosion, was based on the Corrodkote test (ASTM B 380-85). This corrosion test was specified by the American Standards for Testing and Materials, to evaluate the performance of electrodeposited films on steel. Referring to this corrosion testing standard, it was found that Angelucci et al. adapted several parameters of this testing procedure.

The ASTM B 380-85 recommends the following mixture: ferric chloride, cupric nitrate, ammonium chloride and kaolin. This is applied as a slurry on to the coupons. Angelucci et al. (1978) replaced the salts in the slurry with cupric chloride to produce cuprite, nantokite and paratacamite. They ignored the addition of kaolin. Kaolin with its plate like structure, was added to maintain the mixture as a paste, making the spreading of the slurry easier and more even. The non-addition of Kaolin to the cupric chloride might be the reason for the deliquescence.

Angelucci et al. also ignored another step in the ASTM B 380-85. It is stated that the slurry was applied evenly to the surface, and that the coupons were then left to dry for one hour at a relative humidity below 50%, at ambient temperature. This allowed the paste to lose some of its excess water. By ignoring the drying step, the extra water in the paste might cause a more rapid deliquescence of the paste. It should be pointed out, that an exact RH below 50% should perhaps have been stated by ASTM, since the lower the RH the less initial corrosion during drying, and the less the opportunity for variations between samples.

4.10.2 Experimental Procedure

Having established two important deviations from the original ASTM standard, it was thought appropriate to repeat the experimental procedure, applying again a paste but adding kaolin and allowing the paste to dry for 1 hour at ambient temperature, at an RH below 50%. The cupric chloride paste was mixed as follows: 15g $CuCl_2$,15g Kaolin, 20 ml deionised water

Experimental procedure

1. Abrading with 47 micron glass beads
2. ultrasonic acetone bath 100 ml, for 2 minutes
3. infrared drying 5 minutes at 50 ^{0}C
4. weighing (± 0.01mg)
5. application of the $CuCl_2$ paste
6. drying at 35% RH 22°C for 1 hour
7. three coupons exposed for 96 hours at 50°C, 60% RH
8. three coupons exposed for 96 hours at ambient temperature, 55%RH. (55% RH buffered Silica Gel)
9. rinsing 3 times in 100 ml deionised water for 20 minutes
10. infrared drying 5 minutes at 50 ^{0}C
11. exposure for 200 hours to 95% RH ambient temperature
12. rinsing 3 times in 100 ml deionised water for 20 minutes
13. infrared drying 5 minutes at 50 ^{0}C
14. exposure for 48 hours to 95% RH, at ambient temperature

4.10. 3 Experimental Observations

After 24 hours, the paste was still present on the coupons. After 96 hours, there were still no visible changes. The coupons were rinsed three times in 100 ml of deionised water for 20 minutes. They were then infrared dried and assessed visually. Some of the coupons had paste stuck to the surface, which could not be removed by rinsing. This interfered with the gravimetrical assessment and rendered the data inaccurate.

The coupons were then exposed for 200 hours to a 95% RH at ambient temperature to assess the induced corrosion. After 200 hours it was found that there was only minimal corrosion on the surface of the coupons. The resulting copper chloride corrosion again seemed inadequate for use in the evaluation of copper corrosion inhibitors.

The changes to Angelucci et al.'s procedure were of advantage, since they decreased observed deliquescence of the paste. It was thought that the ratio between

$CuCl_2$ and kaolin was perhaps too high. A smaller amount of kaolin would be used for the next experiment.

4.11 Cupric Chloride Paste at 55% Relative Humidity and Ambient Temperature

4.11.1 Introduction

The previous experiments indicated that the relative humidity had to be lowered, and better controlled, and that pure cupric chloride paste produced the best corrosion results. To establish if pure $CuCl_2$ paste would deliquesce, even at a relative humidity below the saturation point of a saturated solution of cupric chloride, an RH of 55% was used. This RH was chosen since it was between 65% RH of a saturated solution and 43% of the activation range of chloride pitting corrosion, according to Scott (1990, 203). The 55% RH was created in a desiccator and the environment was produced by buffered silica gel. It was found difficult to maintain a stable RH, due to the opening and closing of the desiccator when measuring the RH.

4.11.2 Experimental Procedure

1. air abrading with 47 micron glass beads
2. ultrasonic cleaning in 100 ml acetone bath for 2 minutes
3. infrared drying for 5 minutes, 50°C
4. weighing (±0.01mg)
5. applying of the paste 10g $CuCl_2$ in 9 ml of deionised water
6. drying for 1 hour at 35% RH at ambient temperature
7. exposure of 3 coupons for 96 hours to 55% RH at ambient temperature
8. rinsing 3 times in 100 ml deionised water for 20 minutes
9. infrared drying for 5 minutes 50°C
10. exposure for 200 hours to 95% RH at ambient temperature
11. rinsing 3 times in 100 ml deionised water for 20 minutes
12. exposure for 48 hours to 95% RH, at ambient temperature

4.11.3 Experimental Observations

After 96 hours exposure to 55% RH and ambient temperature, the coupons were still covered in cupric chloride paste. It was not possible to weigh the coupons after rinsing off the cupric chloride paste, as some of the paste could not be removed.

The coupons were exposed for 200 hours to 95% RH at ambient temperature. In this period, the coupons produced active chloride corrosion, but this corrosion was not enough to be appropriate for copper corrosion inhibitor testing. The chloride corrosion was removed with a glass bristle brush. The underlying metallic copper was exposed in small areas, indicating the very thin nature of the corrosion produced. The coupons were then placed for 24 hours into 95% RH at ambient temperature, to determine if further paratacamite would erupt. After exposure only one coupon had a very small spot of light green corrosion typical of the paratacamite mineral.

4.11.4 Discussion

This experiment was not successful since it did not produce a large amount of chloride pitting corrosion, but it did indicate a better direction for the experimental work. It clearly indicated that a 55% RH is low enough to stop the deliquescence of the cupric chloride paste and induce a minimal amount of pitting corrosion. Two options were apparent for further experimental work. Either the exposure time of the coupons could be increased when exposed to 55% RH at ambient temperature, or the 55% RH could be maintained and the temperature increased, to allow an increase in the electrochemical corrosion rate.

4.12 Cupric Chloride Paste at 65% RH, Ambient Temperature

4.12.1 Introduction

The problems in the past experiments were either due to the deliquescence of the cupric chloride paste or a diminished corrosion rate, which resulted in no significant pitting corrosion on the coupons. The previous research has shown that the relative humidity of a saturated solution of cupric chloride was 65% ±2%, at ambient temperature. This led to the conclusion that cupric chloride does not deliquesce at a relative humidity below this approximate point.

The following experimental procedure was based on the hypotheses that a dried paste exposed to a closed environment buffered with a saturated solution of cupric chloride, would not readily deliquesce.

4.12.2 Experimental Procedure

1. air-abrading with 47 micron glass beads
2. ultrasonic acetone bath 100 ml, for 2 minutes
3. infrared drying 5 minutes 50 °C
4. weighing (± 0.01mg)
5. application of the $CuCl_2$ paste (30g $CuCl_2$,30 ml deionised water)
6. drying at 15% RH at ambient temperature for 1 hour
7. coupon was placed for 96 hours in a polyethylene box at ambient temperature
8. coupon was placed for 96 hours into polyethylene box with a saturated solution of $CuCl_2$, at ambient temperature
9. rinsing 3 times in 100 ml deionised water for 20 minutes
10. infrared drying 5 minutes 50°C
11. exposure for 200 hours to 95% RH at ambient temperature
12. rinsing 3 times in 100 ml deionised water for 20 minutes
13. infrared drying 5 minutes 50°C
14. exposure for 48 hours to 95% RH, at ambient temperature

4.12.3 Experimental Observations and Discussion

There was a deliquescence of both coupons. The specimen in the polyethylene box that produced its own environment, had less deliquescence than the specimen in the environment buffered with the saturated cupric chloride solution. This showed that the paste very readily accumulated moisture, and that the drying of the paste was not sufficient to prevent deliquesence. After rinsing, both coupons revealed an even corrosion surface, but no local pitting.

The corrosion produced during the 96 hour exposure, transformed into a thin light green probably basic copper chloride corrosion, after exposure to 95% RH at ambient temperature for three days. This even corrosion skin indicated that there was no distinctive pitting corrosion comparable to archaeological surfaces. The experiment was terminated due to the inadequate results.

4.13 Deliquescence of Dried Cupric Chloride Paste

4.13.1 Introduction

To experimentally establish the extent of deliquescence of cupric chloride paste when exposed to 95% RH at ambient temperature, the following procedure was adopted to test the possibility that the Angelucci et al. research team might have allowed the paste to dry, before placing it in 95% RH at ambient temperature.

4.13.2 Experimental Observations and Discussion

A copper coupon was treated in the same manner as the specimens in experiment 4.12.2. The coupon covered with the moist paste was placed into a Petri dish and weighed. The paste on the coupon was allowed to dry for 24 hours at 13% RH, at ambient temperature. A low relative humidity ensured that there was little water left in the paste. Any water left in the paste could have caused a premature deliquescence of the cupric chloride. A more secure way to ensure the drying of the paste would have been to place it in an oven at 105°C. It was not thought advisable to dry the paste in an oven, as this might have changed the corrosion rate during the initial period, when the paste contained water. This in turn might have interfered with the deliquescence of the paste. Nevertheless, this was assessed in subsequent work.

After 24 hours the coupon with the dried paste was removed from the 13% RH and ambient temperature environment, and placed into a 95% RH at ambient temperature. 24 hours exposure was long enough to produce a deliquescence of the paste. The paste had collected 0.327 g of water from the surrounding atmosphere. This was established gravimetrically and did not take into consideration the weight increase due to oxygen uptake during the corrosion process. This again illustrated that the procedure adopted by Angelucci et al. caused the deliquescence of the paste and did not result in a corroded surface with chloride pits similar to an archaeological copper artefact, infested with chloride corrosion.

4.14 Control Test of Paste

4.14.1 Introduction

To reassess all previously acquired results, and to ensure that none of the previously undertaken experiments had unreproducable effects, a study of 8 different treatment variations to produce corrosion pits was undertaken. Due to a lack of space in the test cabinet only one coupon was treated at a time. The coupons were exposed to reagent grade cupric chloride paste, and cupric chloride mixed with kaolin. The specimens were exposed to ambient temperature at 60°C, and 50°C. There was also a variation in relative humidity, 40%, 50%, 65% and 95%. The different RH levels were used to determine the range at which deliquescence occurs, and to what extent a pitted archaeological surface could be produced. Temperatures above ambient temperature should result in a higher corrosion rate, and hopefully in a corrosion surface similar to an archaeological copper artefact. Kaolin in a ratio 1:3 was added to the $CuCl_2$ for two reasons. First, it should allow a better dispersion of paste on the surface of the coupon. This should result in a more even thickness of the paste and as a result, in a more uniform pitting of the surface. Second, it should lead to a smaller amount of deliquescence at an RH around 65%.

4.14.2 Experimental Procedure

For the cupric chloride paste 15g of $CuCl_2$ was mixed with 15 ml of deionised water. The kaolin containing paste had 16g $CuCl_2$ and 4 g kaolin mixed with 20 ml of water. This allowed the paste to be spread easily. The copper chloride ratio to Kaolin was generally 4:1, but in experiment 4.10 the ratio was 1:1 by weight. The increase in cupric chloride should result in an increase in chloride corrosion.

The coupons were treated as follows:

Experimental procedure:

1. abrading with 47 micron glass beads
2. ultrasonic acetone bath 100 ml, for 2 minutes
3. infrared drying 5 minutes 50 °C
4. application of paste
5. drying at an RH below 50% for 1 hour
6. placing the coupons in to the appropriate environment for 96 hours
7. rinsing 3 times in 100 ml deionised water for 20 minutes
8. infrared drying 5 minutes 50 °C
9. exposure for 200 hours to 95% RH at ambient temperature
10. rinsing 3 times in 100 ml deionised water for 20 minutes
11. infrared drying 5 minutes 50 °C
12. half of the surface cleaned with a glass-bristle brush
13. exposure for 48 hours to 95% RH at ambient temperature

	Paste	Temperature	Relative Humidity	Deliquescence after 96 hours
#1	$CuCl_2$	60°C	40%	none
#2	$CuCl_2$	50°C	55%	none
#3	$CuCl_2$	60°C	sealed flask	complete dissolution
#4	$CuCl_2$ and kaolin	50°C	55%	none
#5	$CuCl_2$ and kaolin	60°C	sealed flask	complete dissolution
#6	$CuCl_2$ and kaolin	ambient	65%	some
#7	$CuCl_2$ and kaolin	ambient	95%	complete dissolution
#8	$CuCl_2$ and kaolin	ambient	sealed flask	complete dissolution

Table 4. 5 Treatments of Copper Coupons

The specimens that was placed into a sealed glass flask produced their own relative humidity. An hour of previous drying of the paste was thought to decrease deliquescence. The 65% RH (specimen #6) was produced by a saturated solution of cupric chloride in a sealed container.

4.14.3 Experimental Observations

Coupons 3,5 and 6 were disregarded, due to the deliquescence of the paste. The other coupons were rinsed to remove remaining cupric chloride, and exposed for 200 hours to 95% RH at ambient temperature.

After 24 hours coupons 1 and 8 had an even paratacamite corrosion layer and no pitting. Specimen 2 and 4 had a similar corrosion surface as described by Angelucci et al. (1978). Coupon 4 was slightly more heavily corroded. Coupon 7 had almost no corrosion.

The coupons were rinsed and dried. Half of one side was cleaned with a glass bristle brush, to remove paratacamite, not removed by previous rinsing in deionised water. An attempt was made to remove light paratacamite corrosion only. Specimens 2 and 4 were the only coupons with a surface similar to archaeological material, after paratacamite was removed. The other specimens did not contain sufficient pitting. The areas where the paratacamite was removed, was separated from the rest of the corrosion by a line with a waterproof marker. The specimens were returned to 95% RH at ambient temperature. Two days later none of the coupons had developed chloride corrosion in the cleaned areas. It was thought that the glass bristle brush had removed too much chloride corrosion.

4.14.4 Discussion

Specimen 2 and 4 were judged to be most suitable for further testing. This indicated that a temperature around 50°C and a relative humidity of 55% caused pitting corrosion, as described by Angelucci et al. (1978). Lower RH resulted in a decreased corrosion rate. To increase the corrosion of coupons, the paste should be exposed to 50°C and 55%RH for more than 2 days. Any RH higher than 55% resulted in deliquescence. Kaolin did not prevent the cupric chloride acquiring more moisture. Visual examination suggested that kaolin did not interfere with the chloride corrosion, but had the advantage of making the paste easier to apply to the surface. It also allowed a more precise application, and a more even thickness.

These experiments demonstrate that Angelucci's et al. test results were not easily reproducible. Since unevenly chloride pitted coupons were not readily comparable when treated with a corrosion inhibitor, it was decided to abandon this line of experimental work with cupric chloride paste. The following corrosion tests were based on the findings with 1M cupric chloride in deionised water, as it resulted in a more reproducible testing procedure.

Chapter 5

Corrosion Inhibitor Evaluation Using Nantokite Covered Coupons

This chapter covers the main work undertaken to establish the effectiveness of previously selected inhibitors. Their performance was assessed using elevated relative humidity, at ambient temperature, and increased temperature. Experiments in this chapter were structured towards the identification of the most effective corrosion inhibitor, and to determine drawbacks in the application of specific inhibitors. The experiments conducted were as follows:

The determination of the amount of nantokite needed on copper coupons for further corrosion inhibitor testing.

1. Testing of various concentrations of corrosion inhibitors.
2. Long term corrosion testing of inhibitors.
3. Selection of the most effective corrosion inhibitors for further testing.
4. Long-term exposure to increasing relative humidity and temperature of selected inhibitors.

This corrosion testing procedure used in the following work, tries to simulate corrosion similar to the nantokite in corrosion pits.

5.1 Determination of the Amount of Nantokite needed on Copper Coupons for further Corrosion Inhibitor testing.

5.1.1 Introduction

In previous experiments in chapter 4 it was established that corrosion layers produced by cupric chloride paste were too uneven to be used for standardised testing of corrosion inhibitors. It was therefore decided to test cupric chloride solution for its ability to "grow" a more consistent, uniform thin layer of nantokite and cuprite on the surface of copper coupons. This treatment produced a "controlled" substrate on which to test corrosion inhibitors. These corroded coupons were immersed systematically into ethanol solutions containing selected corrosion inhibitors. The aim was to prevent further oxidation of nantokite to paratacamite. The inhibited surface was then tested for its effectiveness in accelerated corrosion tests. The specimens were evaluated by exposure to an extreme environment of 95%RH at ambient temperature.

5.1.2 Experimental Procedure

Two copper coupons were immersed for four days in a 1M solution of cupric chloride in deionised water. After removal from the copper chloride solution they were dried for 24 hours at 105°C. This procedure produced a layer of nantokite on the coupons. They were then treated with 0.01M solution of BTA in ethanol, or with 0.01M solution of AMT in ethanol. These concentrations were chosen in order to standardise the testing procedure and taken into account the low solubility of AMT. Both coupons were than exposed to 95% RH ambient temperature for 24 hours.

5.1.3 Experimental Observations and Discussion

After 24 hours exposure to 95% RH at ambient temperature, both coupons were completely covered in the characteristic green paratacamite corrosion. The oxidation reaction to paratacamite under these conditions had been previously confirmed with XRD. This clearly indicated that neither inhibitor was able to inhibit the reaction of nantokite to paratacamite when the coupon was exposed for four days to the cupric chloride solution. This led to the conclusion that the test was too severe, since all coupons failed, and that the exposure time to the cupric chloride solution had to be lowered. By reducing the exposure time, the thickness of nantokite should be reduced. The concept was that a thiner layer of nantokite should be more readily protected by the corrosion inhibitor. Thus, the same concentration or film thickness of inhibitor would more adequately cover the relatively thinner nantokite layer.

The following experiment was designed to determine a maximum exposure to cupric chloride solution needed to evaluate BTA and AMT corrosion inhibitors. The exposure time was increased in 24 hour steps using 1M cupric chloride solution. After 24, 48 and 72 hours, coupons were removed form the cupric chloride solution, rinsed, dried, and treated with inhibitor.

5.1.4 Experimental Procedure

Eight copper coupons were air-abraded with glass beads, ultrasonically degreased in acetone and dried under an infrared lamp at 50°C for 5 minutes. The coupons were immersed into 25 ml of a 1 M solution of cupric chloride.

Two coupons were removed after 24 hours from the cupric chloride solution, and rinsed 3 times for 20 minutes in 100 ml of deionised water. The coupons were dried at 105°C for 24 hours, to remove any moisture present in the corrosion layer. A small section was cut from one of the coupons. This section was required to confirm the presence of nantokite. Exposed to 95% RH, this section should react to form paratacamite. One of the corroded coupons was then immersed for 24 hours in 0.01M AMT, the other coupon in 0.01M BTA. Both inhibitors were applied in reagent grade ethanol. The identical amount of inhibitor was chosen arbitrarily to standardise the experiment. It was also thought that a low corrosion inhibitor concentration causes the smallest colour changes on an artefact.

5.1.5 Experimental Observations

After 24 hours exposure to the inhibitor solution, the AMT solution with the precorroded coupon, was discoloured light green, probably due to copper-inhibitor complex. Some of the nantokite from the coupon surface was complexed by the inhibitor into the inhibitor solution. In the bottom of the clear BTA solution there was very small amount of a green complex.

Both coupons were removed form the inhibitor solution and dried for 5 minutes at 50°C under an infrared lamp, to remove moisture. The dry coupons were then placed into a sealed acrylic box used as a humidity cabinet. The relative humidity was 95% at ambient temperature.

After 24 hours the untreated cut section developed the characteristic green corrosion product (paratacamite). The coupon treated with 0.01M BTA was also completely covered with paratacamite corrosion. The 0.01M AMT treated coupon had only one ~1 mm diameter spot of paratacamite corrosion on the whole surface.

After 1 month at 95% RH and ambient temperature, the BTA coupon had corroded slightly more, the AMT coupon had not changed its slightly yellow appearance.

5.1.6 Experimental Conclusion

This experiment showed that a nantokite film grown for one day, was thick enough to indicate variations in effectiveness of inhibiting corrosion with BTA and AMT at high RH. It was concluded that for the following experiments all coupons would be exposed for 24 hours to a 1M solution of cupric chloride.

The initial test clearly showed that BTA, at a 0.01M concentration in ethanol was not effective. The experimental results indicated that an increase in the BTA concentration improved corrosion inhibition. In the following experiments the original 3% by weight conservation treatment was applied. AMT seemed to slow the conversion from nantokite to paratacamite in a 0.01M concentration. Further investigation needs to be carried out to see if an increase in concentration increases corrosion protection. The increase in concentration could however result in increased discolouration. This is a "practical" objective for archaeological conservation.

The experimental results indicated that a one day exposure of copper coupons to a 1M solution of cupric chloride, produces sufficient nantokite to test corrosion inhibitors at 95%RH.

5.2 Corrosion Inhibition Efficiency of Inhibitors on Nantokite Covered Coupons

5.2.1 Introduction

The following experiment on prepared test coupons, was a preliminary step to evaluate the effectiveness of the eight chosen inhibitors in retarding further oxidation of nantokite corrosion to paratacamite. Chlorides are a major cause of deterioration in copper alloy archaeological artefacts. Initial experiments showed that the pre-treatment of copper coupons with cupric chloride was a suitable simulation procedure in the production of a nantokite corrosion layer on metallic copper. These nantokite covered coupons were then treated with corrosion inhibitors. The corrosion inhibition was then tested in extreme relative humidity of ~95%RH. The high RH was chosen, since it is thought that an inhibitor preventing corrosion at this RH will be protective at lower RH for a longer period of time.

Instead of using eight nantokite covered coupons to test each inhibitor as in the previous experiments, only three coupons were used to assess each inhibitor. It is suggested that 3 specimens is the lowest number that should be used, that will allow some confidence in the results. Repetition of the experiment, and choice of the number of specimens used in each experiment were based on recognised variables in the experimental procedure.

Three coupons were treated with the same inhibitor concentrations and under the same procedural steps. At this stage in the investigation repetitions were minimised to 3, since not all parameters recognised during the testing procedure could be exactly monitored. The temperature in the laboratory fluctuated from 16 to 24°C. The relative humidity in the laboratory fluctuated due to temperature changes and other activities. The pH of the deionised water used to rinse the coupons also varied, due to heavy use of the deioniser. Treating all inhibitors in the same experiment ensured that such parameters would be the same and others, like small time fluctuations during exposure to different environments, could be minimised. This was thought to improve the reproducibility of the experiments.

During the experimental procedure an attempt was made to determine the pH values of the various corrosion inhibitor solutions, before and after corrosion inhibition of test coupons. Low pH values could cause the deterioration of copper corrosion products. The pH measurements with a pH meter was not possible, due to the use of ethanol. The pH meter can only be used reliably in aqueous solutions. The titration of the inhibitor solution for pH determination, was beyond the scope of the work presented here.

For the following experiment the mean of the 3 samples was calculated. The mean and the standard deviation (s.d.) can be found in the appendix 4. However, due to the small population size, the standard deviation (s.d) could not be calculated accurately. Fletcher (1991) states that a sample size of 10 is very unreliable (Fletcher, 1991, 64). Furthermore, Mr.C.R.Orton, Reeder in Material and Data Science at the Institute of Archaeology, UCL, advised that descriptive statistics of a population of 3 are of little value (Orton, 1991, personal communication). Nevertheless, the standard deviation is reported in appendix 4, where the mean was used in other calculations.

According to Trabanelli (1970, 171) the effectiveness of an inhibitor in percentage of inhibition (P.I.) can be calculated from the formula below:

$$\text{P.I.}= \frac{\text{uninhibited corr. rate - inhibited corr. rate}}{\text{uninhibited corr. rate}} \times 100$$

The uninhibited corrosion rate is the weight of corrosion product after a unit time on a blank. The inhibited corrosion rate is the comparable ratio for the inhibited coupon. This formula was used to establish the corrosion rate of inhibited coupons in the following experiments. The calculations are based on the data presented in appendix 4. The mean of three samples was calculated. For example, the BTA inhibition percent was calculated as follows:

Weight increase in mg after 24 hour corrosion			
Blank	**Mean**	**BTA**	**Mean**
59.23		46.75	
60.18		51.17	
61.9	60.43	28.78	42.23

$$\frac{60.43-42.23}{60.43} x100 = 30.12\ \%\ \text{inhibition with in 24 hours}$$

Zero inhibition equates with complete corrosion equal to the blank. In this case 30% corrosion inhibition of BTA would be considered a poor performance.

5.2.2 Experimental Procedure

The following is a list of steps:

1. air-abrading of coupons with 47 micron glass beads
2. degreasing in an ultrasonic bath in 100 ml acetone
3. drying for 5 min at 50°C under infrared lamp, and 10 min. cooled in a silica-gel buffered polyethylene box
4. weighing to ±0.01 mg
5. immersion into 25 ml of a 1 M solution of cupric chloride in deionised water, 1 day at ambient temperature
6. rinsing in deionised water, 3 x 20 min in 100 ml
7. quick drying in 200 ml ethanol
8. drying for 5 min at 50°C under infrared lamp
9. exposure to 105°C in an oven for 30 min
10. 10 min cooling in a silica-gel buffered polyethylene box
11. weighing to ±0.01 mg
12. immersion in 25 ml ethanol containing 3% BTA, or 0.01 M inhibitor, for AP, AMT, DB, MBI, MBO, MBT, MP. 24 hours at ambient temperature, only partially covered so oxygen can enter

13. drying for 5 min at 50°C under infrared lamp
14. 10 min. cooling in a silica-gel buffered polyethylene box
15. exposure to 95% RH for 24 hours, at ambient temperature
16. weighing to ±0.01mg
17. observational assessment, photographic documentation
18. exposure to 95% RH for 24 hours, at ambient temperature
19. weighing to ±0.01 mg
20. visual assessment, verbal description of changes

5.2.3 Experimental Observations

After 24 hours in the cupric chloride solution, all coupons appeared to have had variable corrosion on the area close to the cupric chloride solution-air interface. This might have been due to a reduced oxygen content in the lower part of the flask. The areas that corroded variably during the cupric chloride immersion also behaved variably when the coupons were immersed into the inhibitor solutions. All coupons had a modified corrosion type in this region (Figure 5. 1). It appeared that the areas initially closed to solution-air interface were more corroded in the inhibitor solution, and had a small amount of nantokite after drying. This variation in corrosion was in a confined area, but on all coupons.

When removing the coupons from the inhibitor solution, it was observed that some were covered with a film deposit, probably inhibitor-copper complexes (Figure 5. 2). The deposit could protect the underlying polymer film, or cause increased corrosion due to a larger surface area and/or local cell reactions. It is well known that particles deposited on the surface of a metal increase the corrosion rate (Jones, 1992, 12).

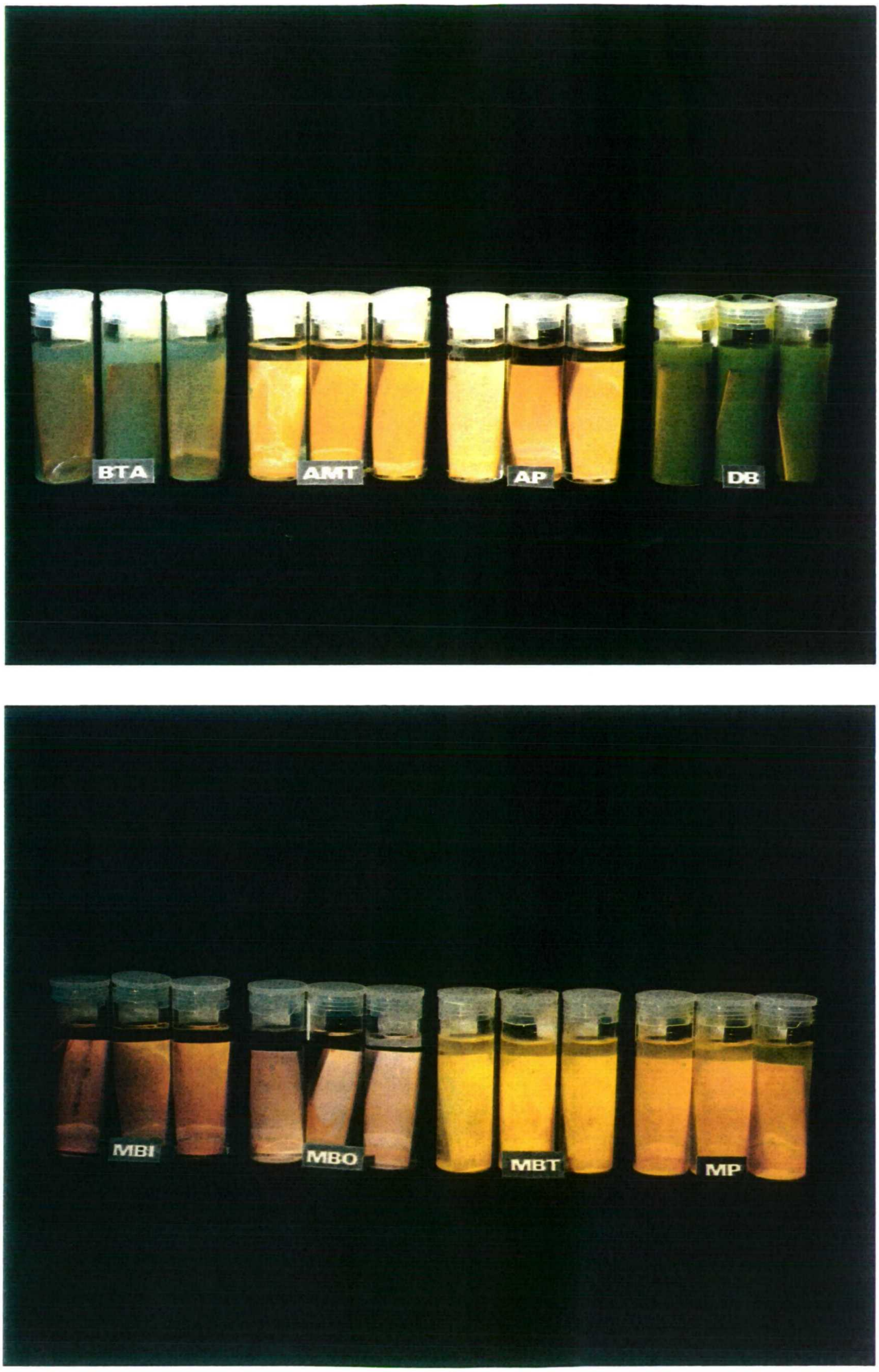


Figure 5. 1 Coupons after 24 hours in Corrosion Inhibitor.

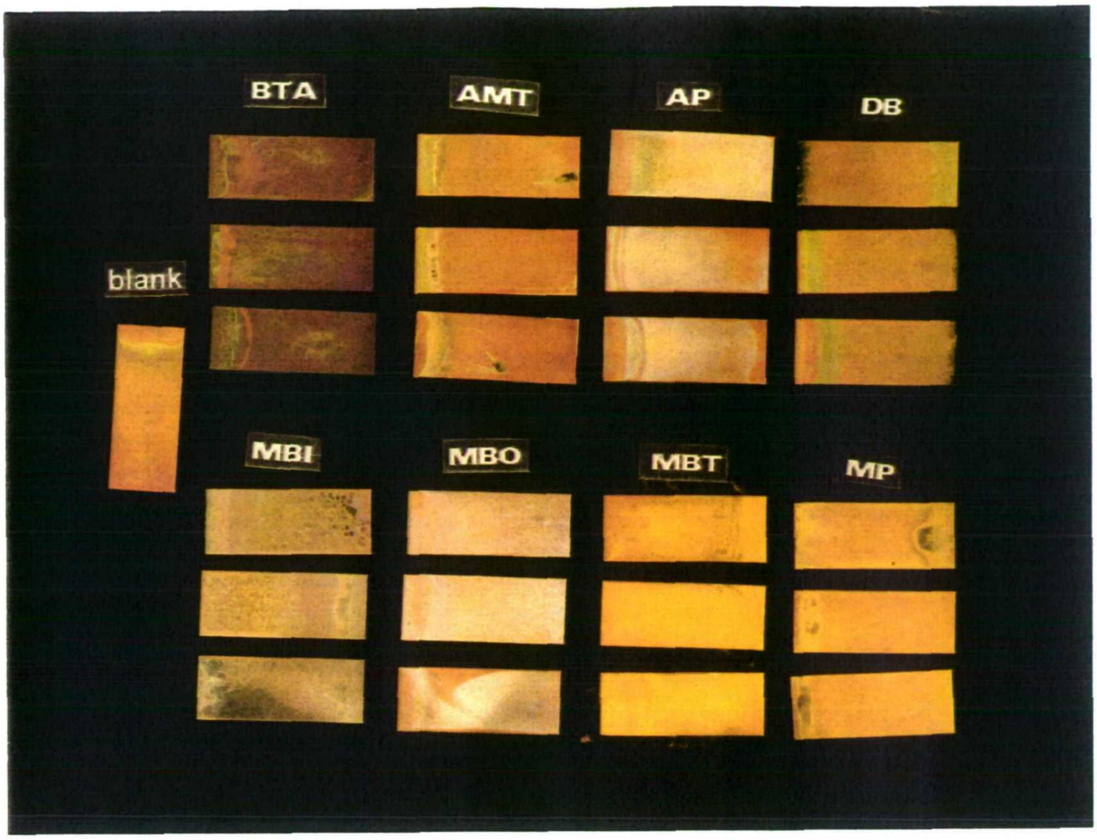


Figure 5. 2 Coupons after 24 hours Corrosion Inhibition and 5 minutes Drying at 50°C.

The coupons were rinsed for 1 minute in a 25 ml solution of reagent grade ethanol. However, not all deposits could be removed by immersing the coupons only into ethanol. One coupon from each group, heavily covered with complex deposit, was cleaned with an ethanol soaked cotton swab. A large amount of the deposit could be removed with the cotton swab. It was decided to only clean one coupon from each group, so the effect of swabbing could be assessed. The swabbing of the surface complicated uniform assessments of the experiment. Swabbing could not be standardised. However, removing the deposits can give an indication of the mechanical properties and stability of the polymer film. Normally archaeological objects are treated with an inhibitor and than rinsed with a solvent, and excess inhibitor is brushed off.

All colours were, wherever possible described according to the Munsell colour chart. The aim of colour matching was to find a treatment, which would cause the smallest changes in colour when compared to a nantokite covered coupon that was not treated with a corrosion inhibitor. Not all colours could be matched exactly, but were noted to the closest matching colour sample represented in the Munsell colour chart. In the following experiment a corroded coupon was used as a "blank". This coupon was corroded in the same way as all the other coupons, but was only dried, and not treated with any corrosion inhibitor. The colour of the untreated coupon represented its initial corrosion colour. The appropriate conservation treatment should result in a colour matching this surface, or the smallest degree of colour change whenever possible.

The experimental observations are divided into single groups, as this may be less confusing, with regard to their behaviour during the experiment. It also facilitates the accessibility of information of specific inhibitors between different experiments. Their colour change after 24 hours in corrosion inhibitor is given in Table 5. 2. The photos taken after corrosion inhibition and 95% RH corrosion are presented in Figure 5. 3. The weight changes after corrosion inhibition and exposure to 95% RH are given in Figure 5. 6.

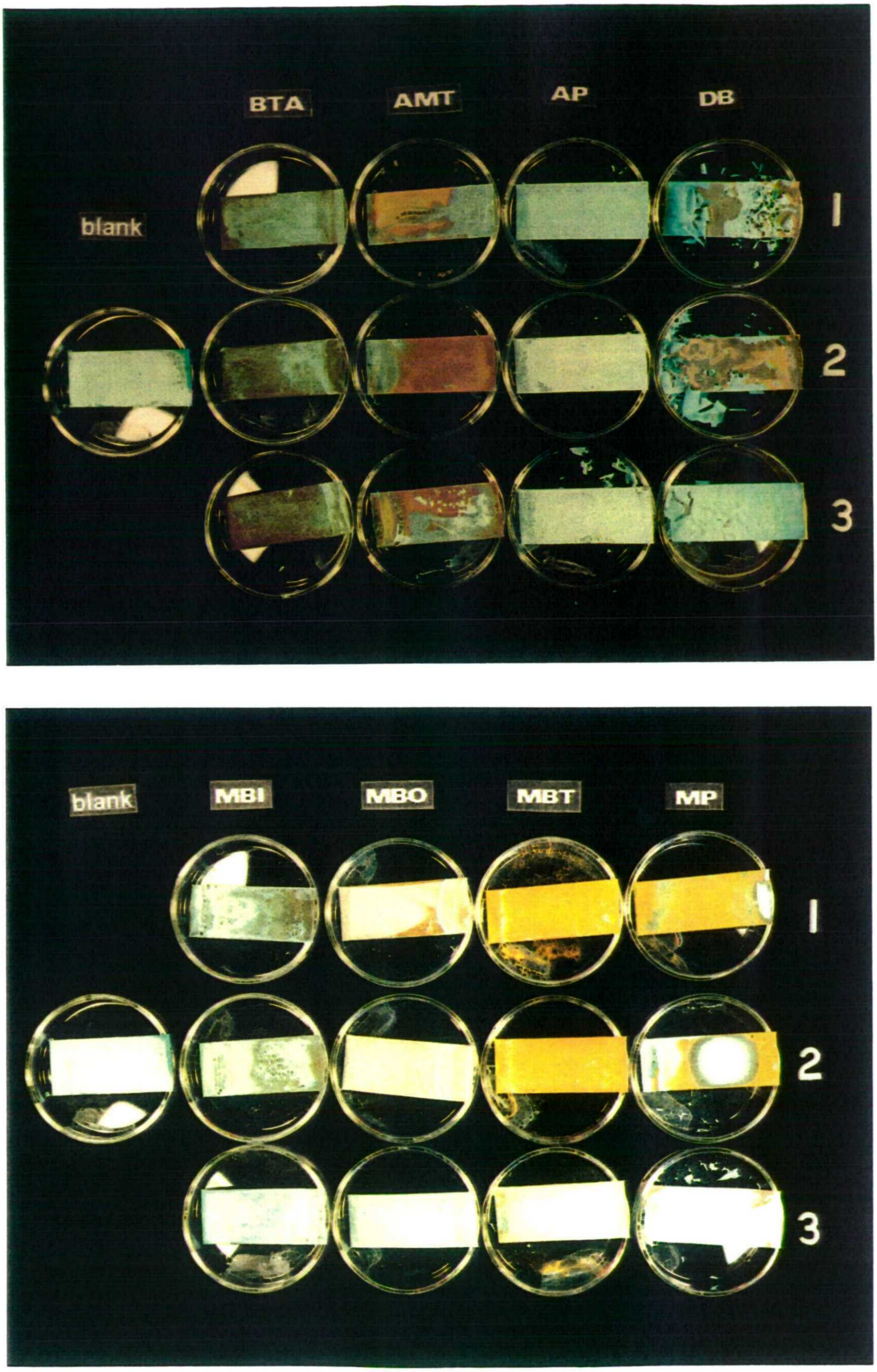


Figure 5. 3 Coupons after 24 hours at 95% RH Ambient Temperature.

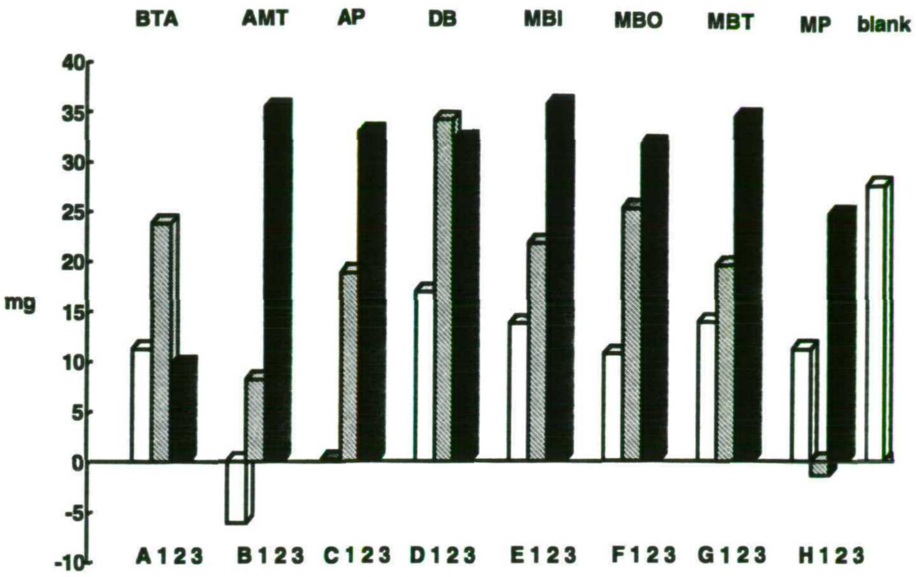


Figure 5. 4 Weight Change of Coupons after $CuCl_2$ Corrosion.

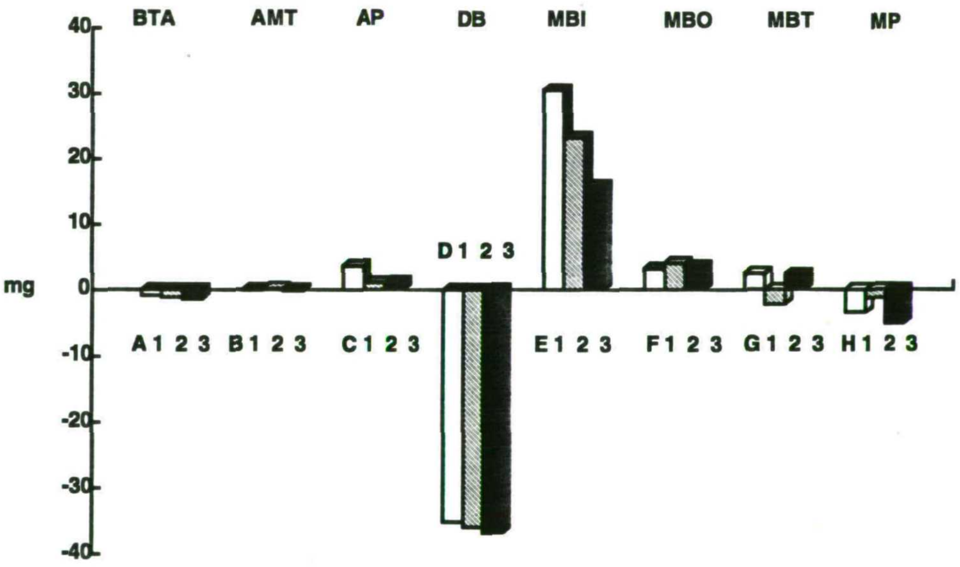


Figure 5. 5 Weight Changes of Coupons after Inhibitor Treatment. The Third Coupon in Each Series had Excess Inhibitor Removed.

	concentration	solution		concentration	solution
BTA	0.25 M	yellow complex	MBI	0.01 M	clear
AMT	0.01 M	clear, sediment of white complex	MBO	0.01 M	clear
AP	0.01 M	clear	MBT	0.01 M	clear yellow
DB	0.01 M	dark olive green	MP	0.01 M	clear strong yellow

Table 5. 1 Colour changes of Inhibitor Solutions after 24 hours treatment.

	Munsell notation	**Munsell colour names**	**Comments**
Blank	2.5YR 4.5/6	red	
BTA	10YR 3/6	dark yellowish brown	
AMT	7.5YR 4.5/6	strong brown	
AP	10Y 7/2	light grey brown	
DB	10YR 5.5/8	brownish yellow	
MBI	7.5R 5/1	grey	flaky complex film
MBO	10R 6/2	pale red	white deposit
MBT	7.5YR 7/8	reddish yellow	
MP	10YR 5/6	yellowish brown	

Table 5. 2 Munsell colour notations of coupons after corrosion inhibition

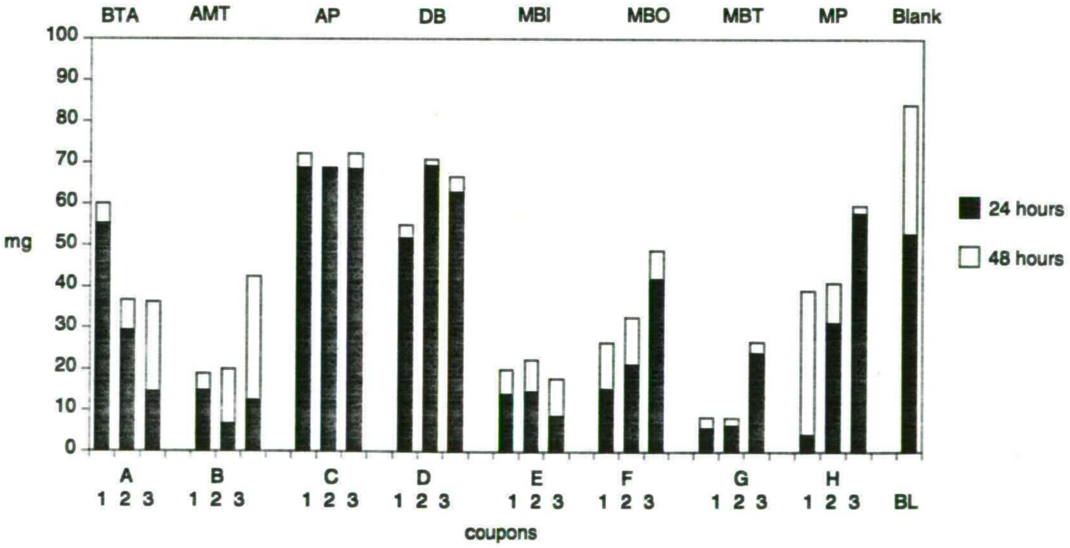


Figure 5. 6 Weight Changes of Coupons after 24 hours and 48 hours at 95%RH

BTA:

0.25M BTA was readily dissolved in 100ml ethanol, and resulted in a clear solution. The nantokite-covered coupons discoloured the solution to a dark olive green after 24 hours exposure. This was probably caused by a complex of copper and BTA. The colour of the corrosion inhibited coupons, after having been dried, was distinctively darker than the "blank" coupon. This colour change gives an indication as to the expected colour change in chloride containing areas on an archaeological copper artefact.

All coupons had paratacamite corrosion on their surface after 24 hours at 95% RH at ambient temperature. This visual result was confirmed gravimetrically, by an increase in weight. Coupon A3 seemed to have a smaller amount of paratacamite corrosion than the other two BTA treated coupons (A1 and A2, see Figure 5. 6). The paratacamite coverage is as follows A1 > A2 > A3. This suggests that this experiment had a lower than expected reproducibility.

After 48 hours all three coupons seemed to have an even amount of corrosion on their surface when they were visually examined. This was confirmed gravimetrically, A1 still had a larger amount of corrosion than the other two coupons.

AMT:

The inhibitor dissolved completely in ethanol after 15 minutes stirring. AMT does not dissolve as readily as BTA. There was a small amount of complex suspended in the inhibitor solution after 24 hours exposure of the nantokite covered coupons. Some nantokite on coupons B1 and B3 was complexed into the inhibitor solution. This missing nantokite caused a weight loss of the coupons. Coupon B2 had no surface corrosion, but showed a small weight increase, probably due to inhibitor adsorbing onto the surface. The areas previously corroded in the inhibitor solution flaked off after being dried at 50°C.

None of the coupons was free of corrosion after 24 Hours at 95% RH at ambient temperature. The corrosion protection of the AMT inhibited coupons was B2>B3>B1. The regions which had a different corrosion at the beginning of their exposure to 95%RH were heavily corroded. These were the ends which had been either in the top of the cupric chloride solution, or areas handled with tweezers while immersing into inhibitor solution.

A further 48 hours at 95% RH caused an increase in paratacamite corrosion. Coupon B3 suffered a large increase in corrosion. This variation shows the low rate of reproducibility of the experiment. The uncorroded areas were similar to the nantokite surface of the blank coupon not previously treated with a corrosion inhibitor.

AP:

The inhibitor dissolved in ethanol and the solution was clear. After 24 hours, the inhibitor solution had not changed its colour when in contact with the precorroded coupon. After removing the coupons and drying them, they were covered in a white surface deposit. The deposit was cleaned off coupon C3 with ethanol. Ethanol removed the largest amount of the white complex, but still left a slight white deposit on the coupon. The removal of excess BTA after treatment is common practice. The object would be rinsed, and swabbed with a cotton swab wetted with ethanol.

After 24 hours at 95% RH, all three coupons were evenly covered in paratacamite. AP did not notably inhibit the oxidation of nantokite to paratacamite. After 48 hours at 95% RH, corrosion increased. The weight loss in C2 was due to a minute loss of corrosion products.

DB:

The inhibitor dissolved completely in ethanol. After 24 hours in contact with the nantokite covered coupons, the solution was very heavily discoloured. The colour was a dark olive-green. This strong colour change in the inhibitor solution is reflected in the high amount of weight loss of all DB treated coupons, due to the dissolution of parts of the nantokite surface into the inhibitor solution. All three copper coupons had a thin black discolouration on the lower end of the coupon after 24 hours. This black line could be removed with ethanol swabs. After drying, the coupons were covered in a yellow deposit On coupon D3 the deposit was easily removed with a cotton wool swab and ethanol.

After 24 hours at 95% RH, Dimethylbenzimidazole did not appear to have inhibited the corrosion of nantokite to paratacamite. The surface of all three coupons was completely covered in paratacamite. After drying some of the paratacamite fell off. This clearly indicates that Dimethylbenzimidazole did not protect nantokite from further oxidation at a 95% RH. After 48 hours the appearance did not change.

MBI:

The inhibitor dissolved in ethanol to a clear solution. The solution was slightly discoloured after 24 hours exposure to the nantokite covered coupon. There was a complex deposit on the bottom of the flask. After drying half of the surfaces of the coupons were covered in a shrivelled surface film. The film was easily disrupted and fell off when dry. The film was easily removed with a cotton swab and ethanol.

When assessing the coupons after 24 hours exposure to 95% RH, E1 and E2 were only slightly corroded. However they had a higher weight increase than E3. This might be due to a hydration of the shrivelled uneven complex film. It seemed that the area with the shrivelled surface film did not contain as much paratacamite as E3, where the surface film was removed. The film on E1 and E2 contained enough MBI to protect the underlying nantokite from further visible corrosion. The coupon E3, when cleaned with ethanol, was heavily corroded. However E3 had a smaller weight increase than E1 and E2.

After 48 hours, all coupons had a larger amount of paratacamite corrosion. MBI seemed not to be useful as a corrosion inhibitor because the protective surface film formed on nantokite and could be easily removed with an ethanol moistened cotton swab.

MBO:

The inhibitor dissolved completely in ethanol and discoloured the solution to a slightly yellow colour. After 24 hours, the colour of the solution in contact with the pre-treated coupons had not changed much. There was a small amount of copper-inhibitor complex on the bottom of the flask. When the coupons were removed from the solution and dried, there was a white deposit on their surface.

After 24 hours at 95% RH, all three coupons were covered in corrosion. Coupon F3, previously cleaned with an ethanol swab, was more heavily corroded, indicating that the inhibiting film was soluble in ethanol, or was not well adhered to the underlying nantokite. This indicated that the nantokite-MBO film was not stable enough to be suitable for the corrosion inhibition of archaeological artefacts. After 48 hours, all coupons were covered in paratacamite and were evenly corroded.

MBT:

The inhibitor was completely soluble at 0.01M concentration in ethanol. A small amount of copper-inhibitor complex had formed in the bottom of the flask, after 24 hours exposure to a nantokite covered copper coupon.

After 24 hours at 95% RH, only G3 was corroded. This was due to the removal of the corrosion inhibiting layer with ethanol swabs. G1 and G2 were only slightly corroded. This did not change after 48 hours exposure to 95% RH. Coupons treated with MBT were more stable in their corrosion inhibition over 48 hours than all the other inhibitors. A disadvantage with MBT treatment was that it caused the coupon surface to become an unsightly reddish yellow colour. The discoloration, and the easy removable inhibitor film made the inhibitor unsuitable for conservation. If the deposit was not damaged or partially removed, MBT would have been the most powerful inhibitor in this concentration.

MP:

The inhibitor solution discoloured and formed a strong yellow colour. The inhibitor did not completely dissolve in ethanol, even after 30 minutes stirring. The solution was still a strong yellow colour after 24 hours exposure to the coupon. There was a large amount of copper-inhibitor complex floating in the inhibitor solution.

After 24 hours at 95% RH and ambient temperature, all three coupons were corroding. The coupon H1 was the coupon with the smallest amount of paratacamite corrosion in the whole experiment. H2 was heavily corroded on one side. The coupon H3 which was previously cleaned with an ethanol swab, was heavily corroded, and seemed not to be protected by the corrosion inhibitor.

After 48 hours exposure to 95% RH, all three coupons corroded evenly, resulting in an even paratacamite coverage.

5.2.4 Discussion

The experiment did not produce entirely conclusive results. None of the inhibitors completely prevented the oxidation of nantokite to paratacamite at 95% RH. The inhibitors can be, generally, divided into two major groups, although there is some overlap:

1) Inhibitors complexing large amounts of nantokite into solution.

2) Inhibitors forming a surface film

The first group is observed to complex nantokite partially into the inhibitor solution. The inhibitor solution of BTA is distinctly green coloured after 24 hours in contact with the copper coupons covered in nantokite. After 24 hours, DB is even more discoloured than BTA. The dramatic weight loss after treatment with DB suggests that this compound complexes large amounts of nantokite into solution. It is suggested that DB could be used as a pre-treatment of heavily chloride infested copper artefacts. During exposure to 95% RH at ambient temperature, DB has shown not to form a protective inhibitor-copper polymer film over the surface of nantokite. This suggests that successive treatments with DB could complex significant amounts of nantokite into the DB solution. The slight discoloration of the inhibitor complex deposit on the surface can be removed by swabbing with ethanol. The following points could be further investigated to reach a conclusive proposal for further use of DB as a chloride removing agent on copper artefacts.

1. Does DB form a more protective film after several treatments?
2. Is DB more effective than sodium sesquicarbonate in complexing copper chlorides into solution?
3. Is the coloured complex completely removable, and does it interfere with the appearance of the surface?
4. Are other copper minerals adversely affected by the treatment with the compound, such as their dissolution or their discoloration?
5. Is DB forming new minerals on the surface of copper artefacts, such as in the case of sodium sesquicarbonate?

These questions were considered beyond the range of this investigation in testing corrosion inhibitors.

The second group of inhibitors were film forming inhibitors. The selected inhibitors were known to form complex films on clean copper specimens. Parallels were drawn to nantokite covered coupons treated with inhibitors. Several selected inhibitors showed lower corrosion rates at a 95% RH. A prime example was AMT: there was a small weight increase, probably due to the inhibitor-copper film forming. This group of coupons that were exposed to a 95% RH, had a lower corrosion rate when compared with the untreated copper coupons. The increase in weight, after the inhibitor treatment, could also have been due to an initial increase in the corrosion rate, when the coupons were immersed into specific inhibitors. This would be an explanation for the dominant weight increase of coupons treated with MBI. The model proposed is that significant amounts of copper go into solution and form a thicker polymer film. The thickness of the polymer film does not necessarily indicate a higher efficiency in preventing further oxidation, since such thick films can be porous, as in case of BTA films formed at low pH (Fang, 1986, 485). However, MBI has shown to be one of the more effective inhibitors, and after 48 hours, is more stable in its corrosion protection than other inhibitors tested, such as MBO, MP and DB. The above described pealing surface film, formed after treatment with MBI, does not seem to be the major factor in protecting the surface from further corrosion. This shrivelled film seems to support a model for a quickly grown thick porous copper-inhibitor complex polymer film. As soon as the film was dried at 50^{O}C, the ethanol in the film was lost and it started to contract, exposing reactive nantokite below and leaving voids between the polymer film and underlying nantokite. Despite the fact that the coupon E3, previously cleaned with ethanol swabs, was visually more corroded than E1 and E2, E3 had a lower increase in weight after 24 hours, and 48 hours at 95%

RH, when comparing its weight with E1 and E2. This suggests a penetration of MBI into the porous nantokite structure.

The drying and shrinking of the film after the inhibitor treatment, might cause damage to the partially inhibited nantokite underneath the film, by physically pulling it off. It is suggested that the polymer film extends into the surface, and does not only remain as a skin on top of the nantokite. Coupon E3 had the tendency to decrease its protection rate after 48 hours. The flaky complex film on coupon E1 and E2, slowed down corrosion after 48 hours, when compared to E3. This might have been due to a physical barrier of the film on E1 and E2. Paratacamite seemed to have developed in the gaps between flakes, suggesting that the film flakes retarded further penetration of moisture and oxygen down to the nantokite.

Removable polymer films were observed on coupons treated with MBO, MBT and MP where the complex film was removed with ethanol swabs. These coupons had a much higher corrosion rate than the undisturbed coupons F-G and 1 and 2.

The most puzzling compound was MBT. MBT formed a strongly coloured yellow powdery complex on the surface of the inhibitor treated coupons. However, this powder was easily removed. The coupon (G3) freed of the complexed yellow powder, was only slightly discoloured when compared with the blank. The complex powder appeared to be very efficient in inhibiting further corrosion at 95% RH. The coupons G1 and 2, treated with MBT, had the lowest increase in weight, due to further corrosion when exposed for 48 hours to 95% RH. Coupon G3, ethanol swabbed and exposed to 95% RH, had a larger weight increase than G1 and G2, but did not have a large increase in weight when compared with coupons treated with the other inhibitors.

During the run of experiments, it was possible to remove parts or all of the protecting corrosion inhibiting films on MBI, MBO, MBT and MP inhibited coupons. It was not possible, however, to control the action of swabbing with an ethanol soaked cotton swab. The amount of ethanol, the pressure, and the contact time with the cotton swab could not be standardised, since it is a manual task. This part of the process was found to be essential. Objects treated with BTA are normally rinsed after exposure to the corrosion inhibiting solution, to prevent the recrystallisation of BTA on the surface and in cracks. The excess, unreacted crystals are easily visible. The rinsing is normally enhanced by swabbing or brushing the surface with a soft brush. During the experiment, it was found that swabbing with ethanol removes excess inhibitor. This inhibitor was, in many cases, complexed with copper ions and discoloured the surface, such as in the case of AP, DB, MBI, MBO, MBT and MP. The discoloration on the BTA treated coupons could not be removed easily. The complex film darkened the BTA coupons extensively (Figure 5. 2). AMT was the only inhibitor which did not greatly affect the colour of the coupons.

In a visual qualitative assessment, the corrosion inhibiting efficiency to prevent the oxidation of nantokite to paratacamite was as follows: AMT > BTA > AP, DB, MBI, MBO, MBT, MP, when the complex film was removed. If the corrosion inhibiting film was not swabbed off with ethanol. MBT was the most protective inhibitor of the selected corrosion inhibitors, but also discoloured most. The only other inhibitor more effective than AMT was MP, but the film could also be removed by ethanol and caused a slight discoloration. AP and DB clearly showed that they were, not effective in inhibiting further corrosion.

5.3 Testing of Various Concentrations of Corrosion Inhibitors

5.3.1 Introduction

The previous series of experiments indicated a practical procedure that may be used to assess corrosion inhibition of selected inhibitor compounds. The subsequent experiments were designed to investigate further at what concentration specific corrosion inhibitors exhibit corrosion inhibition on nantokite covered substrates.

Corrosion inhibitors for copper and copper alloys are applied to prevent corrosion in changing environments. Different environments might require different amounts of inhibitors. It is not known to what extent the inhibitors, chosen in this research prevent corrosion on corroded copper and copper alloy archaeological artefacts because they were generally chosen on the basics of their performance under industrial conditions. In the case of BTA, a 3% by weight solution is generally applied in the conservation of corroded copper alloy artefacts. Madsen (1971, 120) suggested an increase of up to 30% by weight for artefacts that were difficult to stabilise. To be able to compare different inhibitor compounds, the most suitable concentration has to be chosen relative to other dependent variables, such as colour change. In the case of BTA, it was decided to apply it in the concentration of 3% by weight in reagent grade ethanol, since this is the standard conservation procedure. The concentration of 3% by weight BTA is equivalent to 29.78g/L at room temperature, or ~0.25M/L. A molar unit was chosen since it facilitates a comparison with other industrial studies already undertaken, generally using molar weight.

Industrial studies on corrosion inhibitors for copper and copper alloys suggest various concentrations from 0.0001M (MBT, Musiani et al., 1987,191) to 0.01 M (Horner, 1982b,455). The literature generally suggests 0.01M of inhibitor in different industrial service environments. Comparative studies such as Horner (1982,455;1985,547), and Musiani et al. (1987,191) have used these concentrations to compare compounds such as BTA, AP, MBO, MBI, MBT, MP, on clean, uncorroded copper specimens.

With respect to the task of the conservation of copper artefacts, it has to be emphasised that the inhibitors are applied to corroded surfaces. The industrial studies usually completely ignore that fact, that in service environments, the corrosion inhibitor has not only the task of forming a complex structure on a clean copper surface, but also on corroded areas as well. Furthermore, in industrial trials, corrosion is usually stripped off, to prepare for inhibitor treatment.

For testing in this research project, it was decided to apply only two different concentrations of inhibitors to corroded copper coupons. The test coupons were pre-treated with cupric chloride, to form a nantokite layer. The aim of two different inhibitor concentrations in ethanol, was to determine the protective strength of the inhibitor complex film formed on the surface of the artificially formed nantokite layer. The lower concentration was 0.01M of inhibitor. This concentration was chosen since it is the most widely applied concentration on clean copper surfaces in industrial service tests.

A higher inhibitor concentration was selected to account for the acidity of nantokite corrosion, 3.5-4 pH according to Scott (1990,197). Higher concentrations of inhibitor might also be of advantage with regard to the porosity of the nantokite surface. In the case of an archaeological artefact, the porosity of the patina is variable and unknown. It can only be estimated subjectively without resource to further porosity testing. An excess of inhibitor might be deposited in the porous surface and react as a buffer material. As such, it might repair damage in the polymer film at a later stage.

The maximum concentration is mainly governed by the solubility of the corrosion inhibitor. Neither chemical suppliers nor industrial literature provided solubility data of the selected inhibitors in ethanol. The solubility in water is only known in the case of BTA and AMT. BTA is readily soluble in ethanol and in water. The solubility of AMT was determined to be 9g/L IMS at room temperature, and 12g/L at 35°C: the higher the temperature the more AMT was dissolved (Faltermeier, 1992, 13). The concentration of 3% by weight BTA in ethanol was calculated to be ~0.25M/L. In the following experiment it was decided to apply a maximum of 0.25M/L concentration of corrosion inhibitors in ethanol to nantokite covered coupons. Such a concentration enabled the comparison of different inhibitors with the standard 3% BTA treatment. A concentration of 0.25M/L would also indicate if an inhibitor was more effective at a higher concentration. If an inhibitor was not soluble up to 0.25M/L, it was applied as a saturated solution. Should an inhibitor prove to fail at a concentration of 0.25M/L, a decision was made whether the concentration should be further increased, depending on if it was thought to be potentially useful or not.

5.3.2 Experimental Procedure at 0.25M/L Concentration of Inhibitors in Ethanol

The first experimental set was carried out using a concentration of 0.25 M/L of inhibitor in ethanol. Three nantokite covered coupons were treated with the same inhibitor solution. The treatment was applied as follows, according to the inhibitor testing procedure established in the previous chapter.

Following is a list of steps:

1. air-abrading of coupons with 47 micron glass beads
2. degreasing in ultrasonic bath in 100 ml acetone
3. drying for 5 min at 50°C under infrared lamp, and 10 min cooling in a silica-gel buffered polyethylene box
4. weighing to ±0.01 mg
5. immersion into 25 ml of a 1 M solution of cupric chloride in deionised water for 1 day at ambient temperature
6. rinsing in deionised water 3 x 20 min, in 100 ml
7. quick drying in 200 ml ethanol
8. drying for 5 min at 50°C under infrared lamp
9. exposure to 105°C in oven for 30 min
10. 10 min cooled in silica-gel buffered polyethylene box
11. weighing to ±0.01 mg
12. immersion in 25 ml ethanol containing inhibitor (concentrations are in the table below). 24 hours at ambient temperature, only slightly covered so oxygen can enter
13. drying for 5 min at 50°C under infrared lamp
14. 10 min. cooling in silica-gel buffered polyethylene box
15. exposure to 95% relative humidity for 24 hours, at ambient temperature
16. weighing to ±0.01mg
17. observational assessment, photographic documentation
18. exposure to 95% relative humidity for 24 hours, at ambient temperature
19. weighing to ±0.01 mg
20. visual assessment, verbal description of changes

BTA	0.25 M	MBI	saturated solution
AMT	0.01 M	MBO	0.25 M
AP	0.25 M	MBT	0.25 M
DB	0.25 M	MP	saturated solution

Table 5. 3 Corrosion Inhibitor Concentration

5.3.3 Experimental Observations

All coupons had a distinctly different corrosion rates in the cupric chloride solution. This was observed on the lower part of the coupons, situated near the bottom of the flask. The dried coupons were weighed after the nantokite layer was formed. A wide range of corrosion weights was established (Figure 5. 7).

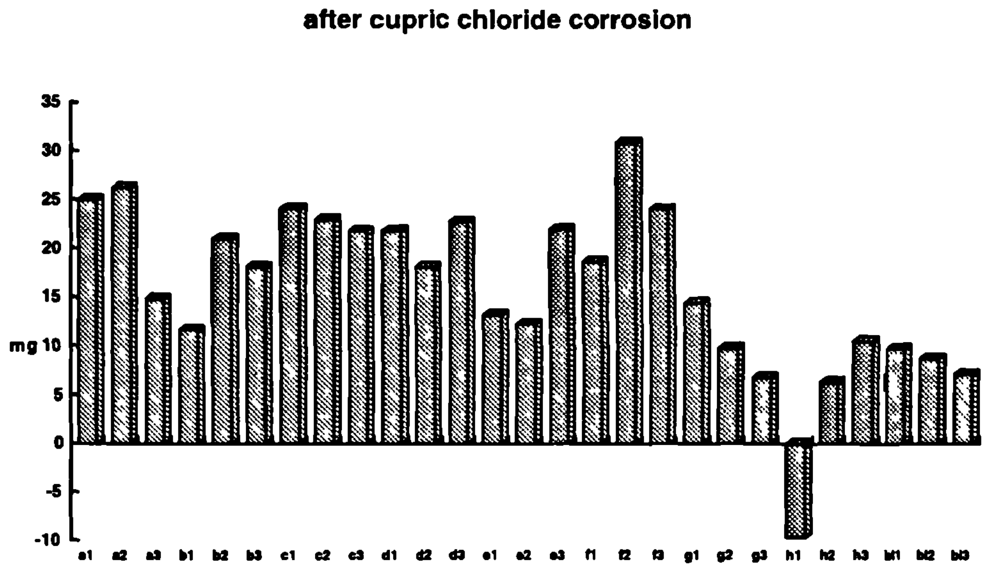


Figure 5. 7 Weight Change after Cupric Chloride Corrosion.

The lowest weight increase due to the nantokite formation, was 6.48mg (h2). The largest increase was 30.95mg (f2). These data was later used to assess variations in corrosion inhibition at 95% RH. The corrosion rate after the cupric chloride treatments varied significantly. Coupon h1 had a loss in weight after cupric chloride corrosion, which was thought to be due to a measurement error. This coupon was still used in the rest of the experiment since the most relevant corrosion changes occur after the inhibitor treatment. In the case of h2, the small weight increase during $CuCl_2$ immersion could explain the low paratacamite contents of coupon h2 after inhibition with MP, after 24 hour exposure to 95% RH and 48 hours at 95% RH (Figure 5. 8). Coupons h1 and h3 had a much higher weight due to paratacamite formation. Photographic records of the coupons after corrosion inhibition and 95%RH corrosion can be found in Figure 5. 9 and Figure 5. 11.

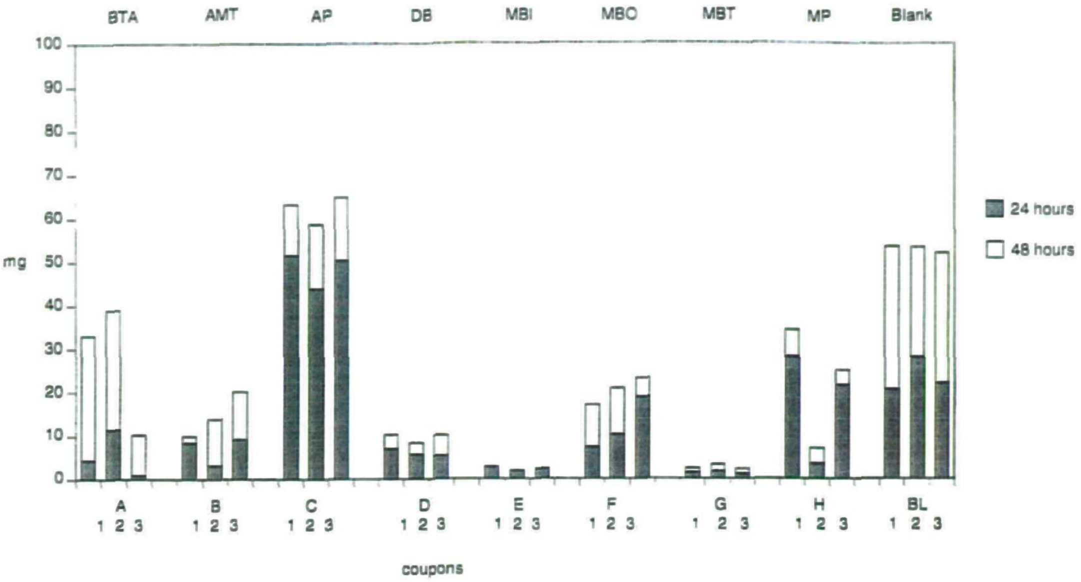


Figure 5. 8 Weight Change after 24 hours and 48 hours at 95%RH.

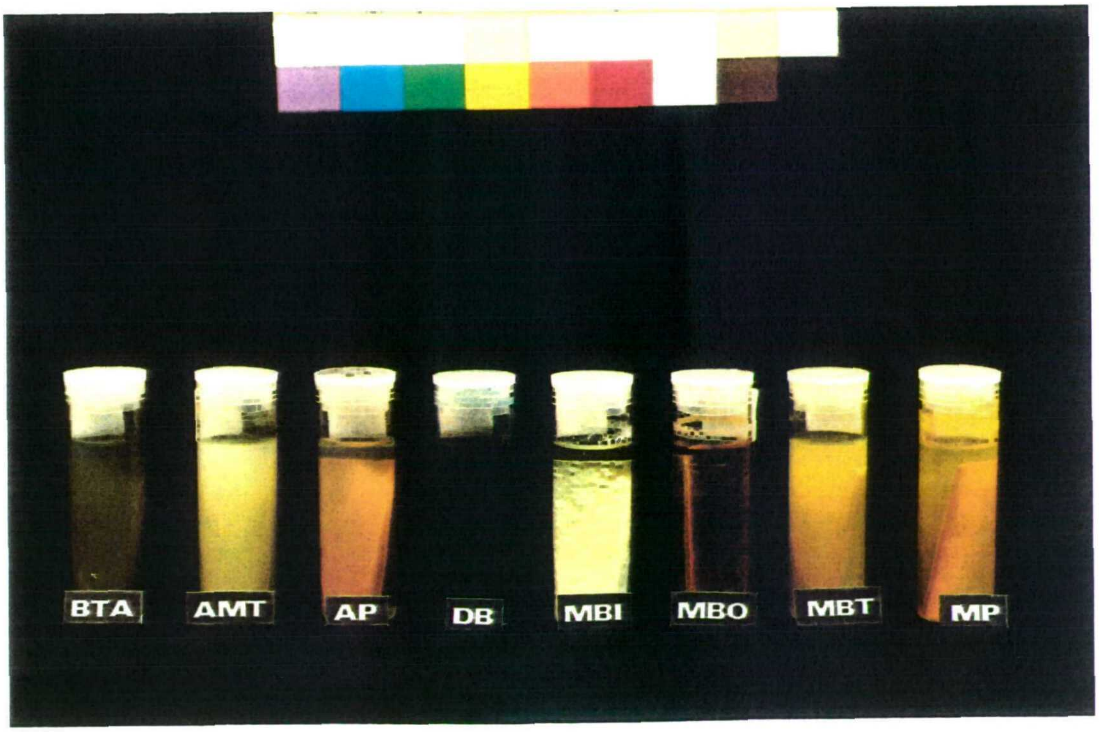


Figure 5. 9 Coupons after 24 hours in Corrosion Inhibitors.

Preparation of corrosion inhibitor solution:

The corrosion inhibitor solutions were prepared from 100 ml reagent grade ethanol added to 0.25M/L powdered inhibitor. BTA dissolved immediately. The other solutions were covered and heated on a hot plate to 50°C in a fume cupboard, to facilitate dissolution. AMT was used in 0.01M concentration. AP dissolved after 2 minutes stirring with an electrical stirrer. DB had to be stirred for 20 minutes before it dissolved completely. MBO and MBT dissolved completely after 5 minutes. MBI dissolved at 50°C, but crystallised out after cooling to room temperature. MBI and MP would not dissolve completely and were filtered after cooling to room temperature. The filtered solutions were applied as saturated solutions to the nantokite covered coupons. The residues in the dried filter paper had an increased weight when compared with the initial amount of inhibitor dissolved. This is probably due to a hydration of the compound.

Some of the inhibitors formed a coloured solution in ethanol. This in turn could be of significance to conservation. The coloured inhibitor containing solution might deposit a coloured material on the surface of an artefact and cause discoloration. The further discoloration and the concentration are stated below:

BTA	0.25 M	clear	MBI	saturated solution	clear
AMT	0.01 M	clear	MBO	0.25 M	clear brown
AP	0.25 M	opaque white	MBT	0.25 M	clear yellow
DB	0.25 M	clear yellow	MP	saturated solution	clear strong yellow

Table 5. 4 Colour Changes of Inhibitor Solutions Before Immersion of Nantokite Covered Coupons.

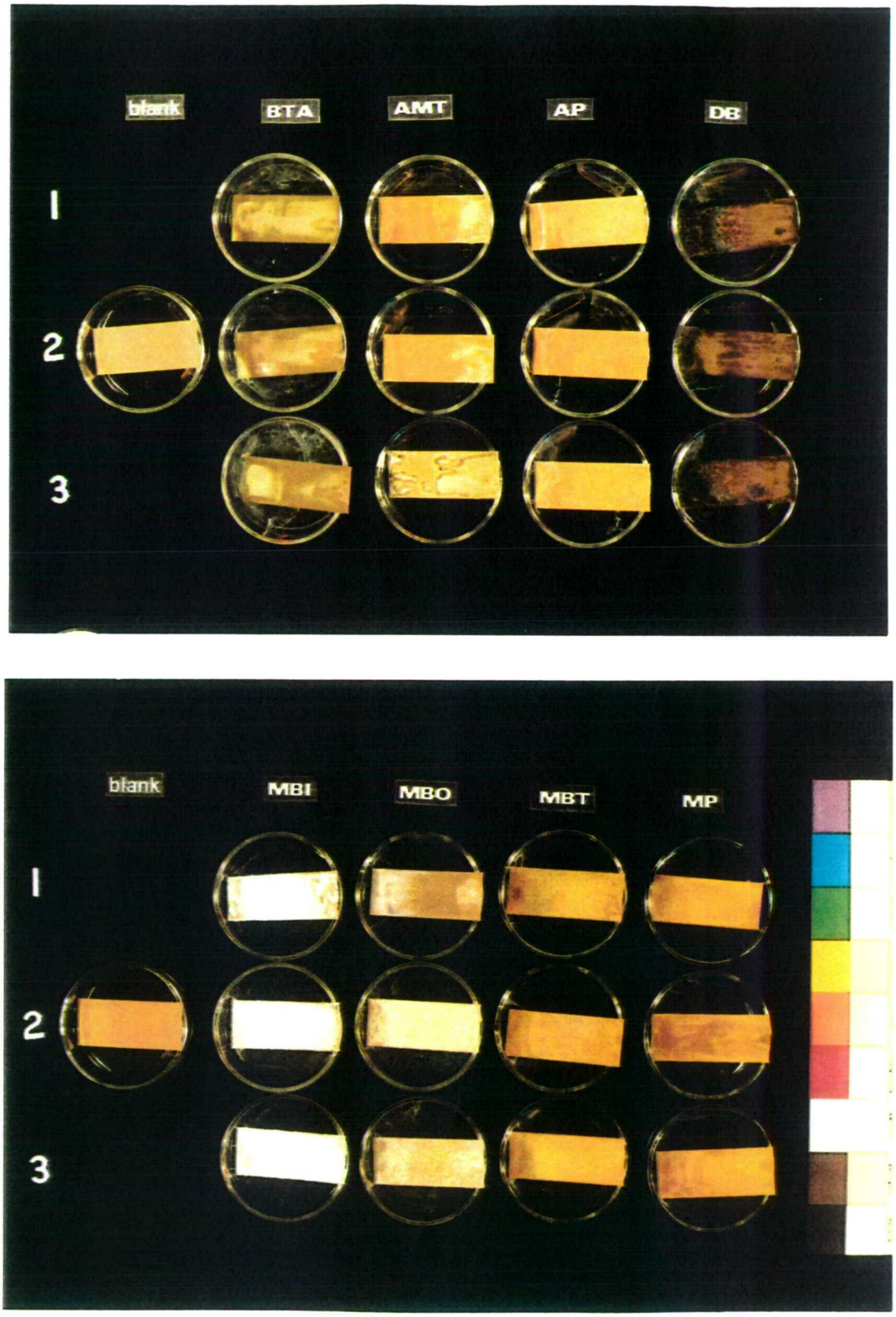


Figure 5. 10 Coupons after 24 hours in Corrosion Inhibitor Solution and Dried 5 minutes at 50°C.

The nantokite covered coupons were immersed in the inhibitor solutions. After 24 hours at room temperature, some of the solutions showed distinct colour changes. These colour changes were thought to be due to copper ions going into solution and forming a complex with the inhibitor (Figure 5. 9). The discoloured coupons after corrosion inhibition can be seen in Figure 5. 10.

	Munsell notation	**Munsell colour names**	**Comments**
Blank	2.5YR 3.5/6	red	
BTA	7.5YR 3.5/2	dark brown	
AMT	2.5YR 3.5/6	red	
AP	2.5 YR 3.5/6	red	
DB	not found	not found	black brown powdery film
MBI	not found	not found	white film
MBO	not found	not found	white green crystallised film
MBT	7.5YR 5/6	strong brown	
MP	5YR 4.5/7	yellowish red	

Table 5. 5 Munsell Colour Notations After Corrosion Inhibition.

ambient temperature 95%RH	**concentration in moles**	**inhibition %**	**inhibition %**	**comments**
		24 hours	**48 hours**	
BTA	0.25	76	48	
AMT	0.01	71	72	
AP	0.25	0	0	
DB	0.25	75	82	film
MBI	saturated	91	96	film
MBO	0.25	49	62	film
MBT	0.25	94	95	
MP	sat	25	58	

Table 5. 6 Corrosion Protection after 24 and 48 hours at 95% RH Ambient Temperature

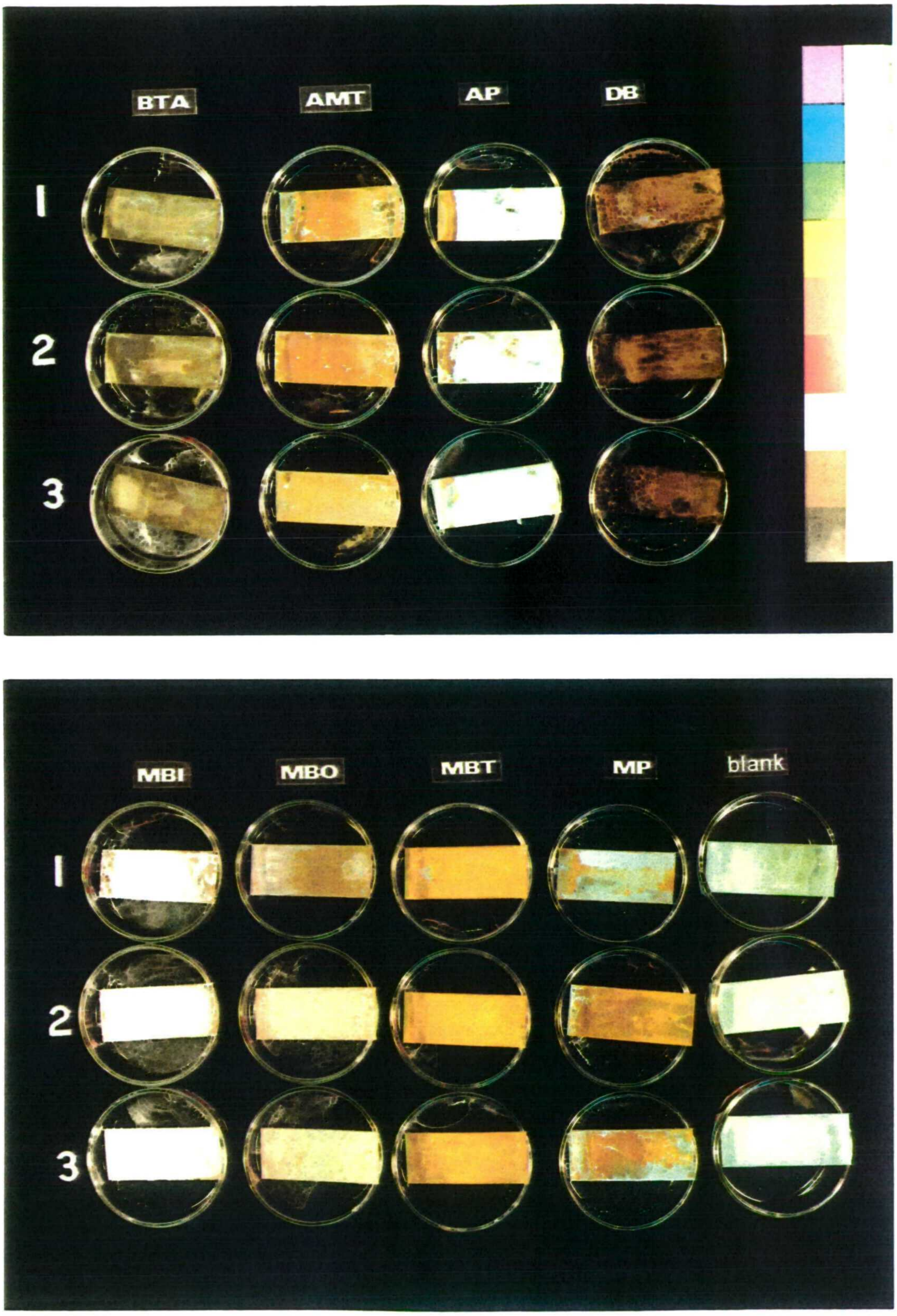


Figure 5. 11 Coupons after 24 hours at 95% RH and Ambient Temperature.

The colours of the coupons after the corrosion inhibitor treatment are listed above in Table 5. 5. The colour change of the coupons are not as relevant as the formation of a disfiguring inhibitor copper polymer film, during corrosion inhibition treatment. The film formation of DB, MBI and MBO is very important since it might reflect the disfiguration of nantokite areas on an artefact. The coupons after exposure to 95%RH at ambient temperature can be seen in Figure 5. 11.

BTA:

The solution had a dark olive green colour, and was still transparent. The dried coupons had an even weight increase due to inhibitor treatment. After 24 hours at 95%RH ambient temperature the coupon was 76% protected. This decreased to 48% after 48 hours.

AMT:

The solution of this compound was clear but B3 had complexed particles floating in the clear, slightly green discoloured solution. Nantokite had been complexed into the inhibitor solution, during corrosion inhibition on all three coupons. This could be clearly seen on the photograph Figure 5. 9, indicating the complexing action of AMT by dissolving nantokite into the inhibitor solution. Coupon b3 with the large amount of complexed particles in the inhibitor solution, was more corroded than b1 and b2. B3 had large areas of nantokite dissolved from its surface, resulting in a patchy appearance. This dissolution was reflected in weight loss after inhibition (-6.66mg, also see Figure 5. 12).

This confirms Ganorkar's et al.(1988) findings, that dissolution of nantokite occurs when treated with AMT. The large variation in weight change of AMT treated coupons, after inhibitor treatment, has not been investigated further.

After 24 hours exposure to 95%RH and ambient temperature, the coupon was protected by 71%. This increased after 24 hours to 72% when compared to the blank.

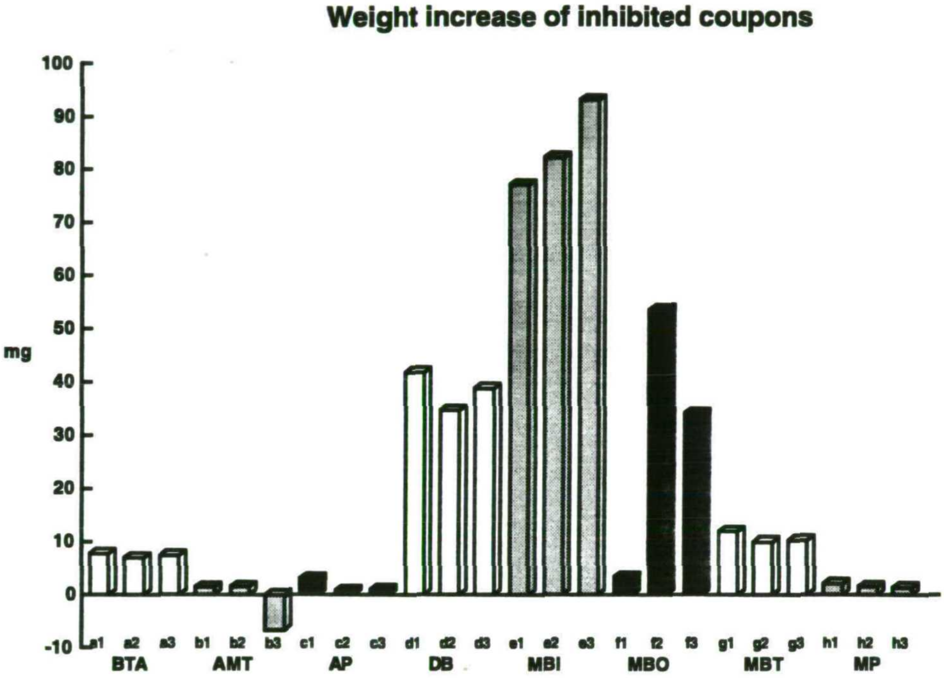


Figure 5. 12 Weight Change after Inhibition.

AP:

There was a very small increase in weight due to the inhibitor. AP caused the smallest weight change. The inhibitor was not a source of visible discoloration on the dried corrosion inhibited coupons. After 24 and 48 hours at 95%RH and ambient temperature, the inhibitor did not protected the coupons.

DB:

After 24 hours inhibitor-nantokite interaction, the solution had a very strong dark green colour. After drying, the surface was uneven, black brown in colour and powdery in texture. It seemed that the inhibitor started to dissolve the nantokite. There was a large weight increase due to the inhibitor. The corrosion inhibition of the disfiguring film was 75% after 24 hours, and 82% after 48 hours.

MBI:

The solution was clear, but slightly greenish after corrosion inhibition. A large amount of white deposit was in the bottom of the flask. The coupons were unevenly corroded in the inhibitor solution. The inhibitor copper film on the coupons was white after the surface dried. The MBI treated coupons had the largest weight increase due to the inhibitor treatment (Figure 5. 12), which was suggested by a thick white inhibitor-Cu complex film on the surface of the coupons. The coupons were corrosion inhibited by 91% after 24 hours exposure, and 96% after 48 hours.

MBO:

The solution was a reddish brown translucent colour, with a white complex floating at the bottom of the flask after 24 hours exposure to the nantokite covered coupons. The coupons had a small thin crystal like film covering their surface. This film was slightly greenish and could not be matched to the Munsell colour chart. The film was very fragile and did not appear to be very protective. After 24 hours the protection was only 49% and after 48 hours 62%.

MBT:

The inhibitor solution changed after 24 hours exposure to the nantokite covered coupons. The solution was yellow and not translucent anymore. There was a complex deposit on the bottom of the flask. After drying, the coupon surface had even discoloration. The corrosion inhibition was very good, after 24 hours the film was 94% protective, and after 48 hours 95%.

MP:

The inhibitor solution was a yellow translucent colour after 24 hours contact with the nantokite covered coupons. There were some needle like crystallites on the bottom of the flask. The inhibitor film was not very protective, after 24 hours it was 25% protective and after 48 hours 58%.

The visual appearance of coupons inhibited with AMT, AP, MBT and MP were considered acceptable for conservation. BTA darkened the surface dramatically. The surfaces treated with DB, MBI and MBO were not visually pleasing.

5.3.4 Discussion

AMT and MBT performed best during the corrosion test. MBT had the smallest weight increase during 95%RH corrosion, supporting the visual assessment of the coupons. BTA, MBO and MP failed to a greater or lesser extent see Table 5. 6. AP failed completely to protect the coupons: this can also be seen in the weight increase after exposure to 95% RH. The corrosion increase is much higher than the blank. This might have been due to pitting in the inhibitor solution.

This experiment has shown the effectiveness of different inhibitors at 0.25M concentration. BTA was at 0.25M and AMT at 0.01M. In the case of DB, MBI and MBO, the 0.25M solution of inhibitor caused a very unsightly inhibitor-copper complex film on top of the nantokite substrate.

5.4 Experimental Procedure at 0.01M/L Concentration of Corrosion Inhibitors in Ethanol

5.4.1 Introduction

In the following experiment, the concentration of 0.01 M was selected and applied to the nantokite covered coupons. This concentration is frequently applied to clean copper substrates in industrial trials (Horner et al. 1982). The lower concentration of inhibitor should minimise the development of discoloration and disfiguring polymer films of the DB, MBI and MBO treated specimens. It would also indicate if MBT is as efficient at a lower concentration. BTA was used at the standard 0.25M solution as used in the conservation of archaeological copper artefacts. In the case of AMT, 0.01M/L is actually the standard concentration suggested by Ganorkar et al. (1988).

5.4.2 Experimental Procedure

The coupons were treated according to the test procedures developed for corrosion testing on nantokite covered surfaces, as stated in the previous experiment.

The only change in the experimental procedure was a change in corrosion inhibitor concentration, as stated above.

5.4.3 Experimental Observations

BTA and AMT were at the same concentrations as in the last experiment. After corrosion inhibition, the AP solution was clear in this experiment compared to a slightly cloudy solution at a concentration of 0.25 M (Figure 5. 13). DB had a smaller amount of green complex formed at 0.01M than at 0.25M, indicating a smaller amount of nantokite being complexed into the inhibitor solutions. The inhibitor solutions of MBI and MBO were both clear: MBO had formed a slight brown colour at a concentration of 0.25 M. MBT and MP also had a reduced cloudy appearence in the inhibitor solution after a 24 hours treatment in a 0.01M concentration, when compared to a 0.25 M concentration. This showed that a concentration of 0.25 M of inhibitor caused more complexing of nantokite into the inhibitor solution in the case of BTA, AP, DB, MBO, MBT and MP. However, in the case of AMT and MBI, it was not possible to compare the concentrations on a visual basis since there was no complex floating in solution.

The inhibited coupons were dried at 50°C for 5 minutes and assessed visually (see Figure 5. 14). BTA darkened the surface. AMT was very similar to the blank coupon. AP was most similar to the blank untreated coupon. With regard to conservation needs, a ranking of surface finish and acceptability could be judged visually as : AP > AMT > MBO > BTA.

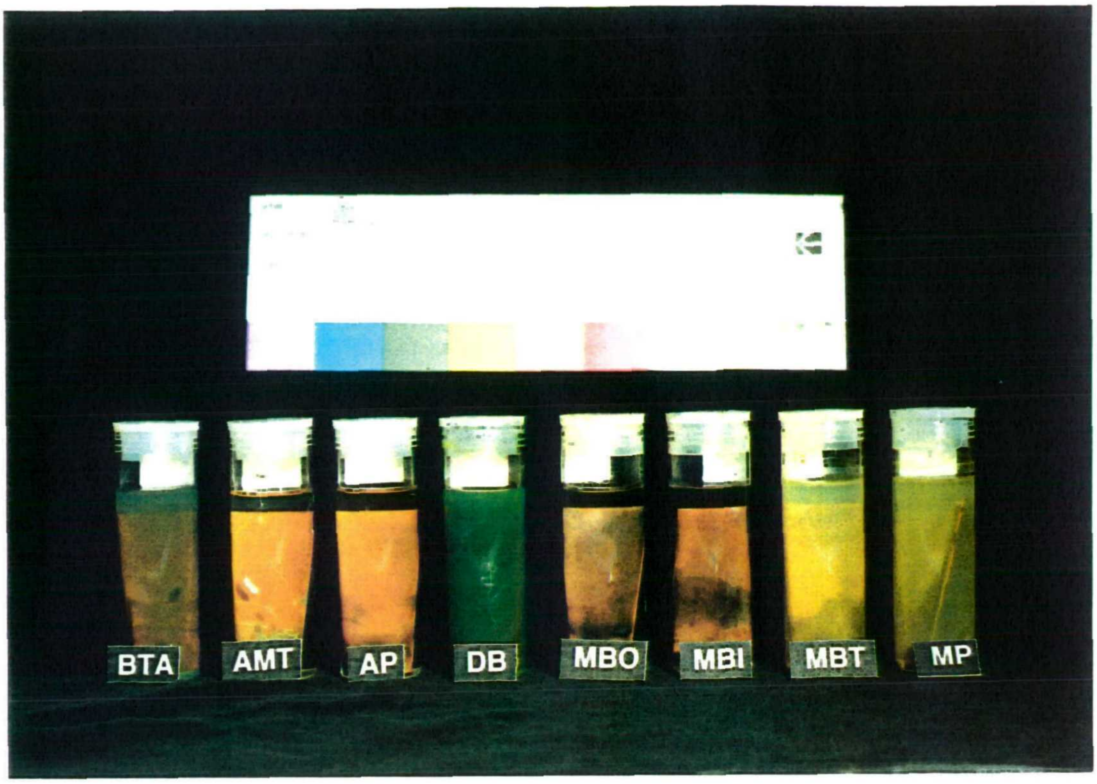


Figure 5. 13 Coupons after 24 hours in Corrosion Inhibitor Solution.

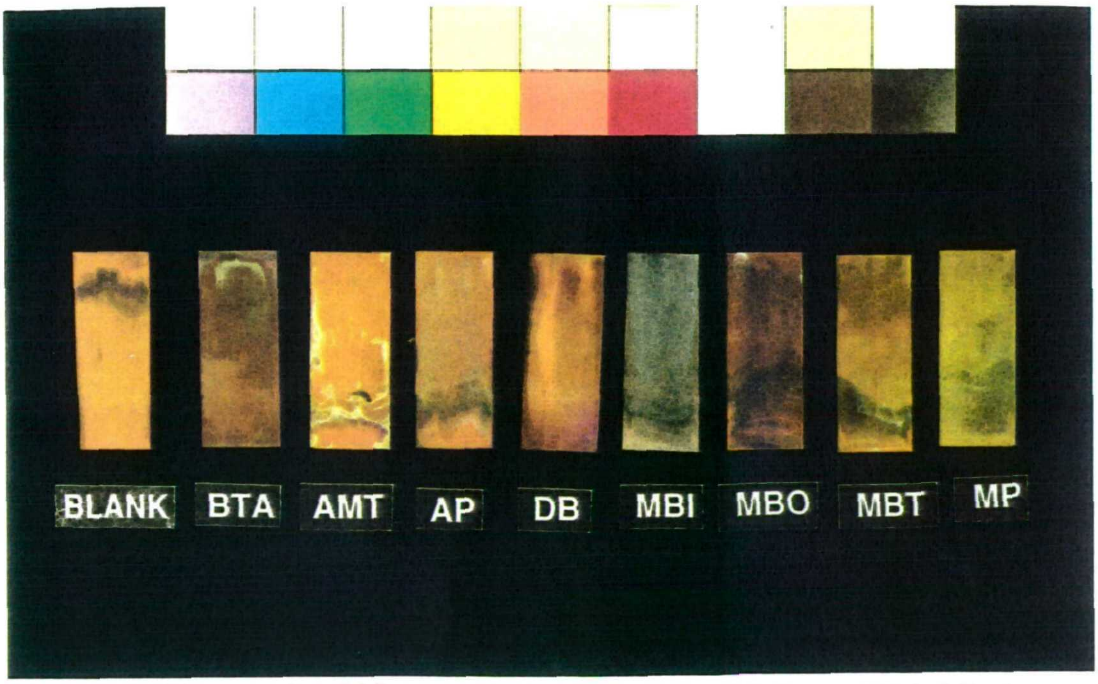


Figure 5. 14 Coupons after 24 hours in Corrosion Inhibitor Solution and Dried 5 minutes at 50°C.

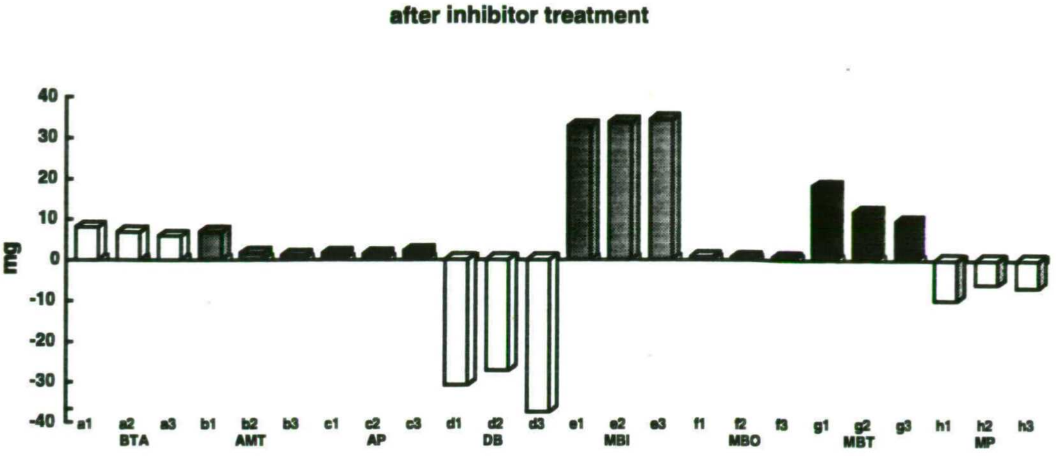


Figure 5. 15 Weight Change after Inhibitor Treatment.

The visual appearance of MBI, MBO, MBT and MP were thought not to be acceptable for conservation (Table 5. 7).

	Munsell notation	Munsell colour names	Comments
Blank	2.5YR 4.5/6	red	
BTA	5YR 3/4	dark reddish brown	more yellow than blank
AMT	5YR 4.5/7	yellowish red	
AP	2.5YR 4.5/6	red	closest to blank
DB	5YR 5/8	yellowish red	
MBI	7.5YR 3/0	very dark grey	white purple surface deposit
MBO	5YR 4/6	yellowish red	small dust size spots on surface
MBT	10YR 4/6	dark yellowish brown	yellow surface deposit
MP	10YR 4/6	dark yellowish brown	yellow surface deposit

Table 5. 7 Colour Change after Corrosion Inhibition.

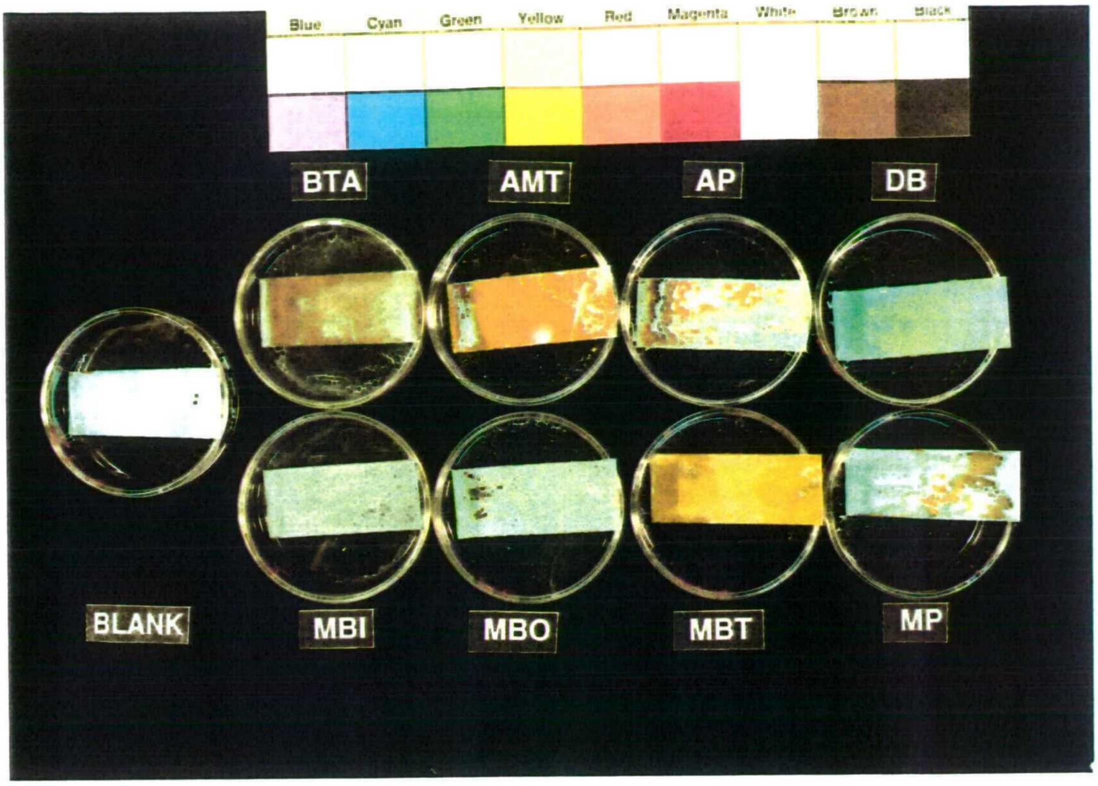


Figure 5. 16 Coupons after 24 hours at 95% RH and Ambient Temperature.

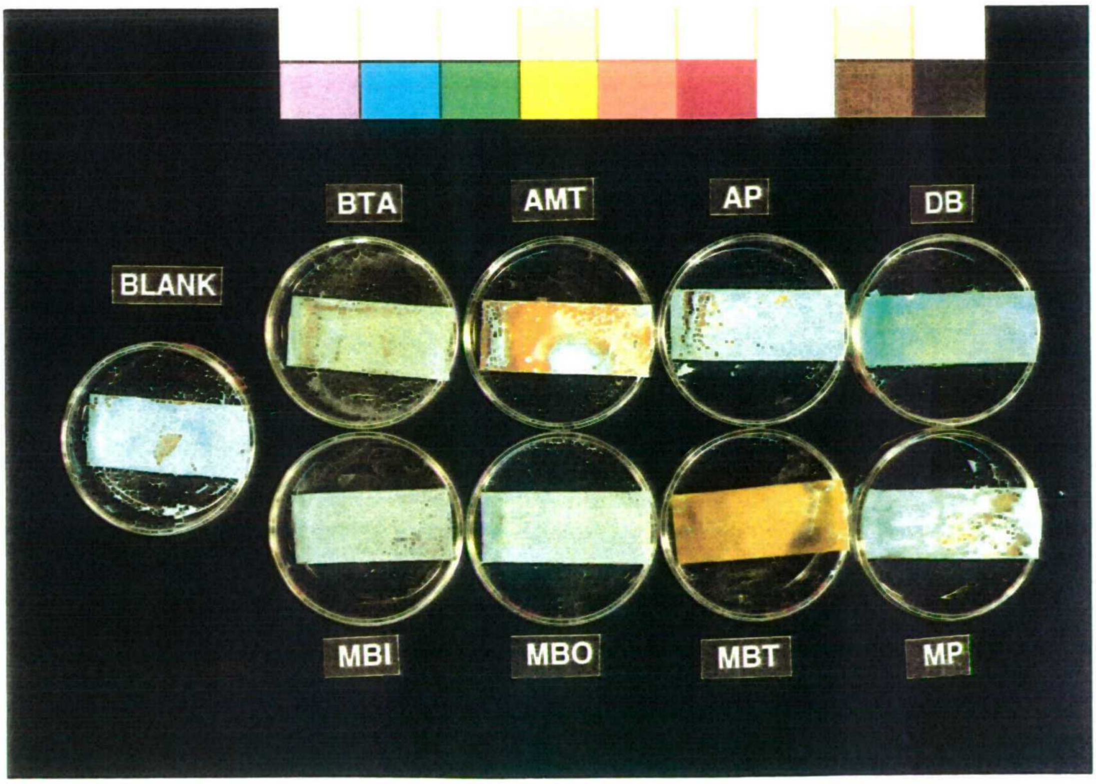


Figure 5. 17 Coupons after 48 hours at 95% RH and Ambient Temperature.

The coupons were assessed after exposure to ~95%RH, at ambient temperature:

The photographic record of the corroded coupons is presented in Figure 5. 16 and Figure 5. 17. The rate of corrosion inhibition was calculated according to Trabanelli (1970, 171) and is listed below.

	Concentration	inhibition % after 24 h.	inhibition % after 48 h.
BTA	0.25M	79	29
AMT	0.01M	78	55
AP	0.01M	27	0
DB	0.01M	0	0
MBI	0.01M	14	0
MBO	0.01M	5	0
MBT	0.01M	95	89
MP	sat	8	4

Table 5. 8 Corrosion Inhibition in Percent after 24 and 48 hours at 95% and Ambient Temperature.

BTA:

After 24 hours at 95% RH the dark coupon was covered in small paratacamite spots and the corrosion protection was 79%. After 48 hours at 95% RH, the surface was covered in paratacamite, and the corrosion protection dropped to 29%.

AMT:

Large areas of the coupon were not covered in paratacamite after 24 hours of exposure to an elevated relative humidity. The protection was 78%. The nantokite areas partially complexed into the inhibitor solution transformed to paratacamite, as did the areas adjacent to it. The amount of paratacamite increased when exposed to 48 hours at the elevated RH, and the protection dropped to 55%.

AP:

These coupons were partially corroded: the surface protection was only 27%. There was more corrosion present than on the BTA coupons. 48 hours exposure caused the surface to completely corrode into paratacamite. There was 0% corrosion protection

DB:

These coupons were completely corroded after 24 hours, and covered in a dense paratacamite layer. This did not change visually after 48 hours.

MBI:

The whole surface was covered in a corrosion layer of paratacamite. The corrosion protection was as low as 14% after 24 hours. The amount of paratacamite had slightly increased after 48 hours at 95% RH, and the corrosion protection was 0%.

MBO:

There was 5% corrosion protection after 24 hours and 0% after 48 hours.

MBT:

The surface was mainly uncorroded: only areas handled previously with tweezers developed paratacamite corrosion. Corrosion protection was as high as 95%. After 48 hours there was a slight increase in paratacamite spots, but there was almost no corrosion present. The corrosion protection dropped to 89%.

MP:

The surface was completely corroded after 24 hours.

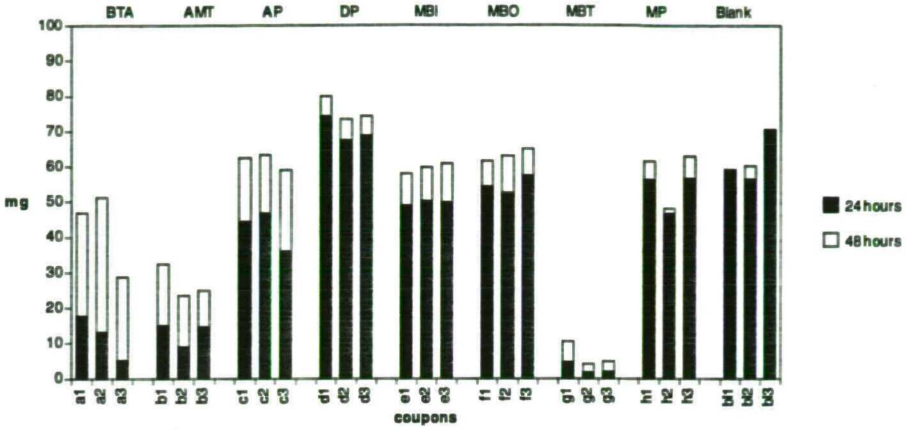


Figure 5. 18 Weight increase after 24 Hours and 48 Hours at 95%RH.

5.4.4 Experimental Conclusion

After 24 hours, MBT (0.01M) was found to protect the surface best from further corrosion. This was also substantiated gravimetrically (Figure 5. 18). In both cases, after 24 hours and 48 hours exposure to 95% RH, AMT (0.01M) was the only other compound protecting the coupons partially from further oxidation to paratacamite. This was more apparent when the coupons were visually examined, after 48 hours. Large areas on the AMT treated coupons were seen to be stable. BTA performed similarly to AMT after 24 hours, but had a distinct increase in corrosion weight after 48 hours. BTA and AP had a much lower inhibiting efficiency than MBT and AMT. However BTA had a lower weight increase due to corrosion, compared to AP.

The inhibitors DB, MBI, MBO and MP under these conditions were considered failures. From this test, the corrosion inhibiting effectiveness of the inhibitors were considered to be as follows:

MBT > AMT > BTA > AP > MBI = MBO = MP = DB.

5.5 Inhibiting Nantokite Corrosion with Various Inhibitor Concentrations

5.5.1 Introduction

The previous tests showed that none of the inhibitors were able to completely prevent further corrosion at 95%RH and ambient temperature. In the table below the inhibitors are listed in accordance to their effectiveness in corrosion inhibition in percent, at specific concentrations.

Corrosion inhibition in %, after exposure to 95%RH, ambient temperature						
Section 5.3	**24 hours**	**48 hours**		**Section 5.4**	**24 hours**	**48 hours**
BTA 0.25	76	48		**BTA 0.25**	79	29
AMT 0.01	71	72		**AMT 0.01**	78	55
AP 0.25	0	0		**AP 0.01**	27	0
DB 0.25	75	82 film		**DB 0.01**	0	0
MBI saturated	91	96 film		**MBI 0.01**	14	0
MBO 0.25	49	62 film		**MBO 0.01**	5	0
MBT 0.25	94	95		**MBT 0.01**	95	89
MP saturated	25	58		**MP saturated**	8	4

Table 5. 9 Different Inhibitor Concentrations and the Corrosion Protection in Percent.

The differences in corrosion inhibition of 0.25M BTA and 0.01M AMT were due to unknown variables in the experiment, such as ambient temperature. It was an indication for the limited reproducibility of corrosion testing. BTA at a 0.25M concentration (3% by weight i.e. the standard conservation treatment), had only a corrosion inhibition of 76-79% on the first day and 29-48% on the second day. Madsen (1971) suggested that an increase, in inhibitor up to 30% by weight, would give increased inhibition for objects that were difficult to stabilise. 30% BTA is equivalent to 2.5M solution. A 1M BTA concentration was observed to produce a very viscous solution.

In the following experiment, BTA and AP were increased to 1M concentrations in ethanol. In this concentration they might be more effective, following Madsen's suggestion to increase BTA concentrations. AP was the only other compound that could be tested at such a concentration. It was found that AMT had a maximum solubility of 0.068M, and MP was a saturated solution below 0.25M. DB, MBI and MBO readily formed unsightly complex films at 0.25M. An increase in concentration apparently only increases the film thickness. A concentration of 0.25M inhibitor did show an increase in polymer film formation on the DB, MBI and MBO coupons. A decrease of inhibitor to 0.01M resulted in a poor inhibition of further corrosion. An intermediate concentration might cause inhibition without causing disfigurement of the coupons surface, due to the polymer layer formed. This needed empirical testing, so DB, MBI and MBO were applied in concentrations of 0.1M.

MBT proved to be effective at 0.25 and 0.01M concentration. However, in both cases MBT caused the nantokite to turn yellow. A decrease to 0.001M might still inhibit further corrosion, but also diminish the discoloration of the surface of the coupons. MP was not very effective in a saturated solution. It was applied at 0.001M to observe if a lower concentration might increase its effectiveness.

5.5.2 Experimental Observations

The coupons were treated as described in section 5.2.2. Figure 5. 19 and Figure 5. 20 show the coupons after inhibition. The discoloration of the inhibitor solutions is listed in the Table 5. 10.

Solution	concentration	before inhibition	after inhibition
BTA	1M	clear	very dark olive green
AMT	0.068M	clear	clear, white complex on bottom
AP	1M	milky white	clear , needle shaped crystals
DB	0.1M	yellowish	very dark olive green
MBI	0.1M	clear	clear
MBO	0.1M	yellow brown, clear	clear very slightly yellow-brown
MBT	0.001M	clear	clear, slightly cloudy complex
MP	0.001M	yellow	clear, slightly cloudy complex

Table 5. 10 Colour Changes of Corrosion Inhibitor Solutions after Corrosion Inhibition.

In the following section, the coupons are described and assessed according to their appearance after inhibiting and drying

BTA:

During the corrosion inhibitor treatment, the nantokite was complexed into the inhibitor solution and the metal substrate was etched, in the area of the coupons closed to the inhibitor solution air interface. The other half was still covered in nantokite. The remaining nantokite was dark olive green. The surface of the coupon was slightly glossy due to the inhibitor.

AP:

The coupons were covered in inhibitor crystals due to a supersaturation of the solution and evaporation of ethanol.

DB and MBI had a very unsightly surface appearance not usually acceptable for conservation. The table below lists the Munsell notations and comments on the surface of the coupons, after inhibitor treatment and drying.

	Munsell notation	**Munsell colour names**	**comments on structure of surface**
Blank	2.5YR 4.5/4	weak red	even surface
BTA	5Y 2.5/1	black	nantokite area only, top corroded to metal surface, glossy surface
AMT	5YR 4.5/5	yellowish red	more yellow than blank, but close to blank
AP	2.5YR 4.5/4	weak red	areas not covered in AP crystals, crystals ~8mm
DB	5Y 2.5/1 to 2.5Y 6/8	dark to light olive green	powdery surface, exfoliating on bottom end
MBI	not found	white	mould like structure, spongy
MBO	2.5YR 4.5/4	weak red	small amount of inhibitor crystals on bottom end
MBT	10YR 5/3	brown green	deposit 5Y 7.5/7 yellow green
MP	2.5Y 6/4	light yellow brown	even surface

Table 5. 11 Surface of Coupons after Corrosion Inhibition.

The coupons that were thought to have an acceptable surface appearance were AMT, MBO, MBT and MP. The ordering would appear to be MBO > AP > AMT, MBT > MP. BTA, DB and MBI were thought to be not acceptable due to the discoloration of the surface.

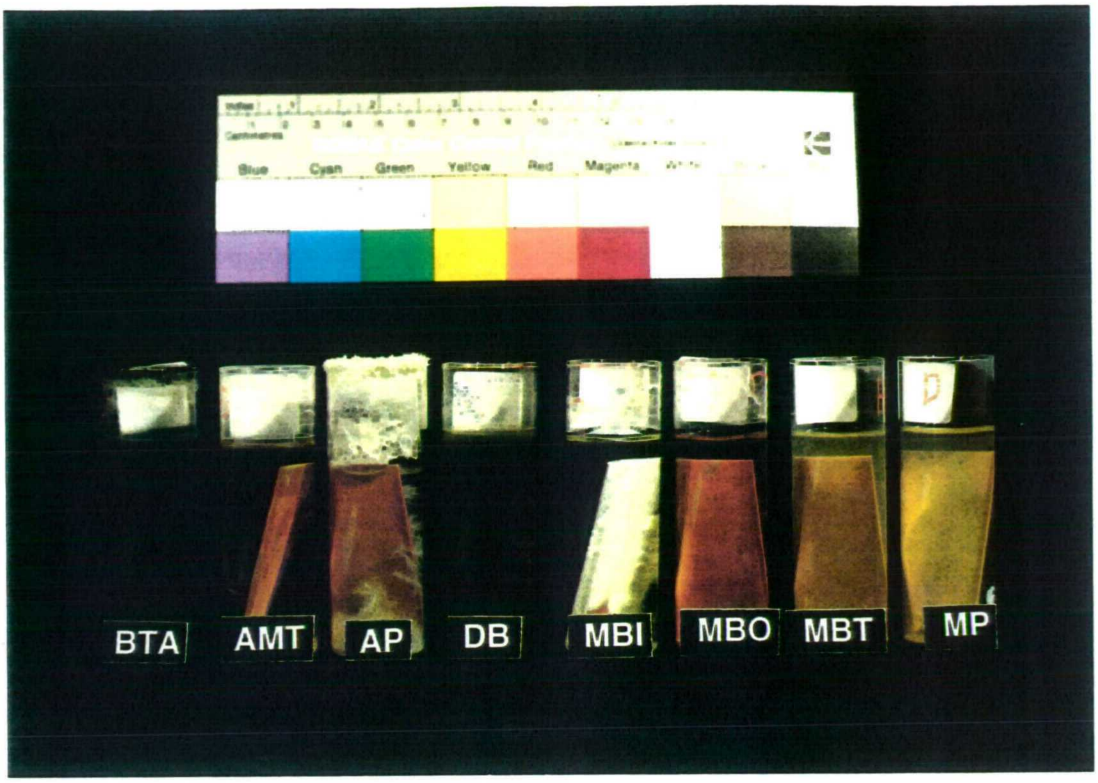


Figure 5. 19 Coupons after 24 hours in the Corrosion Inhibitor Solution.

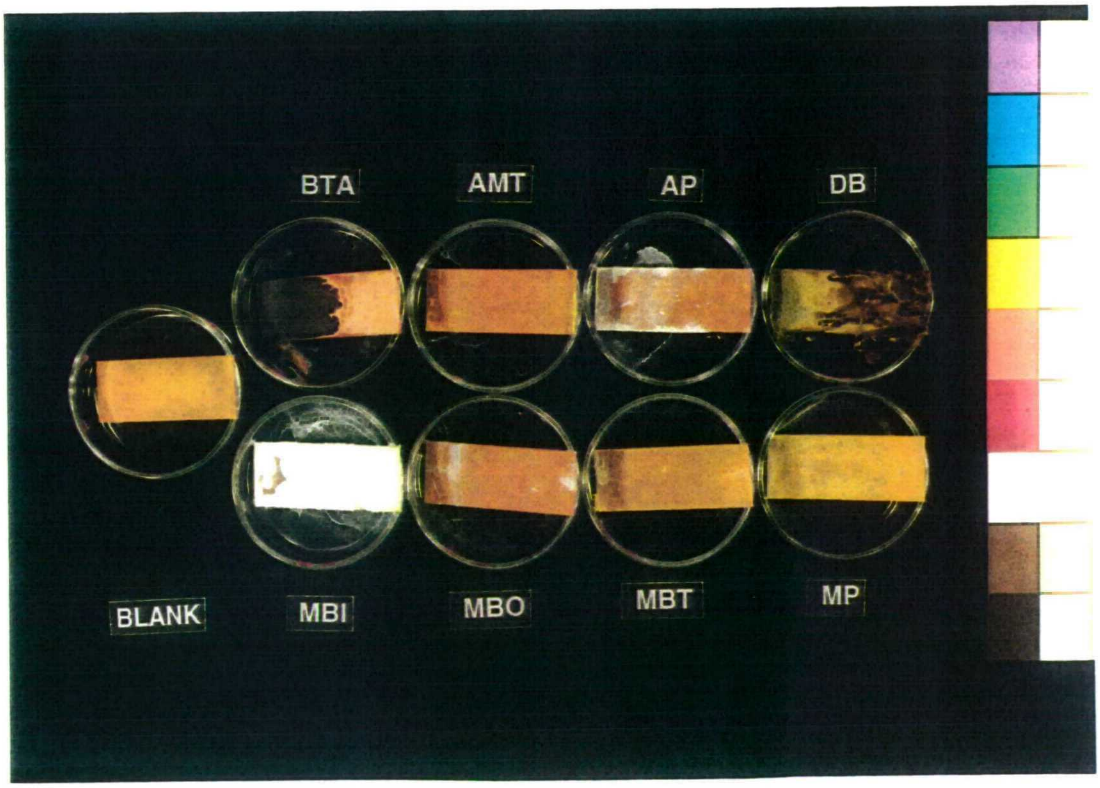


Figure 5. 20 Coupons after Corrosion Inhibition and 5 minutes Drying at 50°C.

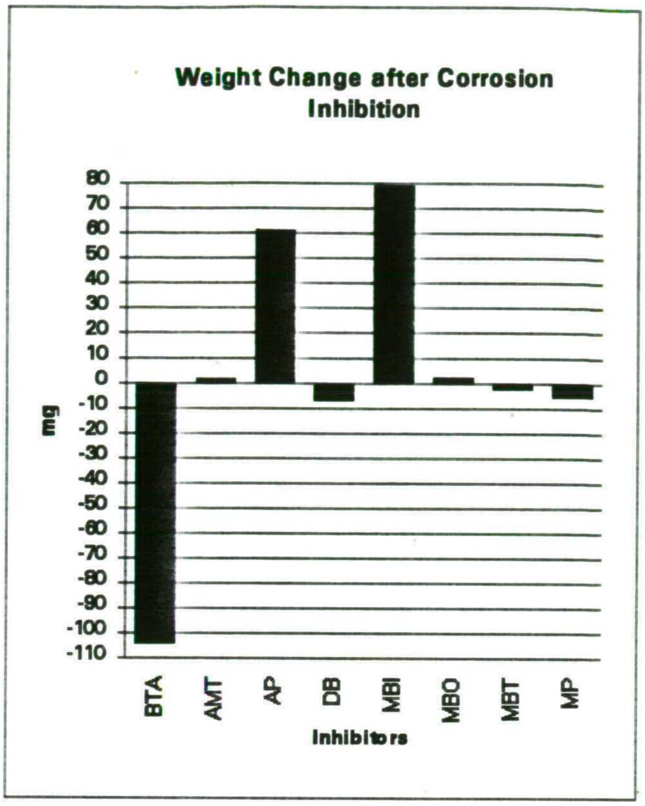


Figure 5. 21 Weight Change in mg after 24 hours in Corrosion Inhibitor Solutions.

Corrosion Inhibition in Percent:

	concentration	after 24 hours 95%RH	after 48 hours 95%RH	comments
BTA	1M	100%	100%	etched and stripped surface
AMT	0.068M	60%	53%	
AP	1M	86%	78%	AP crystals on surface film
DB	0.1M	73%	72%	flaked and corroded film
MBI	0.1M	100%	100%	white complex film
MBO	0.1M	93%	81%	
MBT	0.001M	11%	8%	completely corroded
MP	0.001M	4%	4%	completely corroded

Table 5. 12 Corrosion Inhibition in Percent and Comments on the Surface Appearance

Exposure to 95% RH at ambient temperature:

After having been treated with the corrosion inhibitors, the coupons were exposed to 95% RH at ambient temperature for 24 and 48 hours.

BTA:

After 24 hours, the bottom end of the coupons had very small areas of paratacamite. There was no paratacamite on the stripped metallic areas, and on the dark green discoloured nantokite. After 48 hours there was only a slight increase in paratacamite.

AMT:

All coupons were covered in small amounts of paratacamite after 24 hours exposure. There was only a slight increase in paratacamite corrosion after 48 hours.

AP:

The three coupons were partially corroded after 24 hours. There was an increase in parlatacamite after 48 hours.

DB:

The complex layer was flaking off exposing paratacamite underneath. There was an increase in corrosion after 48 hours.

MBI:

The white areas were stable. The nantokite areas not covered by the white film started to develop paratacamite. This paratacamite increased after 48 hours.

MBO:

Small amounts of paratacamite started to develop. MBO and BTA were the coupons with the smallest amount of corrosion. There was an increase of paratacamite spots after 48 hours.

MBT and MP were completely corroded.

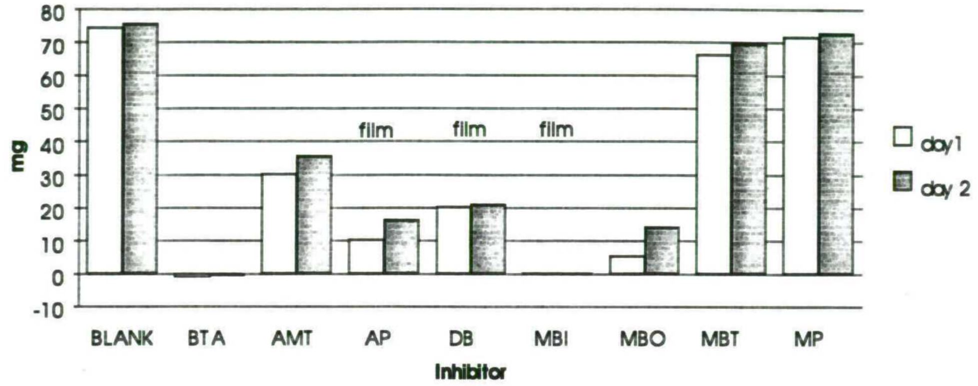


Figure 5. 22 Corrosion Rate in mg after 1 and 2 days at 95%RH Ambient Temperature.

5.5.3 Conclusion

The experiment revealed an important detail: The 1M solution BTA resulted in a loss of nantokite and an etching of the coupon down to the metallic substrate. This dissolution might not only occur on nantokite but it also suggests that the solution might attack other copper minerals on an artefact. The same might be the case with other inhibitors when applied in high concentrations.

5.6 Long Term Experiments with Varying Concentrations

5.6.1 Introduction

The experimental work summarised indicated that none of the inhibitors were able to completely prevent the reaction from nantokite to paratacamite at ~95%RH. The Table 5. 13 displays the corrosion inhibitor effectiveness. The mean of each set was calculated. It should be emphasised that very small weight changes due to paratcamite corrosion do not necessarily indicate good performance of an inhibitor for archaeological metals. The good performance might be due to a disfiguring inhibitor complex, such as in the case of DB, MBI and MBO at a 0.25M/L concentration. This disfiguring film formation is marked as “film” in Table 5. 13.

The data compiled in this research indicates that MBT in 0.01M and 0.25M concentrations leads to the best corrosion inhibition. DB and MBI seem to slow paratacamite conversion as well, but this is at the cost of an unacceptable corrosion inhibitor film forming on a nantokite substrate.

Corrosion protection in percent for three experiments, the coupons were corrosion inhibited and exposed to 95%RH, ambient temperature:

	concentration in moles	**inhibition %**	**inhibition %**	
		day1	**day 2**	**Section 5.3**
BTA	0.25	76	48	
AMT	0.01	71	72	
AP	0.25	0	0	
DB	0.25	75	82	film
MBI	saturated	91	96	film
MBO	0.25	49	62	film
MBT	0.25	94	95	
MP	saturated	25	58	
				Section 5.4
BTA	0.25	79	29	
AMT	0.01	78	55	
AP	0.01	27	0	
DB	0.01	0	0	
MBI	0.01	14	0	
MBO	0.01	5	0	
MBT	0.01	95	89	
MP	saturated	8	4	
				Section 5.5
BTA	1	100	100	corroded during inhibition
AMT	0.068	60	53	
AP	1	86	78	film
DB	0.1	73	72	film
MBI	0.1	100	100	film
MBO	0.1	93	81	
MBT	0.001	11	8	
MP	0.001	4	4	

Table 5. 13 Coupons Treated in Different Concentrations of Inhibitors and Exposed for 24 hours and 48 hours to ~95%RH.

5.6.2 Experimental Procedure

The subsequent experiment was based on the data previously collected, and an attempt was made to further determine at what concentrations specific inhibitors might be more effective. For this experiment a humidity chamber with temperature and humidity control was available. (Fisons Humidity Chamber Model 280/CT/DEG-

2-R10-D½/100°C 750x750x500mm, updated using Eurotherm 910D digital 3-term programming controller with humidity and temperature control). This allowed the selection of specific relative humidities at which coupons treated with selected inhibitors could be evaluated.

The experiment was undertaken in the same manner as stated before. The only changes were made to 3 major variables:

a) the concentrations of the inhibitors

b) the relative humidity and

c) the duration of the exposure to an elevated relative humidity.

During this experiment a set of 3 blank coupons covered in nantokite were immersed for 24 hours in solutions of inhibitor in reagent grade ethanol. BTA was used in the standard 0.25M concentration. AMT was applied at 0.01M. AP was again applied at a 0.25M concentration, to confirm previous data, and determine at what RH level the complex film breaks down, or fails to protect the reactive substrate. DB, MBI and MBO were applied at a 0.1M concentration, since all three formed an unsightly complex film at 0.25M and proved to be ineffective at 0.01M concentration. MBT was applied at 0.25M since the data showed maximum effectiveness at this concentration. MP was applied in a saturated solution to determine the RH threshold at which corrosion starts to occur.

Inhibitor Concentrations			
Inhibitor	**Concentration**	**Inhibitor**	**Concentration**
BTA	0.25M	**MBI**	0.1M
AMT	0.01M	**MBO**	0.1M
AP	0.25M	**MBT**	0.25M
DB	0.1M	**MP**	0.25M

Table 5. 14 Inhibitor Concentrations Selected.

The corrosion chamber allowed the control of two parameters, relative humidity and temperature. It was expected that the lowest relative humidity at which an inhibited coupon would start to fail should be at around 70%RH. This RH was thought reasonable as a starting point, since an inhibited coupon should withstand such an environment. It was decided to raise the relative humidity by 10% , after 24 hours, if none of the inhibitors failed.

The temperature of the chamber was kept at 20°C. A higher temperature might have lead to accelerated corrosion. Corrosion due to the low resistance of an inhibitor film to temperature may have confused the results. It would have been difficult to determine if the deterioration of an inhibitor film was due to the increase in relative humidity or temperature.

5.6.3 Experimental Observations

After 24 hours in the corrosion inhibitor solutions, some inhibitors produced a complex film which seemed unattractive, due to discolouration. BTA darkened the coupons, DB formed a porous dark complex film and MBI formed a white coating. None of these inhibitors would be appropriate in these concentrations in conservation. The other inhibitors were thought to present an acceptable appearance.

The table below indicates the weight change as a mean calculated for each set of corrosion inhibited coupons in milligrams (see also Figure 5. 23):

	24 hours 70%RH	48 hours 70%RH	72 hours 70 %RH	96 hours 80%RH	120 hours 80%RH	144 hours 90%RH	168 hours 90%RH	192 hours 90%RH	216 hours ~100%RH
BLANK	2.2	16.9	24.3	35.1	37.8	47.2	47.1	49.6	64.4
BTA	-0.7	-1.3	-1.5	-1.4	-1.3	2.1	2.4	4.6	8.5
AMT	0.2	0	0.2	0.6	0.7	1.2	1.3	2.4	7.3
AP	-3.8	-3.9	-3.8	-3.5	-3.3	15	20.2	24.5	46.3
DB	1.3	6.1	7.5	12.9	14.4	17.7	18.6	20.9	23.4
MBI	0.2	0.9	1.2	1.6	1.6	2.4	2.3	3.4	13.3
MBO	0.2	0.2	0.2	0.4	0.8	1.7	2.1	2.7	5.5
MBT	0.5	0.9	1.1	1.8	2.2	2.9	3.3	3.8	6
MP	0.6	0.7	0.8	2.4	3.6	16.1	19.8	22.6	37.6

Table 5. 15 Weight Increase in mg During 9 days of Exposure to Elevated Relative Humidity.

	24 hours 70%RH	48 hours 70%RH	72 hours 70 %RH	96 hours 80%RH	120 hours 80%RH	144 hours 90%RH	168 hours 90%RH	192 hours 90%RH	216 hours ~100%RH
BTA	100	100	100	100	100	96	95	91	87
AMT	91	100	99	98	98	97	97	95	89
AP	100	100	100	100	100	68	57	51	28
DB	41	64	69	63	62	63	61	58	64
MBI	91	95	95	95	96	95	95	93	79
MBO	91	99	99	99	98	96	96	95	91
MBT	77	95	95	95	94	94	93	92	91
MP	73	96	97	93	90	66	58	54	42

Table 5. 16 Corrosion Inhibition in Percent after 9 days of Exposure to Elevated Relative Humidity.

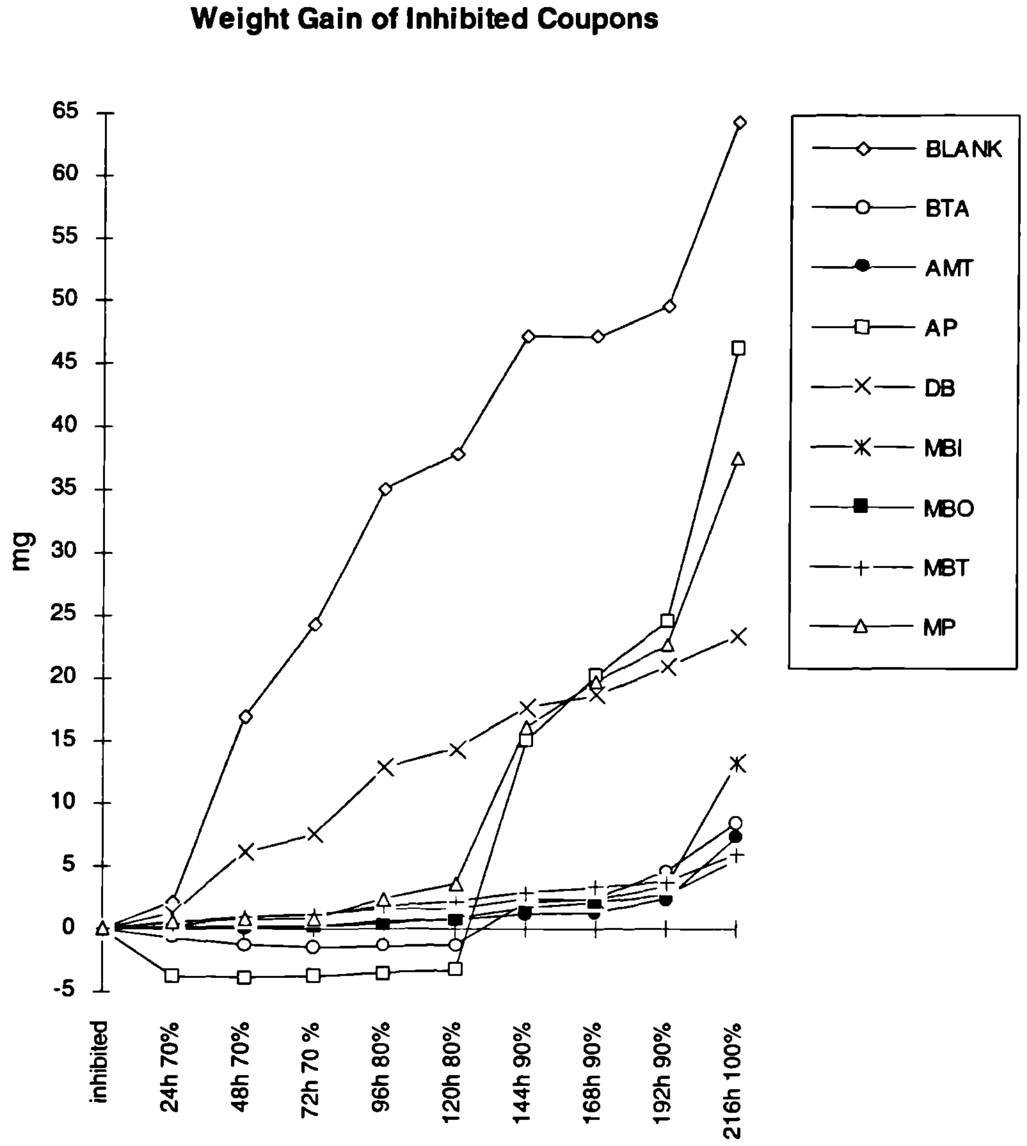


Figure 5. 23 Weight Increase of Coupons During 216 hours of Exposure to Increasing Levels of Relative Humidity.

After 24 hours exposure to 70% RH, only the DB inhibited coupons corroded. After 72 hours most inhibitors protected the coupons up to and between 95 and ~100% RH. Only DB started to fail, and only protected up to <70%RH.

After 24 hours at 80%RH, the first drastic changes in corrosion rate started to occur. DB was still the inhibitor with the largest increase in corrosion. This was followed by MP. After 48 hours at 80% RH, DB and MP were still the inhibitors with the largest weight increase as a measure of corrosion.

After 24 hours at 90% RH; this environment immediately showed the effectiveness of other inhibitors. DB had the largest weight increase of corrosion, this was followed by MP and AP. Only at 90% RH did AP started to corrode. The other inhibitors were still protective. After 48 hours at 90% RH; AP, DB and MP had almost the same amount of corrosion. After 72 hours at 90% RH, AP started to develop more corrosion than DB and MP. The others seemed relatively stable at this high relative humidity. After three days at 90% the relative humidity seemed not to have much effect on coupons treated with BTA, AMT, MBI, MBO and MBT.

After 24 hours at 100% RH; AP, DB and MP had the highest corrosion rate in mg/day. MBI also started to corrode heavily. BTA, AMT, MBO and MBT clearly showed less corrosion (see table Table 5. 16).

5.6.4 Experimental Conclusion

After 24 hours at 70% RH, BTA and AP lost weight. It is not understood completely why this happened. It is suggested that this weight decrease might be due to the delayed evaporation of parts of the solvent or inhibitor. BTA, for example, has been suggested as a vapour phase inhibitor for the corrosion inhibition of artefacts (Keene, 1985). This suggests that unreacted or uncomplexed BTA does "evaporate" slowly. Since the coupons were not rinsed after treatment with inhibitors, it was thought probable that some of the unreacted inhibitor remained on the surface of the coupons. This characteristic of BTA might explain the behaviour of AP, but this will have to be assessed further.

The coupons that had been immersed in ethanol alone, as a control, had an almost linear weight increase during paratacamite corrosion. DB had a lower corrosion rate than the uninhibited coupons, but still an almost linear weight increase from the start of the experiments. All other inhibited coupons were more or less stable when they were exposed for 72 hours at 70% RH followed by two days at 80% RH.

The first inhibitors other than DB to start increasing in corrosion rate were AP and MP. A relative humidity of 90% caused the films to fail, suggesting that these inhibitors were able to protect chloride corrosion containing artefacts for a short period of time at an RH below 90%. BTA, AMT, MBI, MBO and MBT slowly increased in weight during 72 hours at 90% RH, but did not completely break down.

Exposure to 100% RH clearly showed MBI failed, suggesting its application be limited to less severe environments. BTA, AMT, MBO and MBT had an almost equal amount of corrosion, indicating their ability in preventing the transformation of nantokite to paratacamite.

This experiment proved that DB is not appropriate as a corrosion inhibitor for chloride containing copper artefacts. AP, and MP have a limited use in a relative humidity below 90%, for a short period of time. MBI could be applied at RH below 100%, however, it should not be expected that the corrosion inhibiting properties would last very long. BTA, AMT, MBO and MBT showed very good corrosion inhibiting properties and are suggested for further evaluation.

5.7 Corrosion Inhibitor Applications of Selected Corrosion Inhibitors

5.7.1 Introduction

The subsequent experiment was conducted on the basis of two objectives. The first objective was the determination of the effectiveness of the corrosion inhibitors selected, and the second the performance of nantokite covered coupons after a second corrosion inhibitor application.

Earlier experiments have shown that some inhibitors are more successful in inhibiting corrosion than others. Their effectiveness was mainly affected by the percentage of relative humidity present in the corroding environment. The higher the relative humidity, then the more likely it is that an inhibitor simply fails under these conditions. Based on the previous data, inhibitors with the highest corrosion inhibition effectiveness were chosen for this experiment. The limited selection was necessary, since five repetitions were undertaken.

AP, DB and MBI were not selected for this experiment. AP, and DB had a low effectiveness, and MBI was either not effective or formed a unsightly white film. The inhibitors chosen for this experiment were BTA and AMT, since they have been used in conservation, and both had proven to be very effective during the previous tests. MBO, MBT and MP were tested again due to their capability in preventing corrosion. MP had a poor performance in the previous experiment, however it was successful in slowing corrosion at an RH between 70% and 80% for 120 hours.

5.7.2 Experimental Procedure

1. air-abrading of copper coupons with 47 micron glass beads
2. degreasing in ultrasonic bath in 100 ml acetone
3. drying for 5 min at 50°C under infrared lamp, and 10 min cooling in silica-gel buffered polyethylene box
4. weighing to ±0.01 mg
5. immersion into 25 ml of a 1 M solution of cupric chloride in deionised water, 1 day at ambient temperature
6. rinsing in deionised water 3 x 20 min, in 100 ml, quick drying in 200 ml ethanol
7. drying for 5 min at 50°C under infrared lamp
8. exposure to 105°C in oven for 1 hour, and 10 min cooling in silica-gel buffered polyethylene box
9. weighing to ±0.01 mg
10. immersion in to 25 ml ethanol/inhibitor. 24 hours at ambient temperature only slightly covered so oxygen can enter
11. drying for 5 min at 50°C under infrared lamp, and 10 min cooling in silica-gel buffered polyethylene box
12. weighing to ±0.01 mg
13. exposure to 70%RH for 24 hours at 20°C
14. drying for 5 min at 50°C under infrared lamp, and 10 min cooling in silica-gel buffered polyethylene box
15. weighing to ±0.01mg
16. exposure to 80%RH for 24 hours at 20°C
17. drying for 5 min at 50°C under infrared lamp, and 10 min cooling in silica-gel buffered polyethylene box
18. weighing to ±0.01mg
19. second treatment with 25ml solutions of inhibitors. 24 hours at ambient temperature only slightly covered so oxygen can enter
20. drying for 5 min at 50°C under infrared lamp, and 10 min cooling in silica-gel buffered polyethylene box
21. weighing to ±0.01 mg
22. exposure to 80%RH for 24 hours at 20°C
23. drying for 5 min at 50°C under infrared lamp, and 10 min cooling in silica-gel buffered polyethylene box

24. weighing to ±0.01mg
25. days exposure to 90%RH for 24 hours at 20°C
26. drying for 5 min at 50°C under infrared lamp, and 10 min cooling in silica-gel buffered polyethylene box
27. weighing every 24 hours to ±0.01mg

The second corrosion inhibitor treatment was applied, based on previous conservation treatments with BTA. In conservation practice, BTA is reapplied when the BTA-copper complex film starts to deteriorate and spots of paratacamite appear. A copper artefact is usually treated once for 24 hours in a 3% BTA solution. Then it can be exposed to an elevated RH, to evaluate the inhibitor film. Should there be any paratacamite formation the treatment is repeated. This procedure could be continued until the object was "stable". In the experiment discussed here, it was decided to treat the coupons once and then expose them to an elevated RH. An RH of 70% was chosen since it was expected that coupons covered in an inhibitor polymer film would not react below this relative humidity. After 24 hours, the RH was increased to 80% to accelerate the nantokite corrosion. This produced paratacamite corrosion on some of the coupons. This stage of corrosion was found sufficient for a second inhibitor application.

After the second treatment, the RH was kept at 80% for 24 hours to observe the stability of the coupons. It was observed that most of the coupons were resistant to this RH, so it was increased the following days to 90%.

5.7.3 Experimental Observations

After the first inhibitor application, the coupons were exposed for 24 hours to 70% RH/20°C. This level of relative humidity proved to be not aggressive enough for any of the test coupons to gain weight. The RH was raised to 80%. This proved successful in producing paratacamite on AMT, MBO and MP treated coupons. All coupons were again treated for 24 hours in a new inhibitor solution. During this process it was thought that the inhibitor might be capable of complexing some of the paratacamite into the inhibitor solution. The paratacamite corrosion on AMT and MP was not removed in the second treatment, so there was no apparent weight loss. The surface of the coupons treated with BTA darkened further after the second 24 hour treatment. The coupons treated the second time with MBO, developed a surface covered in small crystals or a white polymer film. Crystals and white film were found on all coupons twice treated with MBO. Because of the disfiguring inhibitor polymer film on MBO, the weight increased dramatically.

The second treatment with AMT and MBT seemed not to have adverse effects regarding the visual appearance of the nantokite covered coupons.

After the second inhibitor treatment, the MP treated coupons lost weight, probably due to further nantokite dissolution. A further 24 hour exposure to 80% RH/20°C caused the coupons treated with MP to corrode instantly. The corrosion increased during the following three days at 90%RH.

The coupons inhibited with BTA lost weight during exposure to an RH between 70% and 90%. The weight loss of BTA at elevated RH had to be further investigated. AMT and MBT both had a very slow increase in weight during exposure to elevated RH.

5.7.4 Discussion

The effectiveness, and the behaviour of selected inhibitors was tested after a second inhibitor treatment. BTA is known to increase its protectivness after multiple applications (Weisser, 1987). BTA, AMT and MBT have been the most effective corrosion inhibitors for copper covered with nantokite. The exposure to 24 hours at 70% RH and 24 hours at 80% RH, did not result in a significant increase in weight. The coupons were retreated after the second day and again exposed for four consecutive days to an RH between 80% and 90%. None of the coupons that were treated a second time corroded completely. A slight weight increase was detected on AMT and MBT treated coupons. At the end of the experiment, some of the AMT and MBT coupons had minute visible areas of paratacamite corrosion. The BTA treated coupons were difficult to assess visually for paratacamite corrosion, since the surface had an uneven surface coloration, obscuring erupted paratacamite colours.

The coupons treated with MP for a second time, lost some weight after the second inhibitor treatment. This suggested the removal of some of the paratacamite produced at 70% RH and 80% RH, or further dissolution of nantokite. The coupons treated twice with MP immediately corroded, and gained weight when exposed to 80% RH and 90% RH. The data showed that MP is a poor corrosion inhibitor under these conditions. MBO dramatically gained weight after the second inhibitor treatment, due to a disfiguring copper-inhibitor film forming. Such a film is not acceptable for conservation. This led to the conclusion that MBO could not be applied twice to an artefact.

After the first 24 hours at 70% RH the coupons treated with BTA, AMT, MBO and MBT lost some weight. This weight loss after the first inhibition treatment was not due to an experimental error, since the weight loss was observed on all 5 coupons treated with BTA and AMT.

The weight of BTA coupons further decreased after the second application, suggesting that there might have been some nantokite dissolution during the inhibitor treatment. Further weight loss of BTA treated coupons was observed during the following three days at 80% RH and 90% RH. Only the fourth day did the weight decrease stabilise. The complex weight changes of BTA treated coupons cannot be explained satisfactorily yet.

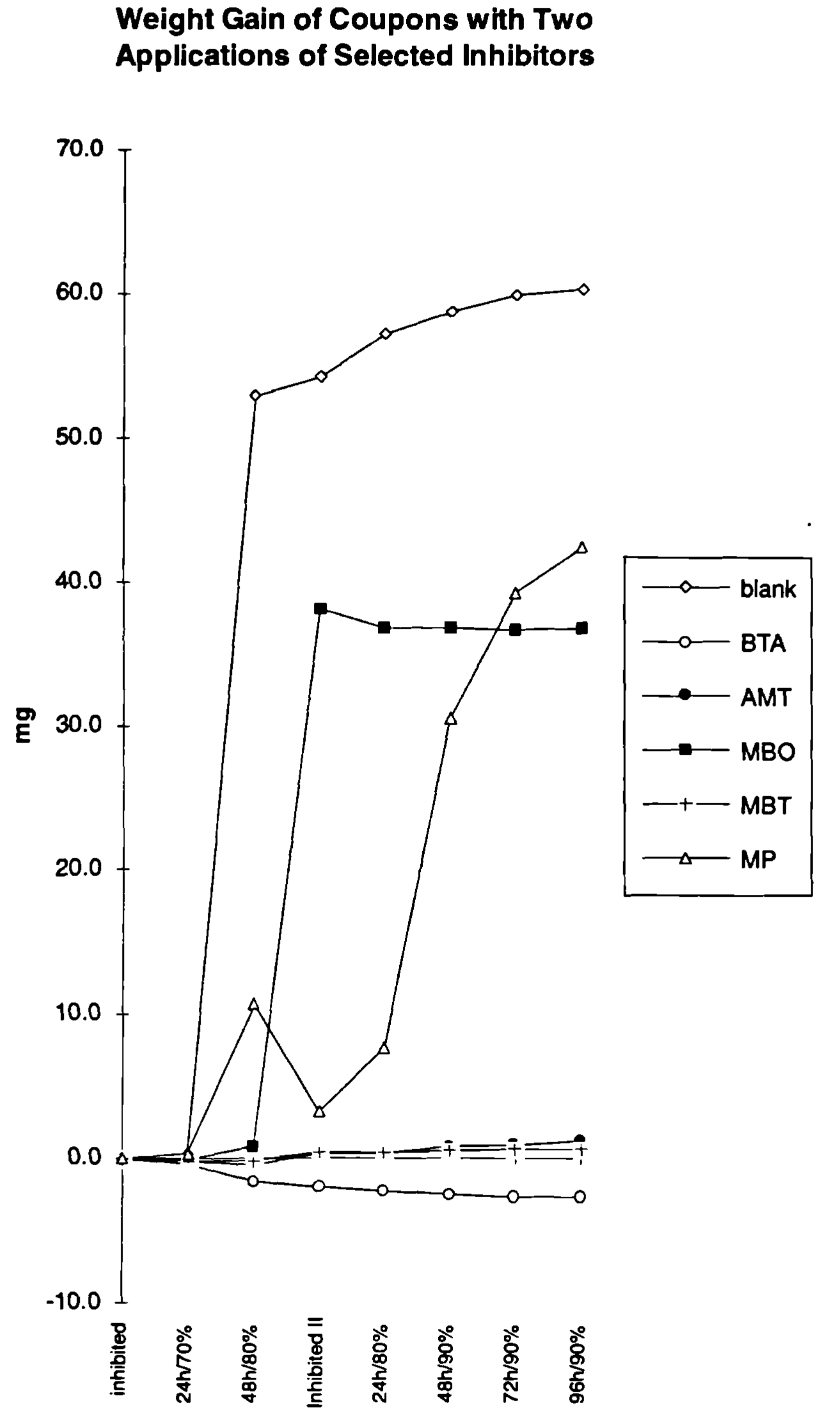


Figure 5. 24 Weight Change of Coupons with two Applications of Inhibitors, and Exposed for 6 days to Selected RH Levels (Initial Weights Within 0.1mg).

5.8 Evaporation of Corrosion Inhibitors

BTA and AP treated coupons lost weight continuously after exposure to elevated RH between 70% and 80%, for 2 to 3 days. A small experiment was performed to assess the evaporation rates of corrosion inhibitors, in an uncomplexed reagent grade form. An increased evaporation of uncomplexed inhibitor molecules might explain the weight loss of BTA and AP in the previous experiment.

Samples of 1g from selected inhibitors were placed in seperate Petrie dishes, and monitored at 20°C/45% RH. The inhibitors were weighed for four days, to an accuracy of ±0.1mg. The weight changes observed are listed in the table below.

in mg	24 hours	48 hours	72 hours	96 hours
BTA	-0.3	-0.2	-0.3	0.9
AMT	-0.3	-0.4	-0.2	-0.3
AP	-17.4	-35.1	-58.9	-75.7
DB	-0.3	-0.4	0.0	-0.1
MBI	0.1	0.2	0.0	0.2
MBO	-1.0	-0.9	-0.8	-0.9
MBT	-0.8	-0.8	-0.5	-0.7
MP	0.7	1.1	0.2	0.6

Table 5. 17 Weight Changes of 1g Samples of Inhibitors Exposed for 4 days 20°C/45% RH.

The data recovered clearly indicated that unreacted AP lost weight by continuous evaporation. BTA lost a minute amount of weight for the first two days and then gained weight. The other inhibitors either gained or lost weight. The maximum weight in the range was +1.1mg and the minimum was -0.9mg.

BTA did not evaporate to a large extent, when in reagent grade form. Maximum evaporation was only about 0.03% by weight, after three days. Coupons treated with BTA lost 20.3%, and coupons covered with AP lost 44.2% of their initial weight gain after inhibitor solution treatment. In both cases the large percentage of weight decrease might, in part, be due to the evaporation of unreacted inhibitor. This is more likely in the case of AP than BTA. However, it is very difficult to estimate the exact weight increase due to the inhibitor treatment, since it is not known how much nantokite was lost in the inhibitor solution. It is difficult then to assess the full extent of inhibitor evaporation on nantokite covered coupons. The results suggest that there must be other parameters governing the weight loss of nantokite covered coupons treated with AP and BTA.

The high evaporation rate of reagent grade AP (7.57% after 4 days) might account for the large weight loss of the AP treated nantokite covered coupons. AP might only complex to a limited extent with the nantokite surface. The high evaporation rate of AP suggests two things. Firstly; AP might be more effective than BTA as a vapour phase inhibitor for the conservation of archaeological artefacts. Secondly; the reason for the low protection rate of AP, when applied in solution, might be due to the evaporation of unreacted AP on the surface of nantokite covered copper coupons. An excess of corrosion inhibitor present on a copper chloride containing surface, might react as a buffer should parts of the inhibitor complex film fail. It was decided not to investigate this aspect any further.

5.9 Long-term Exposure to Raised Relative Humidity and Temperature.

5.9.1 Introduction

The previous experiment has shown that BTA, AMT and MBT are successful inhibitors in preventing corrosion, when nantokite-covered copper coupons are exposed for an extended period of time to high RH. The following experiment monitored the weight loss of the coupons more accurately, after inhibitor treatment. The inhibited coupons were exposed to increasing RH and temperature, to assess the rate of deterioration. The coupons were only treated once with corrosion inhibitors so the initial weight loss could be better observed. Repeated applications in the previous experiment resulted in some weight change due to a second immersion into inhibitor solutions. The coupons were treated, unsing the same testing procedure previously described.

5.9.2 Experimental Procedure

1. air-abrading of coupons with 47 micron glass beads
2. degreasing in ultrasonic bath in 100 ml acetone
3. dried for 5 min at 50°C under infrared lamp, and 10 min cooled in silica-gel buffered polyethylene box
4. weighing to ±0.01 mg
5. immersion in 25 ml of a 1 M solution of cupric chloride in deionised water, 1 day at ambient temperature
6. rinsing in deionised water, 3 x 20 min in 100 ml, quick drying in 200 ml ethanol
7. dried for 5 min at 50°C under infrared lamp
8. exposure to 105°C in oven for 1 hour, and 10 min cooled in silica-gel buffered polyethylene box
9. weighing to ±0.01 mg
10. immersion in 25 ml ethanol/inhibitor. 24 hours at ambient temperature
11. dried for 5 min at 50^{0} C under infrared lamp, and 10 min cooled in silica-gel buffered polyethylene box
12. weighing to ±0.01 mg
13. exposure to gradually increasing RH and Temperature
14. every 24 hours dried for 5 min at 50°C under infrared lamp, and 10 min cooled in silica-gel buffered polyethylene box, and weighing to ±0.01 mg.

5.9.3 Observation and Discussion

The nantokite covered coupons were treated with the following concentrations of inhibitor: 0.25M BTA, 0.01M AMT and 0.25M MBT.

weight change in mg	Inhibited	1 day 10%/20°C
Blank	-1.5	0
BTA	6.9	-0.2
AMT	0.7	-0.2
MBT	10.1	-0.2

Table 5. 18 Weight Change after Inhibition and 1 day at 10% RH and Ambient Temperature.

The table above lists the weight change of coupons after inhibitor treatment, for 1 day at 10% RH and 20°C. The Blank coupons were immersed in reagent grade ethanol, instead of the inhibitor treatment, to compare the corrosion rates. The other coupons were immersed in the inhibitor solutions and they all gained weight, probably due to polymer formation.

One day at low RH caused -0.2mg weight loss in the inhibited coupons (Table 5. 18). This trend of weight loss of inhibited coupons continued. The Blank, AMT and MBT reached their lowest weight after 6 days at 10% RH and ambient temperature. In the following three days the Blank, AMT and MBT showed a continuous weight gain, so it was decided to expose all coupons to 80%RH/20°C. The Blank immediately corroded while AMT and MBT slowly corroded, and BTA continued to loose weight. The weight loss of BTA was observed until the 18th day, when it reached a steady level of 0.017%. In the previous experiment, the maximum weight loss was 0.03% after 6 days. After the 19th day, BTA started to deteriorate when exposed to 85% RH.

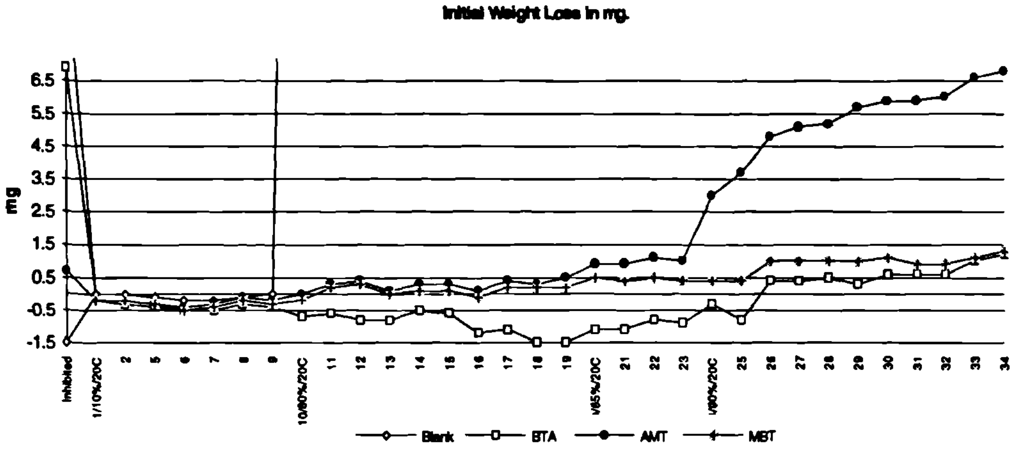


Figure 5. 25 Weight Loss of Inhibited Coupons.

This suggested that BTA film might take approximately 18 days to "cure". At present, in some conservation laboratories, it is common practice to assess the effectiveness of a BTA treatment by exposing the treated objects to a ~95% RH. After 24 hours exposure, an unstable artefact will develop powdery paratacamite on its surface, and will have to be retreated. The present findings might suggest that BTA needs time to fully develop its inhibition potential.

For 52 days coupons were exposed to increasing RH and temperature, to observe their behaviour. BTA and MBT only slowly corroded. 90%RH/20°C caused the AMT coupons to increase drastically in corrosion. The relative humidity and the temperature were changed gradually to increase the corrosion rate (Table 5. 19).

Day	RH %	Temperature in °C
1	10	20
10	80	20
20	85	20
24	90	20
35	95	20
43	95	25
46	95	30
50	100	30

Table 5. 19 Changes in RH and Temperature.

When the experiment was terminated BTA had a corrosion inhibition of 90%, AMT 45% and MBT 95%. These percentages were calculated from a mean of 5 coupons each treated with the same compound. However, not all inhibitors were equally consistent in corrosion protection as can be seen in Figure 5. 26.

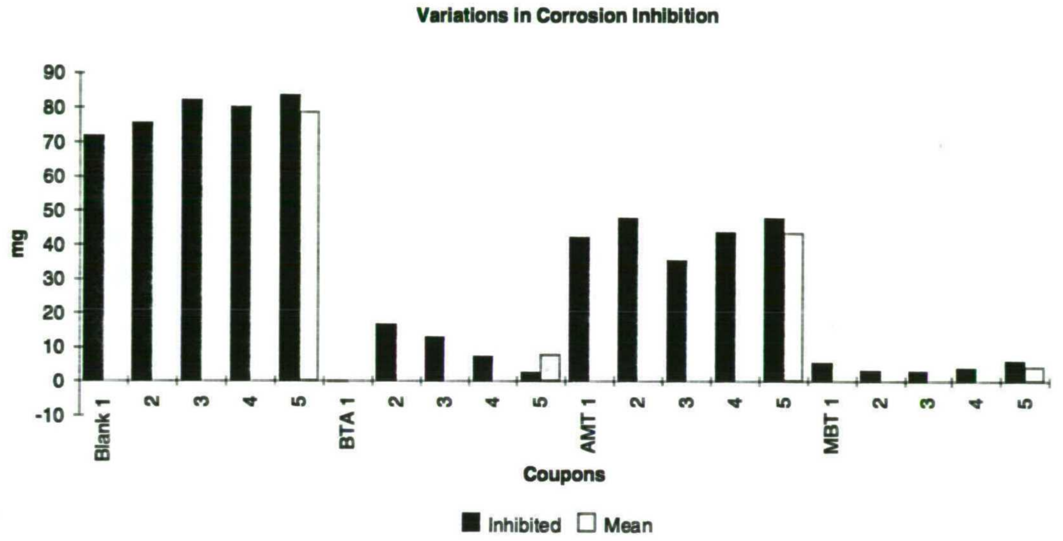


Figure 5. 26 Variations of Corrosion Inhibition on the 52 day.

BTA	inhibition	AMT	inhibition	MBT	inhibition
1	100%	1	47%	1	93%
2	79%	2	39%	2	96%
3	84%	3	55%	3	96%
4	91%	4	45%	4	95%
5	97%	5	39%	5	93%

Table 5. 20 Variations of Corrosion Inhibition on the 52 day

BTA showed some variation in corrosion protection rate (100-79%). BTA coupon 1 did not show a weight increase due to corrosion. This has not been observed in previous experiments. MBT had a much more even corrosion rate, when compared with BTA coupons. This suggested, that a treatment with MBT may be more likely to achieve uniform results. The variable protection rate further suggests that specimens treated with BTA are more likely to result in an unstable film than the coupons treated with MBT. Artefacts containing extensive amounts of chlorides, should be treated with MBT. Added advantages include better corrosion resistance at 95% RH and ambient temperature.

The weight change in mg is plotted in Figure 5. 27. There was an almost linear weight increase of the Blank coupons when exposed to elevated RH. The AMT coupon seemed to be stable below 90% RH at room temperature. However with increasing RH, AMT deteriorated rapidly. BTA and MBT seemed almost equally stable below 95% RH/20°C, and above this threshold MBT seemed to be a better inhibitor. Figure 5. 28 illustrates the corrosion inhibition in percent, and shows the poor results with of AMT under these conditions.

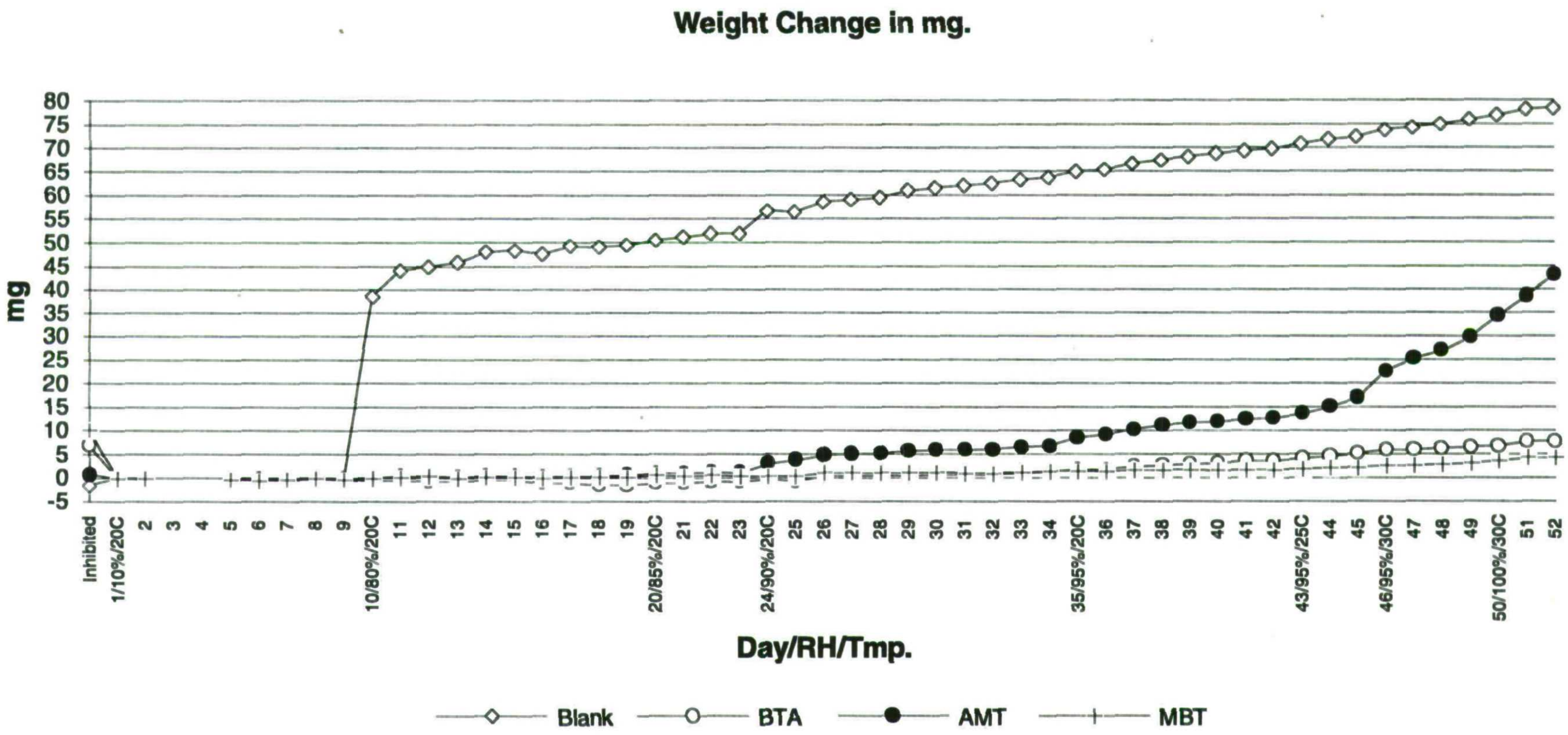


Figure 5. 27 Weight Change of Coupons in mg.

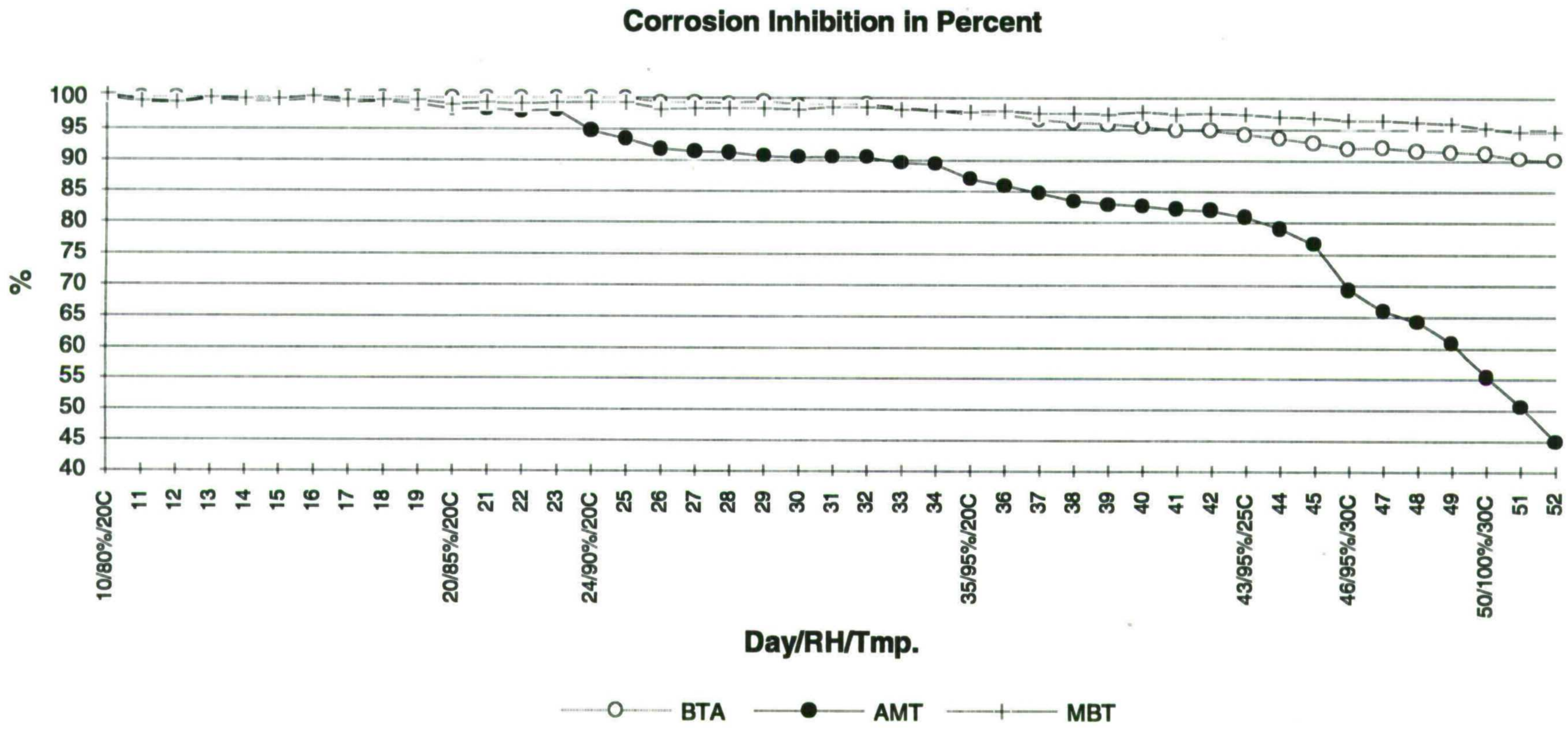


Figure 5. 28 Corrosion Inhibition in Percent.

5.10 BTA and its Corrosion Inhibition After Prolonged Drying.

5.10.1 Introduction

The intention of the following experiment was to determine the effectiveness of BTA after varying periods of drying treated nantokite coupons. In the previous experiment it was observed that BTA lost weight when exposed to an RH lower than 85% at 20°C. This was in conjunction with an improved corrosion inhibition after 52 days. In order to establish the correlation of variably dried BTA treated coupons and improved corrosion inhibition, the following experiment attempted to evaluate various drying times of BTA treated coupons versus improved corrosion inhibition.

5.10.2 Experimental Procedure

Copper coupons were treated as described in section 5.9.2. The coupons were divided into four batches of five coupons. The first batch of BTA treated coupons was dried for 20 days, and the second batch for 5 days at 10% RH and ambient temperature. The third batch of BTA treated coupons, and a batch of blanks were not dried. All coupons were exposed at the same time to 95% RH at 20°C, for 24, 48 and 96 hours.

5.10.3 Observation and Discussion

After corrosion inhibition and drying all BTA inhibited coupons appeared the same visually. Furthermore, no weight loss was observed during the drying period.

This suggests that the weight loss of coupons in previous experiments was probably due to environmental differences in test equipment, for example changes, of temperature in the laboratory. Comparing the experiments 5.3, 5.4 and 5.10, the only change of experimental procedure can be found in the use of a different corrosion chamber. For experiment 5.3 and 5.4, the corrosion chamber was a sealed acrylic box. The relative humidity was produced by means of a glass beaker filled with water, and the RH produced was approximately 95%. The temperature could not be monitored and varied between 16°C and 24°C. From experiment 5.6 onwards, an environmental chamber with humidity and temperature control was available.

weight change in mg	**24 hours**	**48 hours**	**96 hours**
BTA/20 Days	-1.1	1	2.4
BTA/5 Days	-0.8	0.4	1.3
BTA/0 Day	-0.8	-0.2	1.0
Blank	85.1	86.8	87.4
corrosion inhibition %	**24 hours**	**48 hours**	**96 hours**
BTA/20 Days	100	99	97
BTA/5 Days	100	~100	99
BTA/0 Day	100	100	99

Table 5. 21 BTA Dried for 20, 5 and 0 days

Table 5. 21 presents the weight gain in mg during the exposure to 95% RH at 20°C, and the corrosion inhibition was calculated in %. All BTA treated coupons displayed very little corrosion during 96 hours at 95% RH. The small variations in weight change were probably due to variations in temperature during weighing. This suggests, that the "drying process" suggested for BTA is a minor factor for an increase in corrosion protection.

Experiment	24 hours	48 hours	equipment	Temperature
5.3	76%	48%	acrylic chamber	fluctuating 16-24°C
5.4	79%	29%	acrylic chamber	fluctuating 16-24°C
5.10	100%	99%	environmental chamber	20°C

Table 5. 22 Difference of Corrosion Inhibition Percent of BTA Inhibited Coupons in Various Experiments.

Due to unidentified variables in the experimental procedure, BTA developed different amounts of corrosion protection in the experiments listed in Table 5. 22. The variation in corrosion protection in the three experiments was probably due to variations in temperature and RH. The temperature fluctuation in the acrylic chamber (16-24°C) probably had two effects. Firstly, the condensation of water on to the coupons during a drop in temperature and secondly, the expansion and contraction of the BTA-copper polymer film.

A decrease in temperature caused condensation of water in the acrylic chamber. A small amount of water condensed not only on the walls of the chamber, but also on the surface of the coupons. Water on the coupons was not only created by the 95% RH, but also by an increase or decrease in temperature, and the evaporation and condensation of water.

Since there was a small amount of water, it was expected that the pH of the water would be correspondingly low. This low pH would contribute to the breakdown of the inhibitor film, resulting in relatively poor performance.

5.11 Summary of Experiments

The overall comparison of the experiments listed in chapter 5, made it evident that the results of the various experiments only gave an indication of corrosion inhibition performance. As expected, the experiments did not have a high degree of reproducibility. This is due to:

- fluctuations in temperature
- fluctuations in relative humidity
- fluctuations in exposure times
- variations in film properties.

Fluctuations in temperature as related to RH were probably the most significant factors, as explained in the previous section. In the case of the acrylic chamber used, the temperature influenced the RH changes greatly. Variations in exposure time to the corrosive environments are relevant, since an increase in exposure time increases corrosion. However, even in this case, temperature was a more important factor. An increased exposure time, at a high temperature, increases the corrosion rate even further. This supported the initial decision to compare all inhibitors in one experiment, since parameters such as temperature, relative humidity and time were the same for all specimens

The data of different experiments can only be compared with due caution. Small environmental fluctuations affected the different experiments, likewise corrosion tests on copper and coper alloys are recognised to have low reproducibility. Nevertheless, the experiments demonstrated that nantokite covered coupons are an adequate testing procedure, revealing general trends of inhibition percents, when comparing different corrosion inhibitors. The three best performing corrosion inhibitors were BTA, AMT and MBT. The other corrosion inhibitors are in general not very effective at 95% relative humidity. AP, DB, MBI and MBO can be effective corrosion inhibitors when applied in high concentration, between 0.1-0.25M. However they also result in thick inhibitor-copper polymer films. These films are effective at protecting against corrosion, but disfigure the nantokite surface. Such an inhibitor film would be expected to cause extreme visual alterations on an archaeological copper artefact. This would not be acceptable for conservation. MP is not a good corrosion inhibitor in any concentration.

The corrosion inhibitor films formed on MBI, MBO, MBT and MP in experiment 5.2, can be removed with an ethanol soaked cotton swab, suggesting poor stability of the inhibitor film. This removal of inhibitor film is not acceptable for conservation, since artefacts are generally coated after treatment. Lacquering the artefact with a brush could damage the inhibitor film covering the nantokite, but nevertheless the inert coating could in part still serve to prevent corrosion

In experiment 5.6, AP did not corrode until exposed to 80% RH at 20°C, AP and MP corroded greatly between 80% and 90% RH at 20°C, and MBO started to corrode extensively between 90% and 100% RH at 20°C. MBI was either not effective or formed an unsightly white film. DB was not effective at all.

Chapter 6

Atomic Absorption Spectrophotometry of Copper in Corrosion Inhibitor Solutions

6.1 Introduction

The following experiment was designed to determine the extent of copper dissolution from copper minerals in corrosion inhibiting solutions. Benzotriazole (BTA) is a mild acid, so to what extent can it cause copper dissolution? When an archaeological artefact is treated with a corrosion inhibitor, it is common practice to immerse the object in the corrosion inhibiting solution for 24 hours. During this time it is thought that the inhibitor reacts with the surface of the artefact, complexing with copper ions to form a polymer film covering the corrosion surface. Until now no attempt has been made to establish how much copper is lost into the solution during the inhibition treatment. This copper dissolution from various corrosion minerals could actually indicate a partial deterioration of a surface due to corrosion inhibiting solutions.

Ganorkar (1988) observed that nantokite was complexed into solution, during 2-amino-5-mercapto-1,3,4-thiadiazole (AMT) corrosion inhibitor treatment of chloride containing artefacts.

The formation of a nantokite complex, observed by Ganorkar, suggested to the following questions for the research presented here:

- Which new inhibitors react with what mineral to leach copper into solution?
- What minerals are mainly complexed into solution?
- How much of a specific mineral goes into solution?

For the following experiment it was thought feasible to use copper and copper minerals in the inhibitor solution as a means of quantifying mineral dissolution rates. Several techniques were considered to quantify the copper in inhibitor solutions. Atomic Absorption Spectrophotometry (AAS) was thought the most feasible, since the other techniques, such as the titration methods described by Vogel (1989), and the titration kits supplied by all major chemical suppliers (Merck, Aldrich, Fluka) had drawbacks. It was established that the available titration methods used metallic compounds, as indicators. These metals might react with the inhibitor in the solution to be analysed. This would be expected, for example, in the silver nitrate chloride test described by Vogel (1989). Later it was discovered that in many cases the new inhibitors also had a lower solubility in water than ethanol. All inhibitor treatments were applied in ethanol: the titration methods however, were water based. Mixing water with the inhibitor solutions caused a precipitation of the inhibitors, rendering the copper titration inappropriate.

6.2 Experimental Procedure:

For the following experiments archaeological artefacts could not be used, since the effects of the various inhibitor treatments were unknown. An artificial scenario was created to determine the probable "leaching" of copper, from an archaeological patinated copper surface treated in an inhibitor solution. The layers of an archaeological corrosion surface are commonly assumed to be mainly malachite, cuprite, nantokite and copper. In the following experiment the minerals were used as powders in a reagent grade form. The exact particle sizes of the mineral powders were not known. The size range of the powder would be relevant in regard to the ratio of treated surface area, versus inhibitor concentration in solution. Since the particle size was not determined for the reagent powders as received, it could not be taken into account. The copper was used in the form of 99.9% pure copper turnings. Reagent grade copper powder could not be used due to immediate oxidation of the powder when in contact with the atmosphere. In the experiments 0.64g copper turnings, 0.72g cuprite, 1.1g malachite and 1g nantokite mineral powder, were each immersed in 10 ml reagent grade ethanol and inhibitor solutions. The inhibitor concentrations are given in the table below:

BTA	0.25M	**MBI**	0.1M
AMT	0.068 saturated solution	**MBO**	0.1M
AP	0.1M	**MBT**	0.1M
DB	0.1M	**MP**	0.005M saturated solution

Table 6. 1 Inhbitor Concentrations

Previous experiments had shown that the inhibition efficiency of most of the inhibitors were best in the above concentrations. It was also assumed that increased inhibitor concentration would cause increased copper inhibitor complex and might result in higher copper dissolution.

To slow ethanol evaporation, the minerals were exposed to 10ml inhibitor solutions in a covered 100ml pyrex glass beaker at room temperature (17-22 °C) for 24 hours. 5 replicates of each inhibitor-mineral solution were undertaken, to observe the reproducibility of the data.

Each mineral was also exposed for 24 hours to reagent grade ethanol as a blank. This was done to monitor the leaching of copper into an inhibitor free solution, so as to be able to attribute the amount of copper in each inhibitor solution to the effect of inhibitor-mineral interaction.

After 24 hours in inhibitor solution, the minerals were filtered with grade one filter-paper. The solution was then diluted to lower the copper concentration and bring the concentration into an appropriate range for AAS. The inhibitor-mineral solutions were diluted with a solution of 75vol% deionised water and 25vol% pH10 Buffer (BDH). There was no copper detected in the buffer when analysed by AAS.

The atomic absorption spectrophotometer used was a Pye Unicam SP9, software used was Unicam 9178 Atomic Absorption Data Station V1.7 software. A 100mm burner head was used. The detection band for copper was 324.8 nm. These 3 readings of 2 seconds were taken on each solution. Four standard copper solutions were prepared for each inhibitor used containing pH10 buffer, deionised water, ethanol and corrosion inhibitor. Each copper standard had to contain the same inhibitor as the solution being analysed. Copper standards were prepared to calibrate the instrument at concentrations of 5, 10, 20, and 40ppm

6.3 Experimental Observations

The inhibitors were exposed for 24 hours to copper, cuprite, malachite and nantokite. The filtrate had to be diluted with deionised water, since ethanol should not be run straight through the AAS. The flame would be too unstable, rendering the readings inaccurate (Perkin Elemer technical support, personal communication).

When diluting the inhibitor filtrate with deionised water a precipitation of inhibitor was observed. As discussed in a previous chapter, BTA was known to produce a larger polymer structure in acidic conditions. It was assumed that an increase in pH would minimise the polymerisation. This assumption was confirmed when ammonia was added to an inhibitor/deionised water solution. The ammonia however evaporated easily when flowing through the warm nebuliser in the AAS, causing the fine nozzle of the nebuliser to block. Adding pH 10 buffer into the deionised water stopped the inhibitors from polymerizing in the nebuliser and burner of the AAS. The buffer was therefore added to all deionised water used during the experiment. The AAS was rinsed during analysis with a buffer/deionised water solution. A rinsing with deionised water could have caused a percipitation of inhibitor in the nebuliser and mixing chamber.

There was alsmost 0% dissolution of metallic copper in the selected inhibitor solutions, which were in contact with the copper turnings. The low copper concentration suggested that the inhibitor solutions did little damage to the metallic copper. There were only traces of copper detected in DB, MBI, MBO solutions that had been in contact with the metal, suggesting a negligible amount of etching. These small amounts of copper were judged negligible, and considered not to increase excessively the deterioration of a copper surface due to the inhibitor.

The inhibition rate of copper by inhibitors was as follows:

BTA, AMT, AP, MBT, > BLANK > MP > MBO > MBI >DB.

Cuprite however might be slightly attacked by MBI. After treating cuprite the MBI solution contained 166ppm of copper. This represented about 0.26% copper of the cuprite used in the initial mixture. AP (0.06%), DB (0.03%) and MBO (0.15%) were the only other inhibitors that suggested a slight etching of cuprite. The etching by AP, and DB were thought to be negligible.

When filtering the cuprite-ethanol blank, there was an average leaching of 15ppm of copper detected. This was considered improbable, since ethanol should not dissolve any cuprite. The filtrate was filtered once more. The following copper ppm count was 3ppm. This suggested that the cuprite particle size was too small to be retained by the filter-paper grade one. Since there was no visible inhibitor-copper polymer in the filter paper, or in the inhibitor solution, it was thought that there was a polymer formation on the cuprite powder. Since all cuprite-inhibitor solutions were only filtered once during the experiment, all cuprite-inhibitor data was compared to the once filtered cuprite-ethanol Blank.

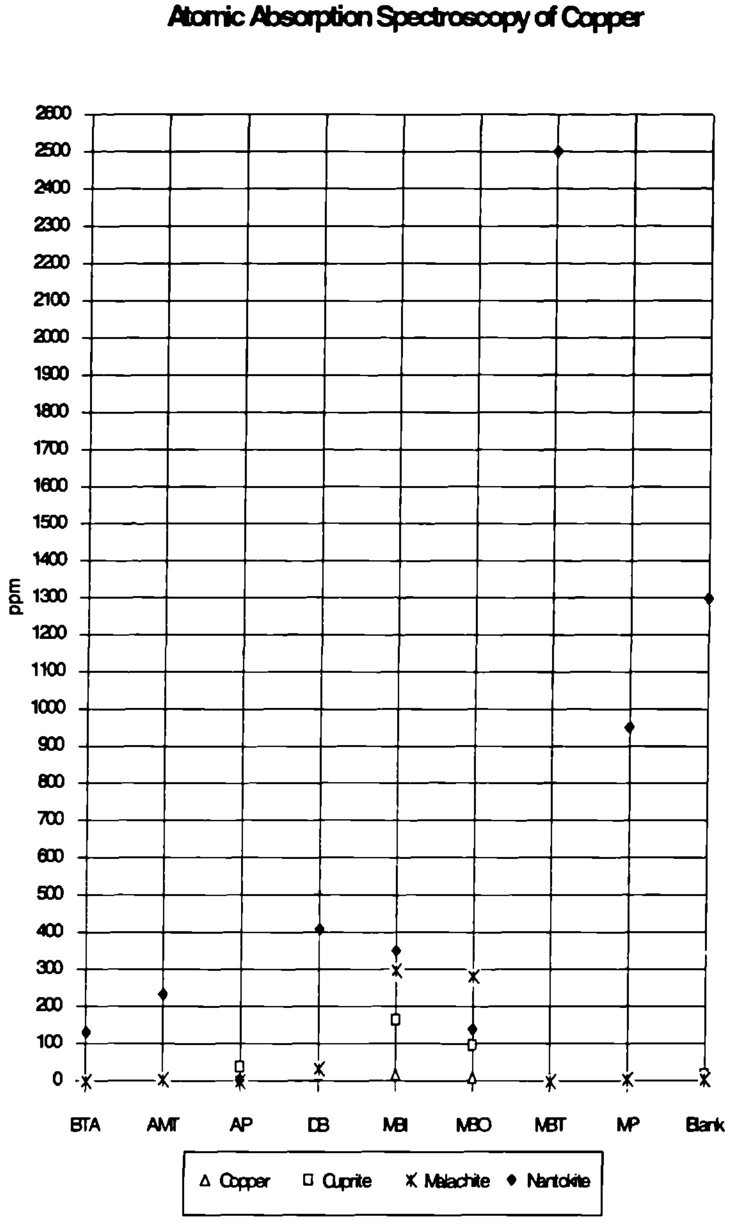


Figure 6. 1 Atomic Absorbtion Cu Count in ppm.

Dissolution %	BTA	AMT	AP	DB	MBI	MBO	MBT	MP	Blank
Copper	0	0	0	0.03	0.03	0.02	0	0	0
Cuprite	0	0	0.06	0.03	0.26	0.15	0	0	0.02
Malachite	0	0	0	0.05	0.46	0.44	0	0	0
Nantokite	0.2	0.36	0.01	0.64	0.55	0.22	3.93	1.5	2.04

Table 6. 2 Copper Dissolution in %.

MEAN ppm	BTA	AMT	AP	DB	MBI	MBO	MBT	MP	Blank
Copper	0	0	0	17	16	10	0	2	1
Cuprite	1	0	36	20	166	95	1	2	15
Malachite	0	1	0	30	295	281	0	2	2
Nantokite	129	231	4	410	352	138	2501	952	1300

Table 6. 3 Copper Dissolution in ppm.

The cuprite-inhibitor data indicated that AP(36ppm), DB(20ppm), MBI (160ppm) and MBO (95ppm) had a copper dissolution higher than 15ppm (Blank), indicating an etching of cuprite. BTA (1ppm), AMT (0ppm), MBT (1ppm) and MP (2ppm) all had a copper count between 0 and 2 ppm (see Table 6. 3) suggesting little complexing reaction with the cuprite, rendering the polymer formed large enough to be retained by the grade one filter-paper, or the copper was complexed onto the cuprite grains.

The protection rate of cuprite by inhibitors was:

AMT > BTA, MBT > MP > Blank > DB > AP > MBO > MBI.

Malachite reacted with MBI and MBO solutions. The resulting copper concentration in the inhibitor solutions after contact with malachite were 295ppm and 281ppm respectively. DB dissolved 0.05%, MBI 0.46%, and MBO 0.44% copper of the original malachite used in the inhibitor solution. The other inhibitors performed well and protected malachite from dissolution.

The protection rate of malachite by inhibitors was:

BTA, AP, MBT > AMT > MP, BLANK > DB > MBO > MBI.

Nantokite had the highest dissolution rate of copper in the selected inhibitor solutions. The largest amount of copper detected was in the MBT solution (2501ppm): 3.93% of mineral went in solution. It was the highest copper count detected during the whole experiment. Ethanol dissolved 2.04% (1300ppm) of the nantokite. This is probably due to the affinity of the mineral for water present in ethanol. Cuprous chloride has a solubility of only 0.006g per 100ml water at room temperature (Scott, 1990).

Nantokite was protected by inhibitors as follows:

AP > BTA >MBO > AMT >MBI > DB > MP > BLANK > MBT.

The tables 6. 2 and 6. 3 list the dissolution rate of copper in percent and ppm. The percentage calculation is based on the dry weight of mineral powder used. The dissolution of copper was expressed as percentage of the original weight of mineral powder used. It should be noted that the surfaces of the mineral grains used are vastly larger than the surface area on an artefact, when it is exposed to a corrosion inhibitor. Thus, reactions on corroded artefacts should be less.

6.4 Discussion

Except for nantokite, the percentage dissolution rate showed clearly that there was no significant deterioration in any of the other mineral powders exposed to the inhibitors. Nantokite was etched in almost all instances (see tables 6.2, 6.3). The inhibitor which might suggest a complexing of nantokite into the inhibitor solutions was MBT, however only 3.93% of the original nantokite went into solution. This does not take into account, an excess of inhibitor in the inhibiting solution, nor the inhibitor-copper complex formation with other mineral species present on the surface.

Ganorkar (1988) indicated the complex formation of copper chlorides into an AMT solution. The AAS analysis showed that there was no excessive copper depletion from nantokite when treated with AMT. AMT-nantokite solutions had only 0.36% copper depletion compared to the much higher dissolution rate of 3.93% when treated with MBT.

AP showed a very low effectiveness in inhibiting nantokite oxidation on copper coupons exposed to an elevated RH. However, during the AAS experiments it was discovered that all minerals were protected by AP in ethanol solution, even the reactive nantokite did not suffer significant copper depletion (4ppm). These findings suggest that, AP might be added effectively to water-logged composite artefacts from marine environments containing copper. There are cases where copper is attached to, for example water-logged wood or water-logged leather. The addition of AP might stabilise the corroding copper and prevent staining of the organic material by copper chlorides. The addition of AP to water-logged material has not yet been tried, but could be researched further. AP could prevent further corrosion of copper but also damage associated materials, such as the organics.

Chapter 7

Minerals Treated with Corrosion Inhibitors and their Colour Changes

7.1 Introduction

Previous experimental work undertaken identified the darkening of mineralised surfaces on copper alloy artefacts treated with Benzotriazole (BTA) (Faltermeier, 1992, 17). This change in surface appearance has not been described qualitatively in the past. There are several reasons for this. Photographic records taken before and after a conservation treatment are usually in black and white. The chance of noticing a slight change in colour on a colour photograph is greater, but not very likely. Rarely is a colour picture taken with a colour reference card (supplied by most colour film producing companies). This attitude towards record keeping in private and public collections, has resulted in a low quality of colour recording for copper and copper alloy artefacts. Conservation records of the past do not assess colour changes due to conservation treatments.

The colour changes due to BTA treatments, have not been accurately assessed by qualitative means. Describing slight alterations in colour poses many difficulties when evaluating experimental work. In the following investigations an attempt was made to qualify and quantify colour changes induced by corrosion inhibitors in the most precise manner possible. Colour changes can not be objectively determined by an observer.

Colour can be perceived differently by each observer. As a simple trial, five people were asked to describe mineral samples treated with different inhibitors, according to their brightness and darkness. This small exercise was undertaken to gain some insight, into how people observe colours differently. The five observers easily identified large colour differences, but the smaller changes were more difficult to recognise. Changes in the light source, the distance of the light source and other factors clearly changed the perception of colour samples.

The Munsell Colour System is used to name and describe colours of soil and ceramic sherds from archaeological contexts. The colour change is qualified by comparing specimens with a set of coloured reference chips. The Munsell colour charts, used in the Institute of Archaeology, only cover a small range of earth and ceramic colours. This range was too narrow for the evaluation of copper minerals. The Munsell Colour Chart is out of print, and the system in general is inadequate. The use of a colour system, hardly accessible to research, limits the accessibility of the data to other researchers. Another drawback in this type of colour matching was the inaccuracy introduced when visually comparing colour chips with powdered minerals. This was largely dependent on the observers'colour perception, and changes in light source.

The discussion of these problems with Dr.D. Saunders (National Gallery, London) led to the application of a colorimeter. This analytical tool is often used at the National Gallery, to compare paint and varnishes of paintings. Schilling (1993) used such an instrument for colour measurements in the tomb of Nefertari in Egypt.

One obstacle encountered when comparing colours, is the choice of descriptive words.

A colour measuring device such as a colorimeter, assigning a numerical value to colour, avoids individual colour perception, results in a higher accuracy, and reproducibility of colour values. The Minolta Chroma Meter CR-200, used in the National Gallery for colour matching, expresses colours in precise numerical values. The instrument relies on modern optoelectronic technology, completely avoiding the subjective variations between individual observers. This tool was ideal for measuring the small variations in colour observed on copper minerals treated with inhibitors.

The Minolta Chroma Meter CR-200 enables accurate measurements to be made of chromaticity (colour and its saturation) and illuminance (light or darkness of a colour) of the surface analysed. It allows a quick objective comparison of samples. The colorimeter uses a diffused illumination and measures the sample in a 0° angle. The consistent illumination is achieved with a pulsed xenon arc lamp inside a mixing chamber, resulting in a diffused lighting over the sample area. Three photocells read the colour. The area measured by the colorimeter is Ø 8mm (Minolta Ltd., 1989, 3). The colorimeter is calibrated with a standardised white ceramic tile provided by Minolta.

The colour can be expressed in the L*a*b*, L*C*H*, or the other older Munsell notations colour system. L*a*b* (CIELAB) is a uniform colour "space" recommended in 1976 by CIE (Commission Internationale de l'Eclairage or

International Commission on Illumination). This is the most widely applied colour standard used in industry today. The CIE colour system closely represents perceived colour and colour differences. Its main advantage is the use of a standardised light source and a standard observer (Billmeyer and Saltzman, 1981, 34). Colour values change under different light sources, due to a difference in the wave-length of each light source.

CIE (1976) introduced the CIELAB system L*a*b*. This system attributes to every colour a numerical value. A positive L* defines brightness and a negative value the darkness of a specimen.

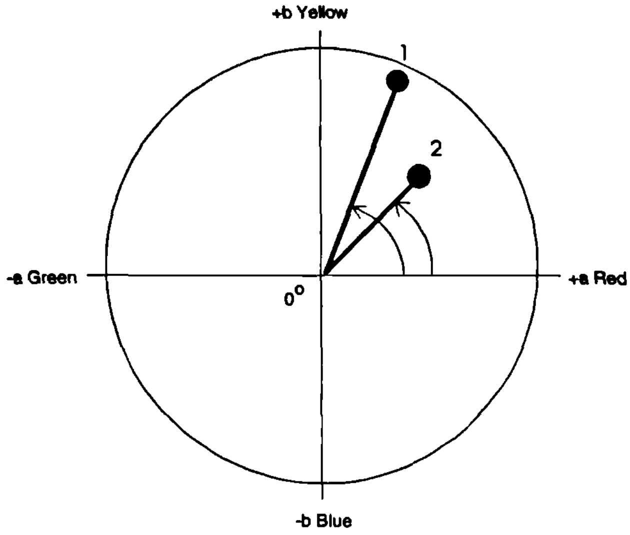
Hue value (H*) defines the quality of a colour usually described by words such as red, yellow, green, blue etc. The Hue angle is measured in degrees, starting with h_{ab}= 0 at +a* (red) and increases anticlockwise (figure 7.1). Hue values are given in terms of a* and b*. L*, a* and b* are orthogonal axes, where positive values of a* represent a red hue and a negative a*, a green hue. Positive b* values are yellows and negative b* are blue values.

Chroma (C*) is used to describe the brilliance of a colour. The lower the Chroma value the duller the specimen, the higher a value the brighter a colour. Chroma is defined as

$C^* = (a^{*2} + b^{*2})^{1/2}$ (Billmeyer and Saltzman, 1981, 34-65).

H*	Hue value, describing type of colour	**C***	brilliance of colour
+a*	red hue	**+b***	yellow hue
-a*	green hue	**-b***	blue hue
L*	Lightness	**E***	overall colour

Table 7. 1 Symbols for Colour Evaluation



(adapted from Billmeyer+Saltzman, 1981)

Figure 7. 1 CIELAB System

Point 1 in the diagram has a larger Hue angle than point 2. The length of the radius indicates the chromaticity of the specimen. The radius to point 1 is longer than the radius of point 2 so it has a higher chroma.

The colour matching with the colorimeter allows a plotting of the different L*a*b* values in the format of a chart, more clearly indicating specific changes in colour. This allows the numerical identification of shifts in Hue and chroma values, pinpointing particular regions of colour changes

To enable the overall evaluation of colour changes between specimens, mathematical equations can be applied. The CIELAB colour difference equation is mainly used for colourants in paints, plastics, textiles and defines ΔE*(overall colour change).

$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ (Billmeyer and Saltzman, 1981, 103).

Calculation of ΔE* has the drawback that some detailed information is no longer reported, such as ΔL*, Δa*, Δb*. To avoid the loss of this complex set of data, two diagrams of the same sets of data are given below. The first identifies ΔL* (lightness), Δa* (red-green), Δb* (blue-yellow) of the minerals treated with different inhibitors. The second plots the calculated ΔE* (overall colour change). ΔE* represents the initial evaluation of a conservation treatment. It documents the overall change of a conservation treatment, indicating the overall change of surface appearance. After this initial ranking, more specific quantification of detailed changes in colour can be made.

Modern colour measuring devices are able to calculate colour differences to one or two decimal places of CIELAB units, where as observers cannot detect colour differences beyond the first decimal point. This fact should be considered when the colour changes for corrosion inhibitors are evaluated. This very important point is mentioned by Billmeyer and Saltzman (1981,105). However, Minolta Ltd. revealed that a professional can detect differences in a ΔE* to 0.3 and a normal viewer ΔE* to 0.65 (Minolta Ltd. personal communication 1995)

It was not expected that a corrosion inhibitor could be found, which did not induce a limited amount of surface colour change in copper corrosion products. It is recognised that all industrial inhibitors react with either copper I or copper II species or in some cases both. The complex formation with these copper ions, and the formation of an inhibitor-copper polymer suggest that a colour change is to be expected following treatment with inhibitors. However the extent of such colour changes could not be readily predicted, and the surface variations may often be hardly detectable to an observer.

7.2 Experimental Work

To evaluate the colour changes induced by corrosion inhibitors, eight selected inhibitors (table 7.2) were dissolved in 50ml of ethanol and exposed to 0.005M dry weight of cuprite, malachite and nantokite.

Inhibitor	molar concentration	Inhibitor	molar concentration
BTA	0.25	MBI	0.1
AMT	0.068	MBO	0.1
AP	0.1	MBT	0.1
DB	0.1	MP	0.005

Table 7. 2 Inhibitor Concentrations

Mineral powders were immersed for 24 hours in the inhibitor-ethanol solution. Treatments of 24 hours are usually used as a standard duration for an inhibitor treatment on an average artefact with a small amount of chlorides in its surface. This is repeated until the object is stabilised and no further active chloride corrosion is detectable. A second set of mineral powders was treated twice for 24 hours with a new solution each day (here after referred to as the 48 hour treatment).

A blank ethanol/mineral sample was included in the experiment. An extra group of minerals was treated for 48 hours with a solution of BTA dissolved in IMS, to indicate colour changes caused by IMS. Most conservation laboratories apply BTA in IMS. IMS is used because it is cheaper than ethanol. To this point there has been no study undertaken evaluating colour changes introduced by IMS. IMS is known to have traces of impurities, it is suggested that these impurities might react with the inhibitor, and so take part in the polymer formation on an artefact. Should IMS enhance colour differences, it should be replaced with ethanol.

After 24 and 48 hour exposures to the mineral, the inhibitor solutions were filtered with filter paper (grade one) and dried in an oven at 50°C for 24 hours. The oven drying should prevent further corrosion due to water present in the mineral slurry. The powder was then placed into a desiccator filled with Silica-gel prior to measurement with the colorimeter.

To better simulate the surface texture of the inhibitor on treated mineral powders, an attempt was made to produce pellets of the treated powder in a hydraulic press. Compact pellets were thought to have a more even surface texture, resembling more closely an archaeological patina. This also might have improved the accuracy of the colour measurements. To produce pellets proved impossibly difficult. The pellets crumbled when attempting to remove them from the press. A binder could not be used, since this would introduce morphological changes, interfering with the colour.

To measure the colour differences the treated mineral powders were spread over filter paper as an even covering and analysed with the colorimeter. The measurement was repeated two to three times to ensure an accurate reading of the surface, and to obtain an average measurement. The tables below indicate the average colour differences of ΔL^*, Δa^*, Δb^* and ΔE^*. The tables are divided into the three main minerals found on chloride infested copper objects, cuprite, malachite and nantokite, and there is a separate table for ΔE*, the overall colour change.

7.3 Experimental Observations

The data resulting from the colorimeter measurements are all calibrated on pure reagent grade mineral powders purchased from Aldrich supplies. ΔL*,Δa*, Δb*, and ΔE* values were calculated from the mineral powder rather than the mineral/ethanol powder. Using mineral/ethanol rather than pure mineral would have confused the comparison since the initial mineral colour would not be assessed.

It was found that the minerals change colour simply when treated with ethanol. This might be due to corrosion in ethanol. Cuprite had a change of 1ΔE* after 24 hours and 1.2ΔE* after 48 hours treatment, Malachite 0.3ΔE* and 1ΔE*, and Nantokite 23.1ΔE* and 16.4ΔE* during one and two 24 hour treatments. These variations in ΔE* after 1 and 2 days treatment, support the use of untreated mineral powder as reference material. Calculating the ΔE* values from the untreated material allowed standardisation of the data and avoided the introduction of experimental errors or changes in corrosion rates, by mineral/ethanol samples.

Considering the shifts in Hue values in the following experiment, they are expressed in positive and negative values of a* and b*. Δa* and Δb* are referred to as changes in red-green and blue-yellow. They do not indicate complete changes form red to green or blue to yellow, only small changes in tone.

7.3.1 Cuprite

After a 24 hour treatment, the colorimeter clearly detected changes in the appearance of the cuprite in all specimens tested. DB and AMT caused the largest shift in colour, according to the calculated ΔE^* values. DB had the most drastic ΔE^*(12.8) change. DB darkened the cuprite most, by -10 ΔL^*, and changed the Δa^* (-5.2), and Δb (4.8) values considerably, causing a slight colour shift to green-blue. AMT caused a darkening of cuprite (-4.7 ΔL^*), and the largest shift to the yellow region (-5.9 Δa^*) over 24hrs. BTA had an average of 5ΔE^*. This is mainly due to a darkening of the cuprite, but there is also a distinctive change in Δa^* (-2.8). AP (0.5 ΔE^*) and MP (1.4 ΔE^*) caused the smallest change in colour.

After two 24 hour inhibitor treatments the largest colour changes were in DB (11.7 ΔE^*) and MBI (13.7 ΔE^*). DB darkened and had a shift to yellow-green similar to the 24 hour treatment. MBI had a large ΔE^* shift, mainly due to a dramatic shift to a dark(-7.4ΔL^*) green (Δ-10.8a^*) spectrum.

The data indicates that BTA/IMS (5.8ΔE^*) caused a slightly greater colour change than BTA/ethanol (5.6ΔE^*). BTA/IMS darkened the cuprite by -0.3ΔL^* more than BTA/ethanol. According to Billmeyer and Saltzman (1981), this is already in a visually detectable range, although the difference is very slight.

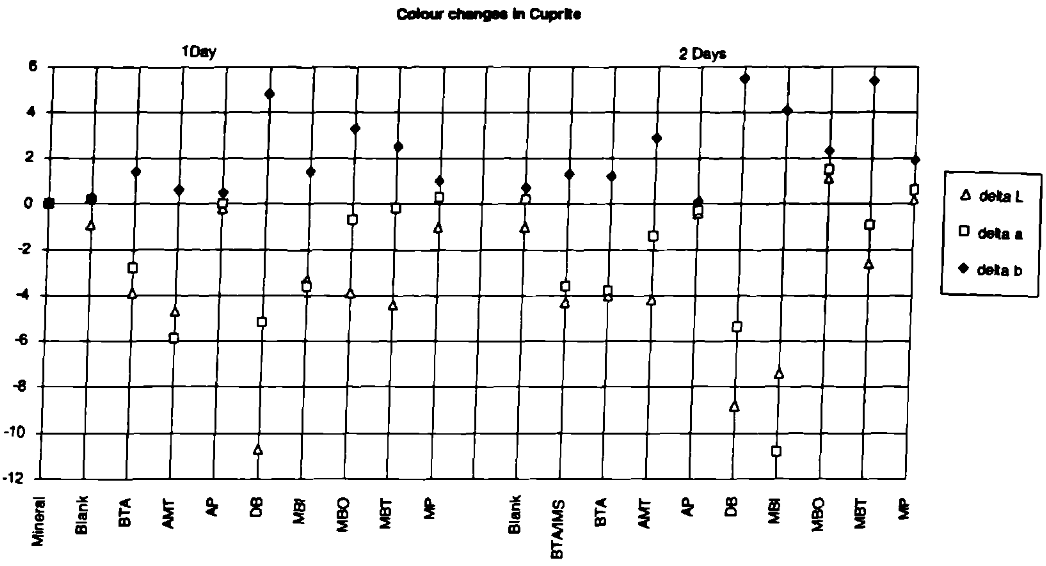


Figure 7. 2 ΔL*, Δa*, and Δb* for Cuprite

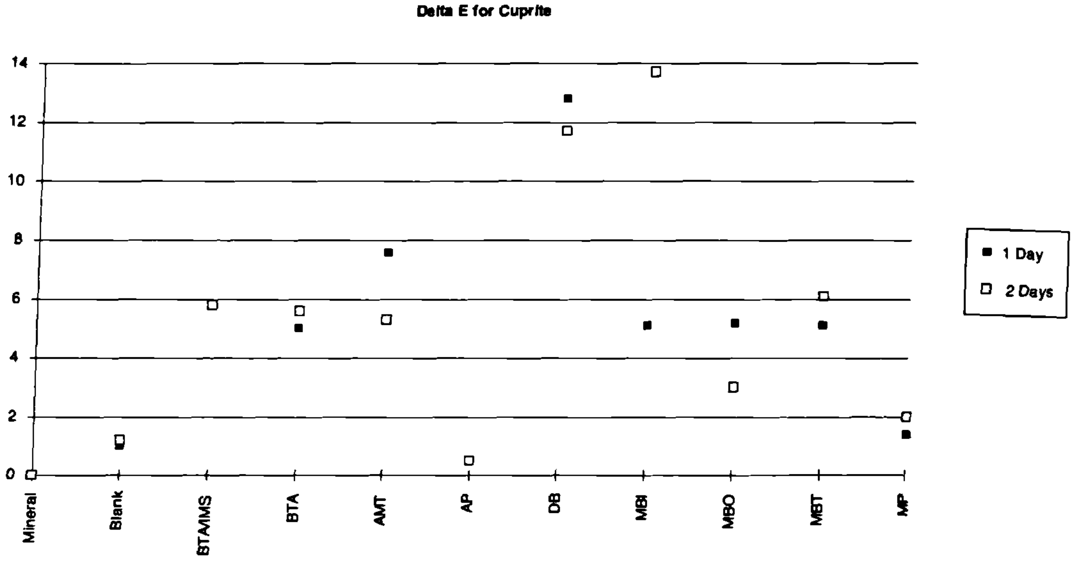


Figure 7. 3 ΔE* of Cuprite (AP has the Same ΔE* for 1 and 2 Days)

The largest discoloration of cuprite was caused by DB after a 24 hour (11.7ΔE^*) and 48 hour (12.8ΔE^*) treatment, and MBI (13.7ΔE^*) after a 48 hour treatment. The inhibitors that caused the smallest colour changes were AP(0.5ΔE^*) and MP (1.4-2ΔE^*).

After two 24 hour treatments, the smallest discolorations were induced by:

AP < MP < MBO < AMT < BTA/ethanol < BTA/IMS < MBT< DB < MBI

7.3.2 Malachite

After 24 hours treatment the basic copper carbonate mineral was mainly discoloured by MBT (11.5ΔE^*) and DB (9ΔE^*). MBT caused a dramatic yellowing of malachite (11.1Δb^*). DB caused a darkening (-5.4ΔL^*) and a reddening (6.8Δa^*) of the mineral.

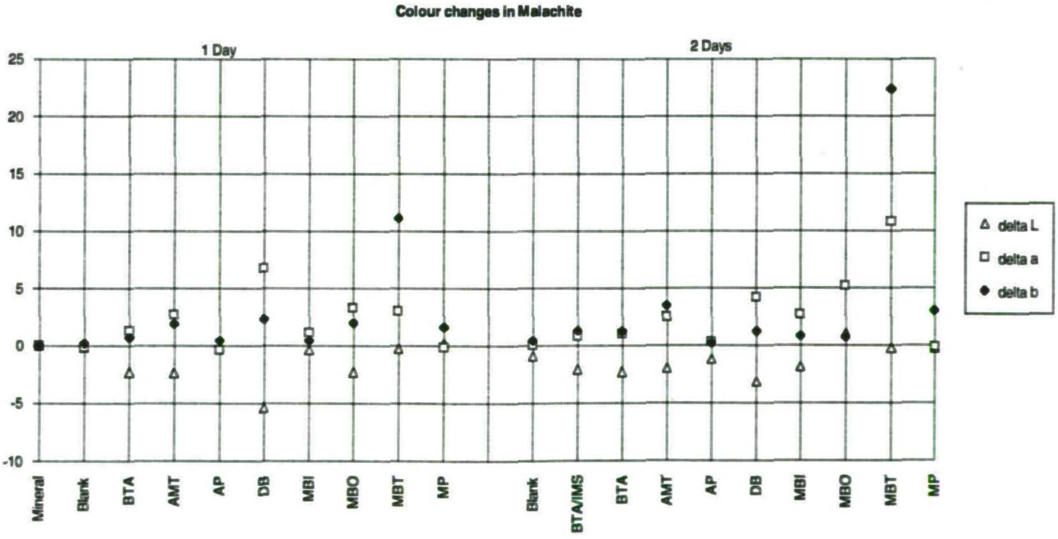


Figure 7. 4 ΔL^*, Δa^*, and Δb^* for Malachite

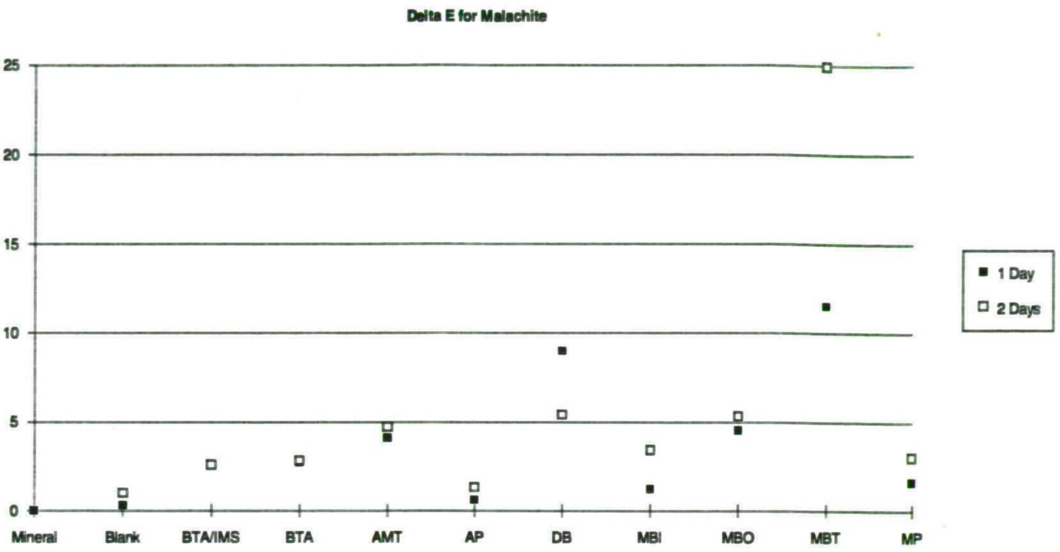


Figure 7. 5 ΔE* of Malachite (1 and 2 Day Treatments of BTA had the Same ΔE*)

After 48 hours MBT had the most dramatic affect on malachite which had a ΔE* of 24.9, whereas the other inhibitors gave values between 1.3-5.4ΔE*. The discoloration was indicated by 10.8Δa* and 22.4Δb*, resulting in a large yellow-red shift. A point of interest worth mentioning is that DB had a drop in ΔE* from 9 to 5.4 during the second 24 hour treatment. It was not known if this was due to an experimental error.

The 24 hour treatment with BTA in ethanol seemed to cause less discoloration when in contact with malachite (2.7ΔE*), rather than cuprite (5ΔE*). When comparing the 48 hour BTA/IMS (2.6ΔE*) and the 48 hour BTA/ethanol (2.8ΔE*) treatments, IMS seemed to cause less colour change. The data indicated that BTA/ethanol (-2.3ΔL*) and AMT (-2 to -2.4ΔL*) caused a distinct darkening of malachite.

It is suggested that MBT could cause the largest discoloration when used on an artefact largely covered in malachite corrosion products. A 24 hour exposure caused a drastic shift into a yellow region, which increased after a repeated treatment with MBT. Inhibitors causing the smallest amount of discoloration of malachite were AP (0.6-1.3 ΔE*), BTA (2.6-2.8 ΔE*) and MP (1.6-3 ΔE*).

The order of degree of colour changes was as follows:

AP < BTA/IMS < BTA/ethanol < MP < MBI < AMT < MBO < DB < MBT

7.3.3 Nantokite

Cuprous chloride showed the largest changes in colour after the treatment with inhibitors or pure reagent grade ethanol. Initially it was expected that there would be no colour change of nantokite powder after treatment with ethanol. The change in colour of the nantokite, when in contact with the ethanol, was probably due to the nantokite reacting with water present in the ethanol. The nantokite powder supplied by Aldrich, had a much higher L* value (75.9), indicating a lighter appearance of the mineral powder than the nantokite treated with ethanol (65.8L*) after 24 hours. Darkening of the powder was not detected after a repeated treatment. Observations indicated that the powder was actually lighter (78.5.L*) than the original untreated nantokite powder after the second treatment.

After a 24 hour treatment, the largest shift in ΔE* was for nantokite treated with BTA in ethanol, 31.7ΔE*, causing the most dramatic darkening (-26.6 ΔL*) of nantokite, and MP (28.2 ΔE*), due to a shift to a dark blue-green (-13.8ΔL*, -11.7Δa*,-23.5Δb*).

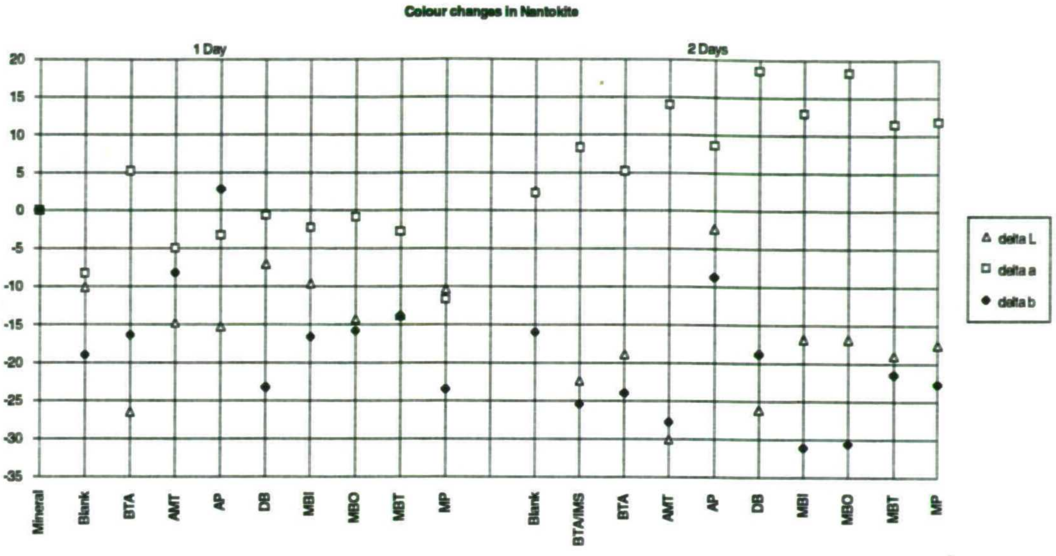


Figure 7. 6 ΔL*, Δa*, and Δb* for Nantokite

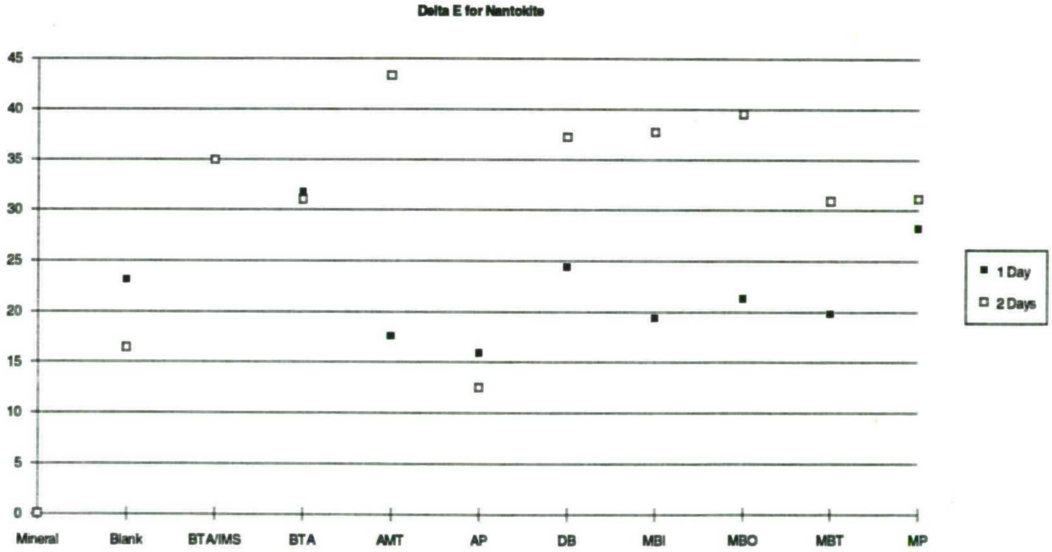


Figure 7. 7 ΔE* of Nantokite

After a second 24 hour treatment, most tested inhibitors increased in colour change. The repeated treatment caused the most distinct colour change in AMT, causing the nantokite to darken and to shift in to a dark red-blue value (43.3 ΔE*, -30.1ΔL*, 14Δa*, -27.8Δb*).

The largest colour changes were expected from treating nantokite with BTA for 24 hours, however, this was not the case, even after 48 hour treatment. This came as a surprise since it was thought that the major darkening of BTA was due to repeated treatments. The colour difference increased when IMS was used as a solvent.

The biggest change of nantokite was detected when it was treated twice for 24 hours with AMT (43.3ΔE*), followed by MBO (39.5ΔE*), MBI (37.7ΔE*), and DB (37.2ΔE*). The smallest colour change expected was thought to occur with nantokite treated with AP(12.5ΔE*). The AP ΔE* value was even lower than the mineral/ethanol blank. A BTA treatment in IMS (34.9ΔE*) caused a larger colour change than BTA in ethanol (31ΔE*).

The smallest colour changes were:

AP < MBT < BTA/ethanol < MP < BTA/IMS < DB < MBI < MBO < AMT

7.4 Discussion

The colorimeter quantified the colour changes that occured when copper minerals were treated with selected corrosion inhibitors. Cuprite, malachite and nantokite changed in appearance when in contact with corrosion inhibitors. Nitrogen containing inhibitors such as BTA, AP, and BD and sulphur containing inhibitors such as AMT, MP, MBO, MBT and MBI all discolour copper corrosion products. Sulphur containing inhibitors do not discolour more than nitrogen containing inhibitors. Cuprite, with an average mean of 5.7ΔE*, and malachite, with a mean of

5.2ΔE* seemed to be almost equally resistant to colour change when treated with corrosion inhibitors. Nantokite (28ΔE*), however, dramatically changed in colour when in contact with the inhibitors. This is thought to be partially due to its affinity for water and oxygen.

The ΔE* calculated mean is a generalisation and does not represent specific inhibitors. It is only used to estimate the resistance of cuprite, malachite and nantokite to colour changes. It shows that nantokite (28ΔE*) is the mineral most affected by inhibitors. It is proposed that this is probably due to the large amount of copper ions in solution. These copper ions easily form polymer complexes with the inhibitor present, redepositing on the surface, and obscuring the colour of nantokite. This is probably due to the fact that dissolved copper ions are used to form the polymer films on copper substrates, and that other elements such as chlorides, are incorporated into the film's matrix.

The most extreme colour change in cuprite was detected when it was treated twice for 24 hours with MBI (13.7ΔE*). The smallest change was detected when cuprite was treated with AP (0.5) for 48 hours. During conservation treatments, it is often found that the original surface of an artefact is retained in the primary cuprite layer (Cronyn, 1990,220). In the author's experience many objects are covered in malachite rather than cuprite, after they have been conserved. Exposing the surface during conservation and treating it with a corrosion inhibitor could cause changes in hue, if the inhibitor is not carefully selected. An artefact with no or low chloride concentration, can safely be treated with an inhibitor such as AP. The data has shown that AP does not change the colour of the surface to a great extent when compared to other inhibitors.

The largest colour change in Malachite was induced by MBT (24.9 ΔE*) after 48 hours. The smallest change was again due to AP (1.3 ΔE*). This suggests that an artefact mainly covered in cuprite and malachite and not containing chlorides, can safely be treated with AP, and the expected colour change would not exceed 1.3 ΔE*. MP also should not cause dramatic colour changes in an object mainly covered in malachite and cuprite, the colour change should not exceed 3 ΔE*. The use of MBT, in the case of an artefact covered in a blue green copper carbonate patina, is not recommended as it could result in the artefact having an excessively blue appearance.

The data lead to the conclusion that an artefact covered mainly with cuprite and malachite, mostly free of cuprous chloride, could be treated with AP (0.5-1.3 ΔE*), MP (1.4-3ΔE*) and MBO (3-5.3ΔE*). More apparent colour changes are to be expected when treating artefacts with AMT (4.1-7.6ΔE*), BTA (2.6-5.8ΔE*). Disfiguring colour changes could occur when treating objects with DB (5.4-12.8ΔE*), MBI (1.2-13.7ΔE*) and MBT (5.1-24.9ΔE*).

In the rare case of an artefact mainly being covered in nantokite, the inhibitor solutions tested will in all cases result in a discoloration of the nantokite covered areas. The smallest discoloration will be caused by a 24 hour treatment with AP (15.9ΔE*), and the largest change with AMT (43.3ΔE*) after two 24 hour treatments. The discoloration of nantokite might be considered a minor drawback when stabilising an actively corroding artefact, however the approach of minimal intervention should be assessed.

Below an attempt was made to classify inhibitors according to the colour change they cause using the ΔE^* mean of 24 hour and 48 hours treatment.

The inhibitors caused colour change as follows:

Cuprite = AP < MP < MBO < BTA/ethanol < MBT < BTA/IMS < AMT < MBI < DB
Malachite = AP < MBI = MP < BTA/IMS < BTA/ethanol < AMT < MBO < DB < MBT
Nantokite = AP < MBT < MBI < MP < MBO < AMT < DB < BTA/ethanol < BTA/IMS

Table 7. 3 Colour Changes due to Inhibitors.

To establish a theoretical ΔE^* for an archaeological artefact covered in 1/3 cuprite, 1/3 malachite and 1/3 nantoktie, the mean of the three ΔE^* values were calculated. This implies that all three copper corrosion products were present in equal amounts on the surface visible to the observer. Such a patina would be found on heavily corroded artefact, containing large amounts of chlorides. An artefact of this kind would require a very reactive corrosion inhibitor, since the chlorides would not only be present in small areas but also underneath large areas of non corroding patina

The smallest discoloration according to ΔE^* of inhibitors/cuprite$^{1/3}$, malachite$^{1/3}$, and nantokite$^{1/3}$ (patina):

Patina: AP < MP < BTA/ethanol = MBO < MBI < AMT < BTA/IMS < MBT < DB

This classification of colour change of the patina induced by inhibitors would change should the surface of a patina contain smaller amounts of nantokite. If the patina only contains 1/10 chlorides and the rest contains equal amounts of cuprite and malachite, the ranging of minimal discoloration would be as follows:

Patina cuprite$^{(4.5/10)}$, malachite$^{(4.5/10)}$ and nantoktie$^{(1/10)}$ =

AP < MP < BTA/ethanol < MBO < BTA/IMS < AMT < MBI < DB < MBT

This kind of patina has been observed by the author, and is thought to be more probable. In the author's experience this sort of corrosion surface is often found on Mediterranean artefacts from saline environments.

The data suggests that AP again causes the smallest amount of colour change when used once or twice on an artefact. AP is the inhibitor that causes the smallest discoloration on objects with or without large amounts of chlorides. AP did, however, not successfully protect copper coupons covered in nantokite when exposed to an RH of 80% for 24 hours.

MP can be used safely on patinas with small amounts of chlorides, for example as stated above. Should the artefact, however, contain large amounts of chlorides MP can be used but a $11.2\Delta E^*$ can be expected on patina containing copper I chloride as 1/3 of its surface area. The larger the chloride content the more colour changes are likely to occur when artefacts are treated with MP.

An artefact containing large amounts of cuprous chloride will change its surface colour when treated with BTA, causing a distinct darkening during a 24 hour treatment. Should the nantokite containing surface be treated with AMT, a slight yellowing of the corrosion product is to be expected.

The inhibitors predicted to cause the largest colour changes in the surface appearance of an object containing cuprite, malachite and nantokite are DB and MBT. The larger the chloride content, the greater the discoloration of the surface. DB is expected to darken the surface of artefacts, mainly due to a darkening of cuprite and nantokite.

MBT is expected to yellow an artefact containing large amounts of malachite, and result in a shift towards a red-blue colour when in contact with chlorides. This suggests that MBT is the corrosion inhibitor most likely to discolour an artefact. This attribute of MBT suggest that it should only be used when all other inhibitors fail.

Nantokite is most affected by corrosion inhibitor colour changes. It has to be argued to what extent colour changes of nantokite are acceptable on a heavily chloride infested object. Considering the vulnerable state of such an artefact, should an inhibitor prove to be very effective in inhibiting further corrosion due to chlorides, then the colour change might be thought of as a minor drawback. However, it has to be considered that these colour changes are irreversible, due to the complex formation of the inhibitor with the copper corrosion products. The complex layer would have to be removed physically to reveal the original mineralised surface. The effects of this depends on the depth of penetration of inhibitors.

Based upon the experimental results, the expected colour changes when treating cuprite malachite and nantokite with selected corrosion inhibitors are as follows:

	Cuprite	Malachite	Nantokite
BTA	slight orange	darker	very dark
AMT	greener	darker orange	slightly darker/yellow
AP	-	-	slightly darker
DB	much darker	much darker	much bluer
MBI	darker	-	slight bluer
MBO	slight yellow	slight darker	slight bluer
MBT	yellow	very yellow	slight bluer
MP	-	slight yellow	much bluer

Table 7. 4Expected Colour changes on Copper Minerals

More accurate data using the ΔL*, Δa*, Δb* system on discolouration are presented in Figure 7.2-7.

Concluding this chapter, AP is recommended for the treatments of artefacts with a highly appreciated patina, which contain very low levels of copper chloride. However, AP is considered to have the lowest effectiveness in protecting from further chloride corrosion. If possible DB and MBT should be avoided, as both can cause severe colour changes of a patina.

Chapter 8

Copper Alloy Artefacts Treated with Corrosion Inhibitors

8.1 Introduction

The ongoing deterioration of archaeological copper and copper alloys in museum environments is mainly caused by copper chloride corrosion and changes in relative humidity. In the previous chapters, copper corrosion inhibitors, selected from the industrial literature were assessed for their suitability in archaeological conservation. Three inhibitors adequately prevented further copper chloride corrosion on copper test coupons. Benzotriazole (BTA, Madsen, 1967), 2-amino-5-mercapto-1,3,4,-thiadiazole (AMT, Ganorkar 1988) and 2-mercaptobenzothiazole (MBT). MBT was published in the industrial literature as a possible corrosion inhibitor by researchers such as Gajendragad and Agrawala (1975), and Pandit Rao et al. (1987), but had not been assessed for use in archaeological conservation.

This chapter includes service tests on selected available archaeological material. The three selected corrosion inhibiting compounds BTA, AMT and MBT were applied to archaeological copper and copper alloys. Previous measurements such as colorimetric testing, established the tendency of inhibitor compounds to induce colour changes after treatment. This made testing on archaeological metals necessary to substantiate previous findings. The use of archaeological material in previous tests was not appropriate, due to the inhomogenity of the various objects available. The corroded surface of an archaeological copper or copper alloy artefact, is generally very variable. The results arising from corrosion testing on such material were specific for the individual objects treated. The reproducibility of the data is low due to the many differences in artefact corrosion. The data variations to be expected are in the areas of colour changes, and effectiveness in corrosion inhibition of chloride corrosion. This is due to the differences in corrosion products.

The copper alloys available for this experiments consisted of a set of Pre-Inca *naipes* (early form of currency) from Peru and a hoard of Early Iron Age arrowheads form Abu Dhabi, some of which were treated by conservation students from the Institute of Archaeology, UCL. The objectives of the following experiments were to assess corrosion inhibition effectiveness, and the colour changes induced by corrosion inhibitor treatments. It was hoped that the results would reflect the findings from corrosion testing experiments outlined in the previous chapters.

8.2 The Treatment of Copper Alloy Arrowheads

Between 1991-1995 a hoard of copper alloy arrowheads, on loan from Al Ain Museum in Abu Dhabi, UAE, were treated in the conservation laboratory at the Institute of Archaeology, U.C.L.. The arrowheads were grave finds from Quidfa U.A.E. (Ryan, M.Sc., 1991). Quidfa is a site on the east coast of the Oman peninsula. The arrowheads were dated to the later part of the second millennium B.C., in an early Iron Age context. Most arrowheads display incised characters on the flat mid-rib surface.

The arrowheads were thought suitable research material, as they originated from the same archaeological context, with similar composition, and they were known to develop problematic copper chloride corrosion. Most arrowheads were treated by undergraduate conservation students, as the practical laboratory work for the course C345 Conservation of Metallic Artefacts taught by Dr.J.F. Merkel., Table 8.1 lists the Laboratory numbers and the various treatments they received. Eleven arrowheads were treated with BTA, and 4 were treated with AMT.

8.2.1 Benzotriazole treatment

In the authors experience, and through numerous discussions, BTA was identified as not being successful in inhibiting copper chloride corrosion on copper artefacts which contain large amounts of copper chlorides. No published study was found which systematically investigated the effectiveness of BTA on a distinct group of artefacts, from the same burial environment.

The arrowheads formed part of the practical conservation training in the Conservation Department at the Institute of Archaeology, UCL. Second year conservation students treated these arrowheads under supervision (Dr.J.F. Merkel and C.Tubb) to acquire experience in the investigative cleaning and corrosion inhibition of archaeological copper and copper alloys (Table 8. 1). The material was judged appropriate by Dr. J.F. Merkel, since it formed part of a conservation research collection, and displayed a corrosion surface frequently found on copper and copper alloys from chloride containing burial environments. The surface exhibited the typical layered structure of malachite, cuprite and nantokite with paratacamite. The arrowheads were evaluated by visual examination before treatment by each student. The arrowheads were in different states of corrosion, some displayed a thin layer of corrosion surface close to the "original surface", while others were heavily corroded, completely obscuring any surface details. On visual analysis, all arrowheads exhibited copper chloride corrosion. Most of the students tested for the presence of copper chlorides by silver nitrate test (Vogel, 1978, 338). Paratacamite was visible on many surfaces.

The corrosion products were mechanically removed down to a "conservation surface" using a scalpel, abrasive dental wheels and glass bristle brush. Mechanical cleaning of these artefacts was preferred, since chemical cleaning methods might have disrupted fragile parts of the corrosion surface, which still retains designs and tool marks.

Eleven arrowheads were treated with BTA. It was applied in the standard 3% by weight solution (in water or alcohol) as recommended by Madsen (1967). The arrowheads were immersed in the inhibitor solution and left for 1-3 days in a vacuum at 600 millibars. The vacuum immersion method was used to facilitate the penetration of the inhibitor solution into the porous corrosion surface.

The students conservation records revealed that out of 11 arrowheads only 2 were stable in the course of 3 days treatment. It has to be noted that these arrowheads were only exposed to fluctuating RH in the laboratory, the levels of which were not stated in the conservation records. Two arrowheads were treated for 5 days with BTA. It is not specified if they were left in the vacuum for this length of time. One arrowhead was treated for 3 weeks. Four were treated between 2-12 months, and one arrowhead for an unknown amount of time.

The 2 arrowheads treated for up to 3 days were not corroding when exposed to the laboratory environment, with its fluctuating RH and temperature (6479/6, 6518). The arrowheads treated for 7 (6409) and 12 months (6408) were not stable, and had to be retreated. Arrowheads 6408, 6409 and 6427 were treated with silver oxide in IMS. 6408 was treated for 1 and 2 hours in 5% sodium carbonate (Weisser, 1987). Both treatments did not prevent further chloride corrosion. Final stabilisation was achieved by applying silver oxide.

The surface of the arrowheads was finally rinsed with IMS, to remove excess BTA. The immersion time varied between 10 minutes to 3 hours. The stabilised surface was then covered in Incralac. Incralac contains BTA and is thought to give extra physical and chemical protection to the surface (Table 8. 2). Two coatings of Incralac in toluene were applied, the concentration of which varied between 10 and 30%. Incralac was developed by the Copper Research Association and was originally designed as a coating for copper and copper alloys. It found application for both interior and exterior use. The main component of Incralac is Paraloid B44 (methacrylate copolymer) which has a glass transition temperature of 60°C (Horie, 1987). Paraloid B44 has good UV resistance and ageing properties. In conservation treatments Incralac is usually diluted in toluene.

Table 8.1 lists the treatments used to stabilise the arrowheads. The table shows that the treatment time that was needed to prevent further chloride corrosion, varied greatly. To stabilise arrowheads 6479/6, 6510 and 6518, less than one weeks treatment was needed. Specimens 6407, 6408 and 6409 were treated for several months, and only 6407 appeared stable after a 9 month treatment. 6408 and 6409 were not stabilised with BTA. These findings suggest that BTA treatments lasting months, do not necessarily result in a more stable corrosion surface. However, the present research indicates that these surfaces darkened markedly.

The treatments of the Quidfa arrowheads with BTA suggests that artefacts containing large amounts of chlorides should be treated for a week only. Prolonged treatments, lasting several months, do not result in increased protection. The author, however, observed that artefacts can continue to corrode when left unattended for several days in the BTA solutions. If an artefact is repeatedly treated with BTA, then the solution should be changed, preferably every 24 hours, to prevent BTA depletion.

Treated 1992-1995

Lab No.:	Acetone degreasing	Inhibitor treatment	IMS rinsing	Stability after treatment	Protective Coating Incralac/toluene
6408	10 min	3% BTA/IMS 12 mth	3 hrs	not with BTA	2x15% incralac
6407	10 min	3% BTA/IMS 9 mth	X	stable	2X30% incralac
6409	10 min	3% BTA/IMS 7 mth	X	not with BTA	2x15% incralac
6512	1 min	3% BTA/IMS 2 mth	?	?	2X30% incralac
6427	20 min	3% BTA/IMS ? mth	30 min	not with BTA	2x15% incralac
6513	?	3% BTA/IMS 3 weeks	10 min	stable in lab	2x10% incralac
6510	X	3% BTA/IMS 5 days	X	stable in Lab after 2 weeks	2x incralac
6516	5 min	3% BTA/IMS 5 days	30 min	?	2X30% incralac
6479/6	10 min	3% BTA/IMS 3 days	O	effective 55%RH	5% Paraloid B-72
6511	2 hrs	3% BTA/IMS 3 days	30min	?	2x10% incralac
6518	10 min	3% BTA/IMS 3 days	10 min	stable in lab	2X20% incralac
6479/1	10 min	0.01 AMT/IMS 1day, 3% BTA/IMS 2days	O	not after 24hrs AMT but after 2 days BTA	5% Paraloid B-72
6479/2	10 min	0.01 AMT/IMS,1hr/60°C	O	effective 55% RH	5% Paraloid B-72
6479/3	10 min	2x1% AMT,24 hrs	O	effective 55% RH	5% Paraloid B-72
6479/4	10 min	1% AMT, 1 hr/60°C, and 1% AMT 2 days	O	after 1% AMT 2days stable at 55% RH	5% Paraloid B-72

Lab No.:		
6408	1hrs and 2hrs, 5% sodium carbonate and retreated for 1 month 3%BTA, 2x repeated, stable after silver oxide	? = data unknown X=treated O=untreated
6409	stable after silver oxide/IMS	BTA = Benzotriazole
6427	BTA exposure time unknown, 1hrs and 2hrs 5% Sodium Carbonate/Distilled Water and rinsed, stable after silver oxide/IMS	AMT = 2-amino-5-mercapto-1,3,4-thiadiazole
6479/1-6	Silver nitrate tested, the specimens where part of a 3rd year dissertation	mth = month

Table 8. 1 Conservation Treatments on Copper Alloy Arrowheads.

Incralac contains:		
Paraloid B44 (40%)	74%	methyl methacrylate
Toluene	20%	
Ethanol or butyl acetate	5%	
Benzotriazole	0.5%	corrosion inhibitor
Epoxidised Soya bean oil	0.5%	Paraplex g-60, to reduce orange-peel effect

Table 8. 2 Composition of Incralac (Source: Institute of Archaeology, Conservation Handbook.)

8.2.2 AMT Treatment

AMT was assessed for its effectiveness, as a third year undergraduate dissertation (Faltermeier, 1992). Four arrowheads from the same hoard as the previously BTA treated objects, were treated with selected AMT/ethanol concentrations and exposures. The arrowheads were mechanically cleaned and degreased in reagent grade acetone for 10 minutes. AMT was than applied in industrial methylated spirits, as stated in table 8.3.

Arrowhead	**AMT /IMS concentration**	**immersion time**	**temperature**
6479/1	0.01M	24 hours	room temp.
6479/2	0.01M	1 hour	60^0C
6479/3	1%	24 hours	room temp.
6479/4	1%	1 hour	60^0C

Table 8. 3 Arrowheads Treated with AMT

After the AMT treatment, the arrowheads were exposed for 24 hours to ~95% RH at room temperature. Only 6479/2 did not show paratacamite corrosion. This suggested that the treatment described by Ganorkars et al. (1988) could be successful in such cases. Arrowheads 6479/1,3 and 4 had to be retreated.

Since immersion in the 0.01M solution for 1 hour at 60^0C seemed effective, 6479/1,3 and 4 were retreated in this manner. When immersed in the warm inhibitor solution, a yellow green precipitate formed over the nantokite areas. Ganorkar et al. (1988) mentioned the formation of this inhibitor-copper complex. This had to be repeatedly removed with a soft brush. The AMT treatment was assessed by a 24 hour exposure to ~95%RH. The test was too severe and active corrosion was again evident.

Arrowhead 6479/1 was treated for 48 hours with BTA, since Ganorkar et al. (1988, 100) suggested the use of a combined treatment of AMT and BTA, in the case of very unstable artefacts. The 24 hour and the 1 hour treatment at a 0.01M concentration did not result in a stable corrosion surface on specimens 6479/3,4. The arrowheads 6479/3,4 were immersed for 48 hours into a 1% by weight AMT/IMS solution at a 600 millibars vacuum.

After 24 hours exposure to 55% RH at room temperature, arrowheads 6479/3,4 and 5 appeared stable. Arrowhead 6479/1 was not stable at 55% RH, so treatment was halted to prevent disintegration of the object.

All arrowheads treated with AMT were coated with a 5% solution of Paraloid B-72 in acetone (ethyl methyl methacrylate copolymer). Incralac was not applied since it contains BTA, and the complex effects in combination with AMT, have not been studied before.

8.2.3 Discussion of Arrowhead Treatments Between 1992-95

The work undertaken indicated that AMT does not completely inhibit copper chloride corrosion (Table 8. 1). The data also suggested that a 0.01M AMT treatment at 60^{0}C causes the dissolution of some nantokite. It also appeared to cause a smaller amount of discolouration than the 24 hour treatment at 0.01M. The 1% by weight AMT treatment did not adequately protect the artefact. A repeated treatment, however, resulted in better protection. These findings lead to the conclusion that a higher concentration of inhibitor increased the rate of protection.

8.3 Arrowhead No. 6679

This specimen came from the same excavation as the above discussed arrowheads. Ryan (1991) proposed after examination, that the arrowheads were probably cast in a rough shape, and than cold worked and annealed in several cycles.

This arrowhead was treated as part of the Ph.D. research. The arrowhead was very corroded, and covered with brown green corrosion products. Some areas, especially the tip, were covered in pail green corrosion products (copper chlorides). Some markings could be identified along the midrib of the arrowhead (Figure 8. 1). The arrowhead was analysed by J.Ryan (1991) using Atomic Absorption Spectroscopy, and identified as a tin bronze.

Element	**% by weight**	**Element**	**% by weight**
Cu	87.31	Sn	6.54
As	0.19	Pb	0.05
Ni	0.11	Sb	0.001
Fe	0.17	Bi	0.04
Ag	0.0	Cr	0.08
Zn	0.04	Co	0.0

Table 8. 4 Atomic Absorption analysis by J.Ryan (1991)

The surface was mechanically cleaned by an undergraduate student (Howard Wellman) of the Conservation Department, UCL. A silver nitrate test revealed extensive chlorides. The arrowhead was degreased for 10 minutes in reagent grade acetone, and dried.

To establish the effectiveness of 0.1M MBT in reagent grade ethanol, the arrowhead was immersed in 50ml of this corrosion inhibitor solution for 24 hours, at ambient temperature. The arrowhead was removed from the solution and dried under an infrared lamp at 50°C. As in the other experiments, nantokite areas had an unsightly yellow colour. It was expected that the inhibitor would have penetrated further into the porous corrosion product layers and that this would decrease the yellow discolouration when applied to corroded archaeological metals.

Corrosion resistance at 90% RH was tested by an exposure for 24 hours at 20°C. After 24 hours, only 4 small areas contained light green paratacamite corrosion. The paratacamite was removed with a glass bristle brush, and the same MBT treatment was repeated. After the second treatment the arrowhead was still somewhat unstable.

To assess the reaction between MBT and BTA it was decided to apply 0.25M BTA to the arrowhead. 0.25M BTA/reagent grade ethanol was applied for 24 hours at ambient temperature. The arrowhead was than stored for 40 days at 10%RH, in Silica-Gel.

Previous experiments in chapter 5 showed that nantokite covered coupons treated with BTA, lost weight over a period of 18 days. This occured during the first 10 days at 10% RH. They were then exposed to an increasing RH. In this experiment the BTA treated coupons displayed a higher degree of corrosion inhibition than the AMT treated coupons, when exposed to a slowly increasing RH (up to ~100%RH, on the 52nd day, Figure 8. 3).

Figure 8. 1 Copper Alloy Arrowhead Before Treatment.

Figure 8. 2 Copper Alloy Arrowhead After Inhibitor Treatment.

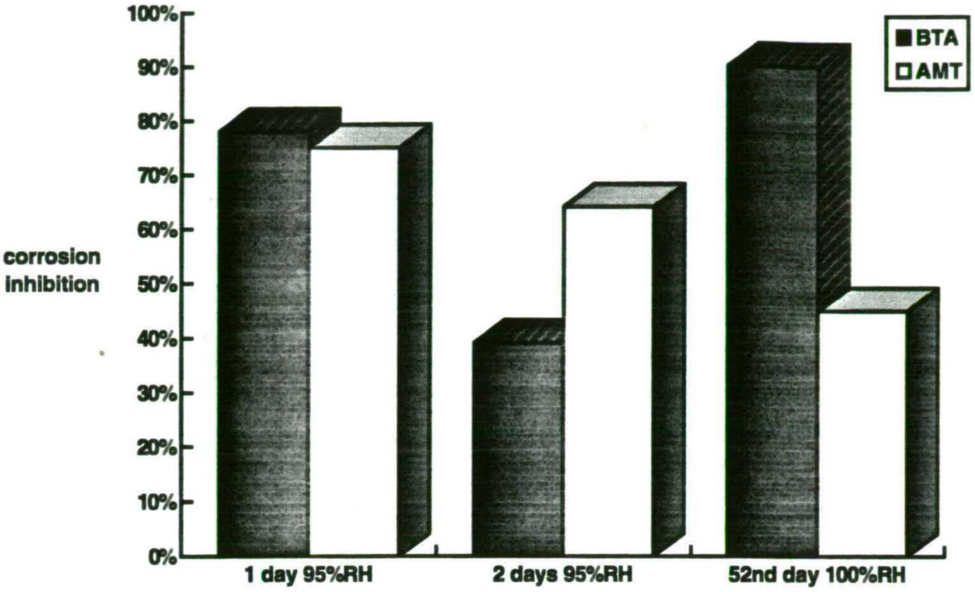


Figure 8. 3 Corrosion Inhibition After 1,2 Days, and 52 Days. (The Inhibition Percent was Calculated Based on the Blanks)

Figure 8. 3 shows the corrosion inhibition of nantokite covered coupons treated with BTA, or AMT. In the initial experiments, nantokite covered coupons were treated with corrosion inhibitors and subsequently exposed for 1 day and 2 days to 95% RH, at ambient temperature. In these experiments AMT outperformed BTA in corrosion inhibition effectiveness.

In experiment 5.7 coupons were dried for 10 days at 10% RH, and then exposed to increasing RH for 52 days. On the final day the RH was set at ~100% and at the end of this period, BTA showed a higher protection rate than AMT.

The BTA treated arrowhead was dried for 40 days and exposed for 24 hours to 90%RH, at 20°C. The arrowhead appeared stable, but the surface had darkened in colour after the BTA treatment. The nantokite covered regions, previously yellowed by the MBT treatment, darkened slightly after the BTA treatment.

The experiment on nantokite covered coupons reported a higher degree of corrosion inhibition due to MBT, rather than BTA. While large nantokite areas on the artefact were readily protected by MBT from further corrosion, smaller areas were reactive. However, BTA stabilised these corroding areas. Colour changes were evident after both MBT and BTA treatments. The nantokite was very yellow after the MBT treatment, but the whole surface darkened after the BTA treatment (Figure 8. 2).

8.4 Copper Alloy Bracelet No. 6672

The bracelet was on loan from the Al Ain Museum, Abu Dabi, UAE. The find was excavated from a similar grave hoard to that at Quidfa, UAE. It is dated to the Iron Age, about 1300-300 BC. The object was approximately 89-92mm in diameter, and had a cross section of 20-28mm. Ryan (1991) suggested that the artefact was cast tin bronze. His atomic absorption analysis results are listed below. The surface was highly corroded (before conservation Figure 8. 4 and after conservation Figure 8. 5).

Element	% by weight	Element	% by weight
Cu	88.12	Sn	8.85
As	0.001	Pb	0.06
Ni	0.001	Sb	0.026
Fe	0.075	Bi	0.05
Ag	0.0	Cr	0.02
Zn	0.02	Co	0.05

Table 8. 5 Atomic Asorption Analysis by Ryan (1991)

The bracelet was cleaned mechanically by a conservation student (Howard Wellman) from the Conservation Department, UCL. The surface was cleaned with

Figure 8. 4 Copper Alloy Bracelet Before Treatment.

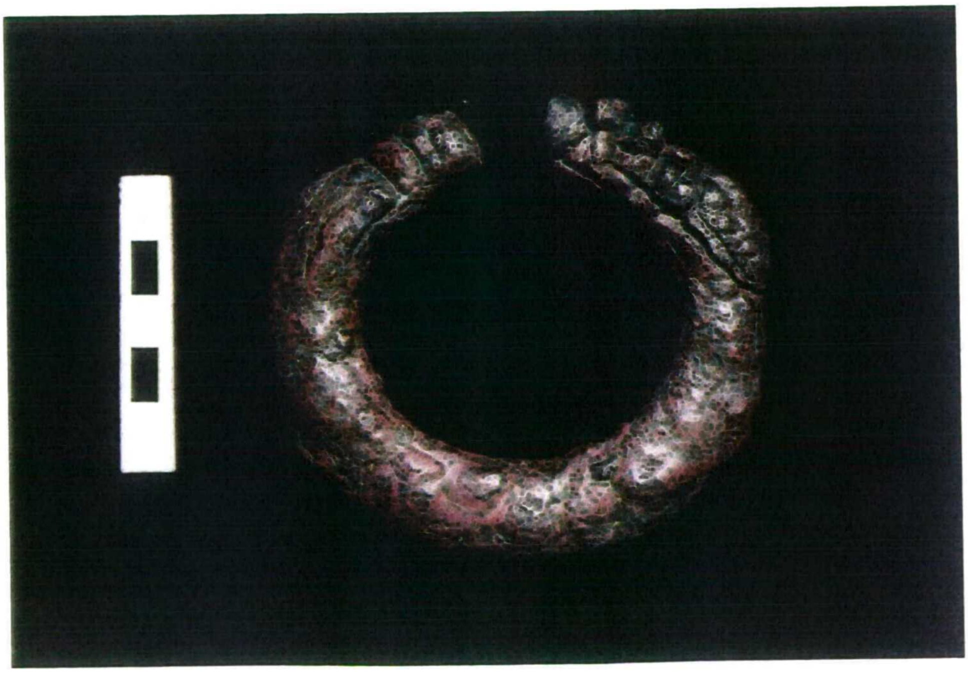


Figure 8. 5 Copper Alloy Bracelet After Conservation Treatment.

scalpel and glass bristle brush. The silver nitrate test on loose corrosion products revealed the presence of copper chlorides.

The object was degreased for 10 min in reagent grade acetone and air dried. To stabilise the nantokite, the bracelet was immersed for 24 hours in 300ml 0.068M concentration AMT in reagent grade ethanol. Subsequent exposure to 90%RH at 20°C, produced new paratacamite. Exposure to 90% RH created extreme conditions, however, it was found necessary to ensure maximum corrosion inhibition. The paratacamite was removed and the treatment repeated. Renewed exposure to 90%RH at 20°C resulted in further paratacamite corrosion in the same small areas. This clearly showed that AMT is not effective in completely preventing copper chloride corrosion during a 24 hour exposure to 90%RH at 20°C. It was decided to use BTA on the bracelet.

After a 24 hour immersion in 0.25M BTA/reagent grade ethanol, the bracelet was dried for 40 days at 10%RH in Silica-Gel. This was followed by a 24 hour exposure to 90%RH at 20°C. After retreatment, there was no visible paratacamite corrosion. However the surface of the bracelet was darkened by the BTA treatment (Figure 8. 5).

8.5 Colour Changes of Corrosion Products on Naipes

8.5.1 Introduction

The naipes used in this study were excavated by Prof. Izumi Shimada from a tomb in Batan Grande, Peru. They were similar to Ecuadorian axe-moneys. This group was dated to late Middle Sicán (ca. A.D. 900-1050). Metallographic and EPMA analysis showed that these naipes were made from a copper-arsenic bronze hammered sheet. The naipes were stacked or sometimes bundled in textile when buried (Merkel, 1995, personal communication).

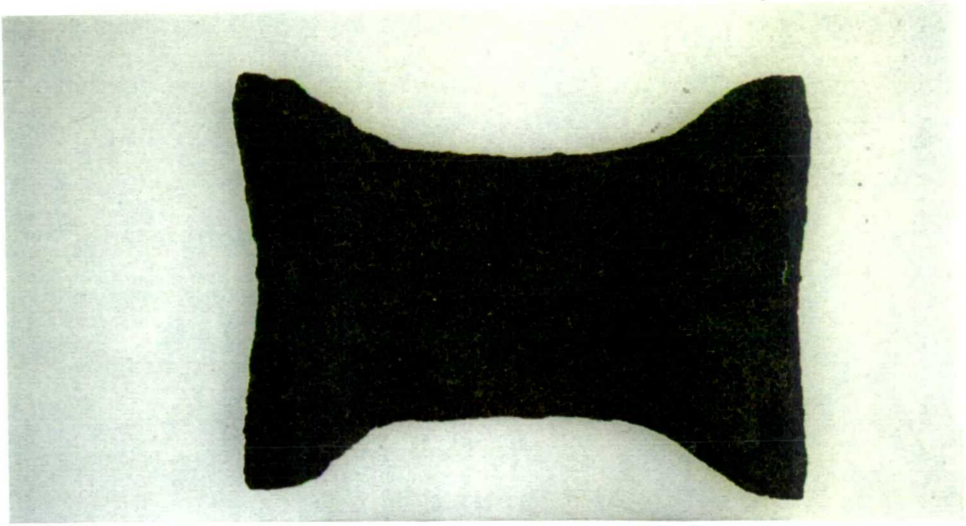


Figure 8. 6 Naipes Before Conservation Treatment (Original Size).

The naipes were cleaned using a scalpel and glass bristle brush under a binocular microscope with 20x magnification, to remove the surface deposits and excess corrosion products. The surface was cleaned to a level where the conservation surface was judged appropriate. Tool marks became apparent at this level. The removed corrosion products were used to analyse for copper chlorides, with the silver nitrate test. The silver nitrate solution did not produce a positive result, indicated by a white precipitate. On the basis of this result and a visual assessment of each fragment, it was concluded that there was little copper chloride present. Since there are literally thousands of naipes which have been excavated in Batan Grande, it was agreed that the naipes fragments could be divided into three sections and cut with a jewellers saw into similar sized pieces, for further testing. This was considered a valid but destructive use of selected naipes fragments. However, since the naipes had been previously sampled, analysed, and were part of a huge hoard of similar finds, it was possible to use them for this kind of experimental work. It was decided to use three naipe fragments, in an attempt to limit damage.

8.5.2 Experimental Procedure

1. Visual assessment of corrosion surface
2. Cleaning of three fragments with scalpel and glass bristle brush
3. silver nitrate test
4. cutting fragments with jewellers'saw into three similar sized pieces
5. 10 min. degreasing of surfaces with acetone
6. immersion in inhibitor solutions.
        Segment a) of each fragment untreated,
        Segment b) treated for 24 hours in inhibitor,
        Segment c) treated for 48 hours in inhibitor,
   Concentrations: BTA 0.25M, AMT 0.068M, MBT 0.1M in 25ml reagent grade ethanol.
7. rinsing for 10min in ethanol
8. photographed, colorimetric evaluation

8.5.3 Experimental Observations and Discussion

The visual assessment, after drying the specimens, clearly identified the BTA treated fragments as the most pleasing surfaces. The AMT treated fragments had a yellow appearance. As previously determined, MBT clearly was not acceptable in the conservation of archaeological copper and copper alloys, on the basis of colorimetric aspects of the treatment. The sections treated with MBT turned yellow. The yellow appearance of AMT and MBT was most likely due to the sulphur present in the

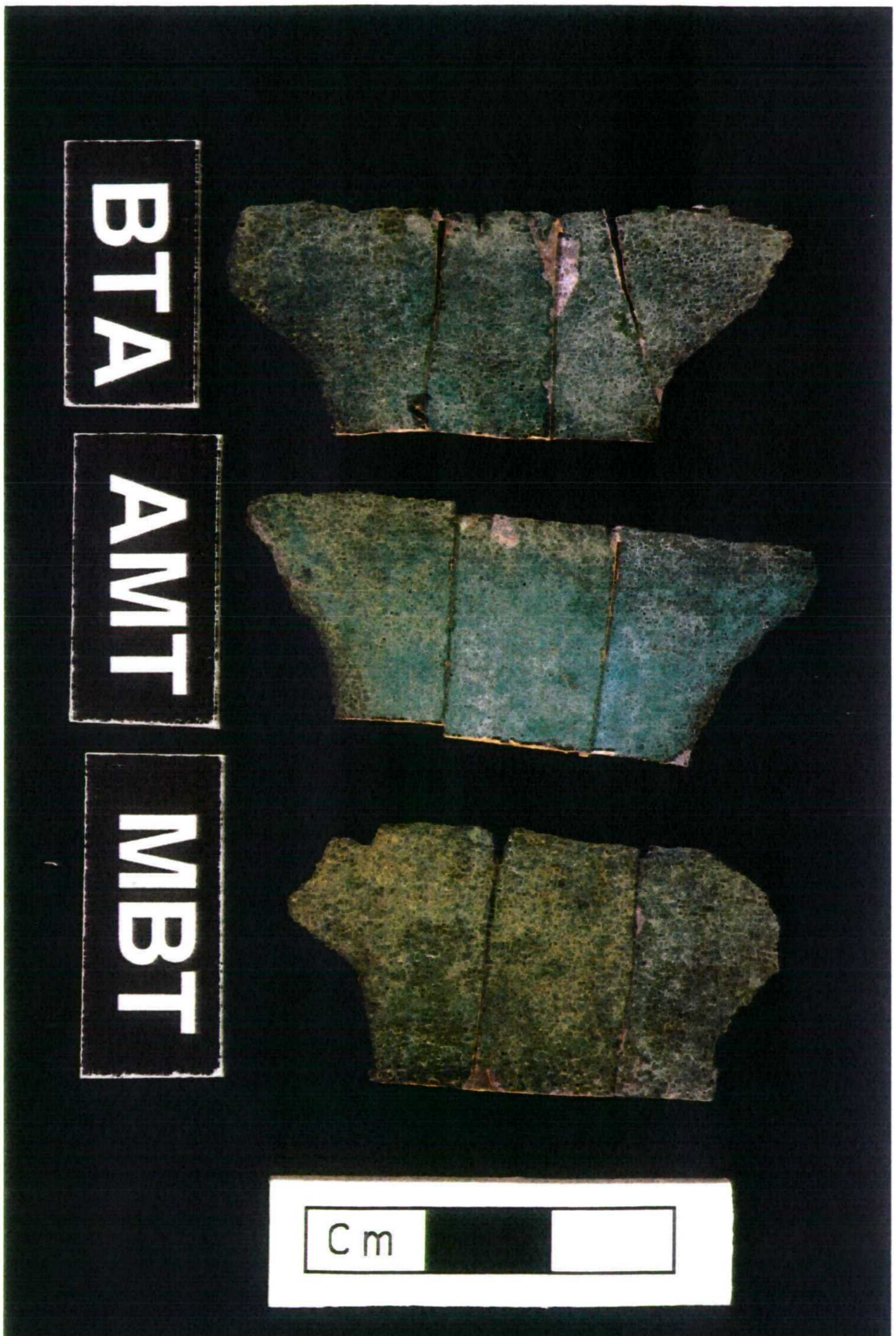


Figure 8. 7 Naipes After Treatment

corrosion inhibitor. This visual assessment was confirmed when using the Minolta Colorimeter CR-200 in the National Gallery in London.

The colour changes detected with the colorimeter varied greatly. This was due to the inhomogeneous nature of the corrosion surface on the samples. Each specimen was measured 10 times and an average was calculated. The L*, a* and b* values are given in Figure 8. 8.

BTA seemed to shift into the blue (-b) region after 1 and 2 days treatment. AMT and MBT clearly yellowed (+b) the surface after the treatment. The data suggested that a repeated treatment with AMT and MBT would increase the yellow of the treated surface. MBT also seems to cause a shift into the green region (Figure 8. 8).

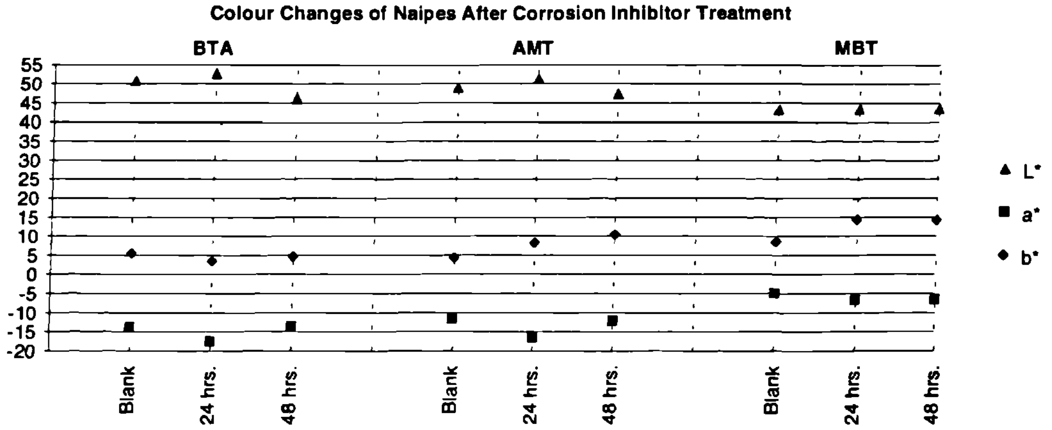


Figure 8. 8 Colour Measurements After Inhibitor Treatment.

The ΔE* calculated on the basis of ΔL*, Δa* and Δb* confirmed the initial visual assessment. BTA had a smaller change in ΔE* than both mercapto compounds

AMT and MBT. MBT seemed to cause a slightly less overall colour change than AMT. This result confirmed the earlier findings in chapter 7, that AMT and MBT both caused a yellowing of the corroded surface.

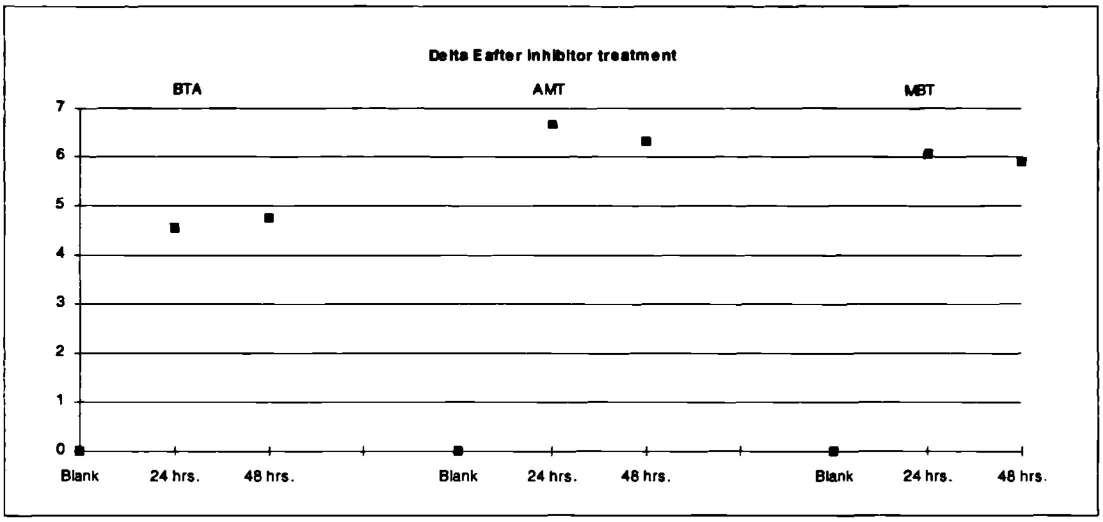


Figure 8. 9 ΔE* Values After Inhibitor Treatment.

An increase in ΔE* after a two day treatment with BTA was expected. However, the decrease in ΔE*, after the second treatment in AMT and MBT, could not readily be explained. This was possibly due to the inhomogeneity of the corrosion products on the specimen surface. Figure 8. 10 illustrates the variations in colorimeter readings on the untreated BTA section 1a. The second measurement has a -a* shift, clearly affecting the overall average, and so affecting all ΔE* calculations. The data available, nevertheless, represents an overall trend. This trend reflects what a conservator has to expect when treating a corroded copper or copper alloy with BTA, AMT and MBT.

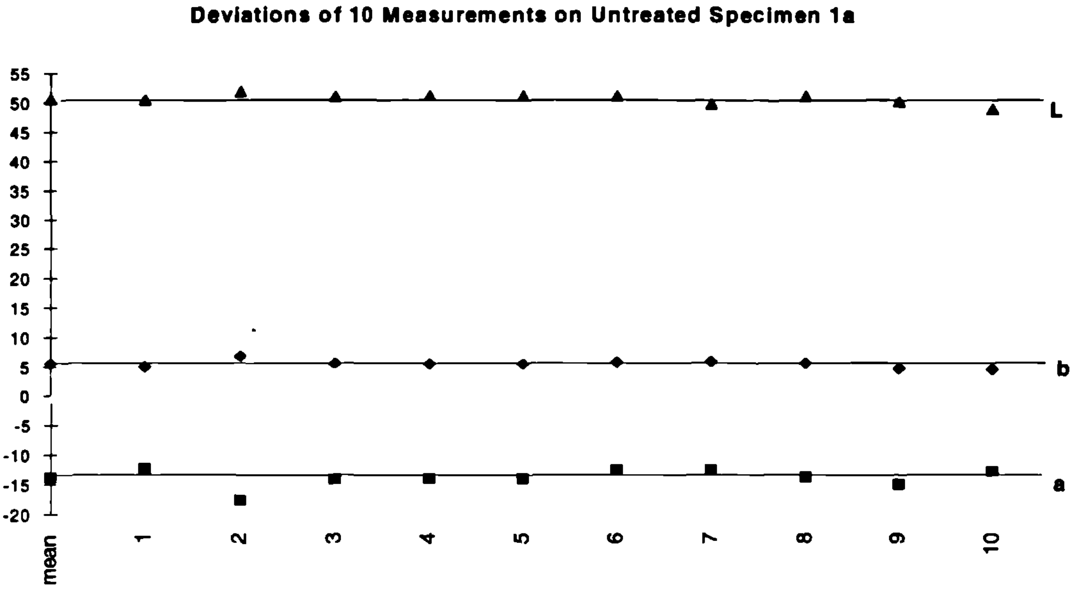


Figure 8. 10 Deviations in L*, a* and b*, After 10 Measurements on Untreated Sample.

The data given above is based on the 3 naipe fragments used (Figure 8. 10). Each sample had an approximate surface area of 5cm^2. Ten colour measurements were taken, and a mean was calculated. It was not surprising that the data varied. This was due to the uneven corrosion surface, and the number of measurements taken. In a normal conservation treatment, it is not possible to "sacrifice" an artefact to such an extent.

8.6 Conclusion

BTA, AMT and MBT did not inhibit the corrosion of nantokite instantaneously. BTA and AMT were known to be partially ineffective when applied to heavily chloride containing artefacts. The newly tested MBT was not as successful as indicated by previous experiments. Previous trials have shown MBT to be more effective than BTA and AMT, when applied to nantokite covered coupons. Large nantokite areas were protected by MBT, but small pinprick sized areas were still actively corroding.

A major drawback of the inhibitors was their discolouration of the corroded surface. All three inhibitors cause discolouration on the naipes, which confirmed the previous findings in chapter 7. AMT and MBT caused a yellowing which was not considered acceptable on archaeological artefacts. It is important to note that BTA darkens the surface of artefacts.

It is difficult to say if BTA is a better inhibitor than the other compounds with regard to corrosion protection, since the arrowhead #6679, and the bracelet #6672 were previously treated with another inhibitor. The previous small survey of BTA, and AMT treated arrowheads in table 8.1, indicated that BTA and AMT did not prevent instantly further corrosion. A long period of immersion in the inhibitor solution can cause more intense discolouration. Mercapto compounds were found to cause the most severe discolouration, mainly on nantokite.

Chapter 9

Discussion and Conclusion

This research on standardised testing developed from the need to find a better method to counteract copper chloride corrosion on archaeological copper and copper alloy artefacts. The transformation of cuprous chloride (nantokite) to basic copper chloride (paratacamite) is recognised as the most destructive form of corrosion on copper artefacts in museum exhibitions and storage. Since 1967 BTA has been applied in aqueous or alcohol solutions to copper artefacts, to prevent further corrosion. However, in many cases BTA was not able to prevent further damage. The only alternative inhibitor suggested as being any better in the conservation literature was AMT (Ganorkar et al., 1988). The research presented here had the aim of systematically testing new corrosion inhibitors for copper and copper alloys archaeological artefacts. This standardisation of corrosion testing for archaeological conservation required several new innovations, such as the simulation of reproducable corroded test coupons and assessment of film discolouration on artefacts.

9.1 Selection of Corrosion Inhibitors and Suitable Corrosion Tests

To identify suitable corrosion inhibitors for copper and copper alloy archaeological artefacts the following sources were screened: Chemical Abstracts, Science Citation Index, Patents, Industrial-, and key journals. Eighty two corrosion inhibitors for copper were listed, for use in aqueous or chloride containing environments. A list of conservation requirements was proposed in chapter 2.2 and assessed relative to the available published data on the corrosion inhibitors. This resulted in the selection of 8 inhibitors (Table 9.1) for further investigation.

Nitrogen based inhibitors	*Formula*	*Abrev.*
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

Table 9. 1 Selected Corrosion Inhibitors

The published literature clearly indicates that sulphur containing compounds are more effective in inhibiting copper corrosion (Thierry and Leygraf, 1985, 1013). This was confirmed in the systematic corrosion tests. The literature sighted, also indicated that the type of corrosion testing procedures used in industrial research were only in part suitable for testing in archaeological conservation. Researchers mainly used electrochemical techniques, such as potentiostatic or potentiodynamic techniques (Wranglen, 1985, 241) , for the qualitative assessment of the effectiveness of a corrosion inhibitor and for comparative studies. This type of corrosion testing is not useful for archaeological material since it utilises electrical connections on clean copper sheets. Excavated archaeological copper artefacts are typically covered in a variety of copper corrosion products, which to some degree should be preserved intact as the noble patination on the artefact. Archaeological material should not be used for extensive corrosion testing, due to its historical and academic value, as well as its compositional inhomogeneity.

The detailed survey of the relevant corrosion testing literature was necessary to assess the range of applications of potentially useful inhibitors. There are many standard corrosion testing procedures in the literature. Standard tests in general use are the British Standards Institute (BSI), Deutsche Industry Norm (DIN), International Standards Organisation (ISO) and the American Standards for Testing and Materials (ASTM). BSI and ASTM have the largest selection of corrosion tests for coatings on metallic substrates. However no specific standard has been designed for corrosion inhibitors. The only conservation corrosion test listed for the testing of copper corrosion inhibitors was designed by Angelucci et al. (1978). This test was adapted from the Corrodkote Test (ASTM B 380-61T). Angelucci et al.(1978) reported that the corroding paste ($CuCl_2$ and deionised water) developed a deeply pitted chloride surface, after 96 hours at 90-95%RH at room temperature. Furthermore, Angelucci et al. reported that there was no difference if the paste were exposed at room temperature and 50°C.

After repeated attempts however it was not possible to reproduce the results of Angelucci. The $CuCl_2$ paste deliquesced at 90-95%RH and ambient temperature. Only an RH threshold of 55% stopped the deliquescence of the paste, and induced a small amount of chloride pitting on copper coupons. With closer examination, it became apparent that copper coupons with an unevenly pitted corrosion surface were not suitable for corrosion testing. The main disadvantage of Angelucci et al. testing procedure was the unevenness of the corrosion surface. Uneven pitting of test specimens renders comparison of different inhibitor treated nantokite coupons difficult. To overcome the unevenness in sample preparation, a new corrosion testing procedure was adapted.

The new corrosion test for the testing of corrosion inhibitors for copper and copper alloy archaeological artefacts, utilised cupric chloride in deionised water as the corroding agent. Reagent grade copper coupons were immersed in a 1M solution of cupric chloride.

1. air-abrading of 99.9% pure copper coupons (20x50x1mm) with 47 micron glass beads
2. degreasing in an ultrasonic bath in 100 ml acetone
3. drying for 5 min. at 50°C under infrared lamp, and 10 min. cooled in a silica-gel buffered polyethylene box
4. weighing to ±0.01 mg
5. immersion into 25 ml of a 1 M solution of cupric chloride in deionised water, 1 day at ambient temperature
6. rinsing in deionised water, 3 x 20 min in 100 ml
7. quick drying in 200 ml ethanol
8. drying for 5 min. at 50°C under infrared lamp
9. exposure to 105°C in an oven for 30 min.
10. 10 min cooling in a silica-gel buffered polyethylene box
11. weighing to ±0.01 mg
12. immersion in 25 ml ethanol containing corrosion inhibitor, 24 hours at ambient temperature, only partially covered so oxygen can enter
13. drying for 5 min. at 50°C under infrared lamp
14. 10 min. cooling in a silica-gel buffered polyethylene box
15. exposure to 95% RH for 24 hours, at ambient temperature
16. weighing to ±0.01mg
17. observational assessment, photographic documentation
18. exposure to 95% RH for 24 hours, at ambient temperature
19. weighing to ±0.01 mg
20. observational assessment, photographic documentation

Table 9. 2 New testing procedure for the evaluation of corrosion inhibitors for copper and copper alloy archaeological artefacts

The test was adapted from several standard testing procedures described in BSI, DIN, ISO and ASTM. Specimen requirements are mainly taken from BS- 6917:1987 and ASTM G1-90. The main advantage of the new procedure is its "relatively good" reproducibility. In the Angelucci et al.(1978) test, the coupons had to be assessed visually. In the conservation literature, Green (1995) reported that the assessment of metal coupons by different observers leads to a variety of results. The interlaboratory comparison of the Oddy test was used by Green (1995) to assess storage and display materials. In this article, she discusses some of the disadvantages and errors of insufficiently standardised testing procedure for archaeological conservation.

The developed testing procedure for copper corrosion inhibitors, has been standardised to produce repeatedly a 20-25 micron thick nantokite layer covering the copper substrate. The nantokite in turn, is covered by a 5-10 micron thick layer of cuprite, with little intergranular corrosion evident. This chloride corrosion is much more even than the pitting corrosion reported by Angelucci et al. (1978). Such a coupon can then be readily tested with the application of selected corrosion inhibitors. The failure of the inhibitor film is indicated primarily by green spots of paratacamite. The new test is not only useful for corrosion inhibitors, but it can also be used to assess protective coatings such as Paraloid or Incralac, on corroded test coupons. It is more appropriate for archaeological conservation than for testing on clean metallic coupons.

9.2 Corrosion Testing of 8 Corrosion Inhibitors on Nantokite Covered Copper Coupons

The corrosion testing procedure outlined, was conducted using various corrosion inhibitor concentrations in reagent grade ethanol. Corrosion inhibition in percent (P.I.) was calculated according to the equation below

$$\text{P.I.}=\frac{\text{uninhibited corr. rate - inhibited corr. rate}}{\text{uninhibited corr. rate}}\times 100$$

When the corrosion test was performed in an acrylic chamber at 95%RH ±5% at 16-24°C, 0.25M concentration BTA (~3% by weight) was found to result in 78% corrosion protection after 24 hours at 95% RH and 20°C. This was reduced to 39% after 48 hours in the same environment. After 24 hours AMT was 75% protective. However, AMT protected 64% after 48 hours; a better result than BTA. These results were outperformed by MBT in 0.25 M concentration. MBT inhibited corrosion by 94% after 24 hours and 95% after 48 hours.

The effectiveness of the inhibitors during experiments of longer duration was somewhat different. These experiments were conducted in a Fisons Humidity Chamber with programmed temperature and humidity levels. The conditions during these experiment were more stable. After 52 days of steadily rising relative humidity, 10 to ~100% at 30°C, BTA had corrosion protection values of 90%, AMT 45% and MBT 95%.

During the long term experiments, an initial weight loss of inhibitor treated coupons was observed. This weight loss was observed in experiments 5.6, 5.7 and 5.9. Initially it was thought that this might be due to the evaporation of corrosion inhibitor. In experiment 5.8 the evaporation of reagent grade inhibitors was measured. AP was the only inhibitor that was volatile to a limited extent. AP lost 7.6% of its initial weight after 96 hours. The weight loss of the other inhibitors was below 0.1% and considered negligible. These minor fluctuations were probably due to temperature and RH fluctuations. AP could thus have a potential as a vapour phase inhibitor.

When BTA was applied in a concentration of 1M, producing a film which was 100% protective after 24 and 48 hours at 95% RH/20°C. However, some of the nantokite film was dissolved into the inhibitor solution and the surface of the copper sheet appeared to be etched. The remaining nantokite was darkened by BTA. This leads to the recommendation that BTA concentrations should not be as high as 1M, to avoid etching of the surface of an artefact, and the dissolution of corrosion products.

From the selected inhibitors MBT was found to be the best in terms of corrosion protection. Its corrosion protection at 0.25M concentration was 94% after 24 hours and 95% after 48 at 95% RH and 20°C. At a concentration of 0.01M the corrosion protection was 95% (24 hours), and 89% (48 hours). However, it was possible to remove the corrosion inhibitor film with an ethanol soaked cotton swab. Thus it may be considered partially reversible. The removal of inhibitor film was also possible on nantokite covered coupons treated with MBI, MBO and MP, suggesting that the chemical bond was not sufficiently strong. AP, DB, MBI, MBO and MP did not perform well in these corrosion tests and they are not recommended as a corrosion inhibitor for such severe relative humidities above ~95%.

While AP, DB, MBI and MBO form discolouring polymer films over the nantokite when applied in high concentration, these films are in general very protective. However, they are very unsightly, and suggest an unacceptable surface finish on an archaeological artefact. For the most part it was observed that an increase in inhibitor concentration increased corrosion inhibition and an increase in discolouration. Increased concentration can also result in the growth of thick inhibitor-copper polymer films. These films can obscure the surface details, as in case of DB, MBI, and MBO. The layers would not be satisfactorily within the porous corrosion products. The resulting film on the surface of an artefact would be unacceptable in archaeological conservation.

In experiment 5.10, the drying and the initial weight loss of BTA treated nantokite coupons, was further investigated to determine inconsistencies in experimental procedures, and to improve the reproducibility of the results. It was thought that the initial drying of BTA treated artefacts might increase the corrosion protection of BTA. This could not be substantiated. The weight loss of inhibitor treated coupons was found to be due to the differences in experimental procedure. For the first experiments an acrylic chamber was used. A relative humidity of ~95% was produced by placing a glass beaker filled with water into the sealed chamber. The temperature could not be controlled and fluctuated between 16-24°C. From experiment 5.6 onwards a humidity chamber with RH and temperature control was available. The humidity chamber resulted in more consistent results.

9.3 Atomic Absorption Spectrophotometry of Copper Minerals in Corrosion Inhibitor Solutions

Ganorkar et al. (1988) observed that AMT complexes nantokite into the inhibitor solution. It was thought possible that not only nantokite can be complexed in large amounts into the corrosion inhibitor solution, but also other corrosion products, since inhibitors are known to form complexes, not only with copper I, but also with copper II. This could result in a partial dissolution of noble patina, removing some of the detail or other evidence mineralised in the surface corrosion. The selected inhibitors had to be assessed for the following factors:

Which inhibitors complex specific minerals into solution?

Which mineral is most likely to be dissolved?

How much of the mineral goes into solution?

The minerals tested were copper, cuprite, malachite and nantokite. The minerals were in reagent grade form. The mineral powders (5mM) were immersed in 50 ml of inhibitor in reagent grade ethanol.

Nantokite/inhibitors solutions of MBT had the greatest concentration of copper in solution (2500 ppm).

Copper, cuprite and malachite were not attacked when immersed in BTA, AMT and MBT. However, MBI and MBO dissolved some copper when in contact with cuprite and malachite. This presented a further reason not to use these compounds.

The smallest amount of nantokite was complexed with AP (4 ppm). Overall, AP might be a poor polymer film forming corrosion inhibitor at elevated RH, but it prevents copper depletion in ethanol solution. This suggests its application as a storage medium for water logged material. Frequently waterlogged material is composite in nature. Such material could be stored for prolonged time in AP inhibited solutions, to prevent deterioration before final treatment. AP was also the inhibitor inducing the smallest amount of colour change on cuprite, malachite and nantokite.

The prolonged immersion in AP solutions and the effects on organic material have to be further investigated.

Overall it was found that copper, cuprite and malachite were less likely to be depleted by inhibitor solutions. With the exception of AP however, there is a high possibility of nantokite going into the inhibitor solution. It was concluded that copper corrosion inhibitors do not prevent the dissolution of all copper compounds.

9.4 Minerals Treated with Corrosion Inhibitors and their Colour Changes

BTA has been known to induce colour changes when applied to copper and copper alloy archaeological artefacts. No reference to this could be found in the literature. However, personal experience has confirmed this darkening effect. The more often an unstable artefact has to be treated with BTA, the darker the surface appearance. It was not known which corrosion products were affected and to what extent the colour changes disfigure the surface. The aim of this part of the research was to assess qualitatively and quantitatively, colour changes due to corrosion inhibitor treatments. This has not been done for the conservation of metallic artefacts. For many years archaeologists have used the Munsell Colour System to describe the colours of soil and ceramic sherds from an archaeological context. The colour changes are qualified by comparing the specimens with a set of colour reference chips from the Munsell Colour handbook. For conservation, this form of colour matching had several drawbacks. For example,

1. The Munsell Colour System available had a limited colour range
2. The Munsell Colour System is out of print

3. The colour matching varies greatly, depending on a standard observer, and a standard light source
4. The data cannot be quantified
5. It is difficult to compare data

Colorimeters overcome these problems. Schilling (1993) has used this technique for the colour measurment program in the tomb of Nefertari. In this study, a Minolta Chroma Meter CR-200 was used to assess the colour changes induced by corrosion inhibitors. The CIELAB system was applied to evaluate the data. This is the most widely used system in industry.

Cuprite, malachite and nantokite were treated with corrosion inhibitors and dried. The minerals were in powdered form since archaeological material is to inhomogeneous. The colour values were then individually measured. Three readings were taken and a mean calculated. The data is presented as ΔL*, Δa*, Δb* and ΔE* (Chapter 7).

The powdered minerals changed colour when treated with reagent grade ethanol. This was probably due to a change in surface texture. All minerals changed their colour when in contact with corrosion inhibitors. Of the selected inhibitors, AP caused the least overall colour change. The greatest colour changes have to be expected when treating cuprite with DB and MBI, and malachite with DB and MBT. The colour of nantokite is always changed when in contact with an inhibitor. The smallest change was observed with AP and the greatest change with AMT and BTA.

BTA, AMT and MBT are the most effective inhibitors. BTA caused a darkening of cuprite, malachite and nantokite. The largest amount of darkening was detected on nantokite. The darkening of malachite was more apparent than on cuprite, when treating with BTA. Repeated treatment of objects mainly covered in nantokite and malachite could cause darkening of the overall appearance of the artefact. This correlates with the darkening of artefacts containing large amounts of nantokite when repeatedly treated with BTA.

AMT and MBT caused a yellowing of malachite. The yellowing introduced by MBT was so great, that the compound was not recommended for artefacts covered in a largely malachite containing corrosion surface. In general, the trend confirms that sulphur containing corrosion inhibitors are more likely to cause a yellowing of malachite, according to the data presented here.

Generally, cuprite and malachite are less likely to be discoloured by an inhibitor than nantokite. The inhibitor that caused the smallest colour change was AP, and the inhibitor most likely to cause colour changes was DB.

9.5 Copper Alloy Archaeological Artefacts Treated with Selected Corrosion Inhibitors

The accelerated corrosion tests using cuprous chloride covered coupons identified BTA, AMT and MBT as effective corrosion inhibitors at 95%RH and 20°C. It was decided to assess these inhibitors on archaeological artefacts.

A hoard of Early Iron Age copper alloy arrowheads from Quidfa U.A.E., were treated with BTA and AMT. The data available indicated that the results varied greatly, mainly due to the inhomogeneity of the sample material. In many cases, repeated treatments with BTA, or AMT did not result in a protective inhibitor coating, when tested under extreme conditions of 95% RH.

One arrowhead was treated with 0.01M MBT in reagent grade ethanol. After two treatments the arrowhead had still two "pinprick" sized areas of paratacamite. A 24 hour treatment with 0.25M BTA resulted in the stabilisation of the arrowhead. It is not know if the corrosion protection was due to the combination treatment of MBT/BTA, the repeated treatment, or the treatment with BTA. More testing would be required, since the amount of chloride present in the arrowhead is unknown.

The treatment of a copper alloy bracelet with AMT also did not result in satisfactory corrosion inhibition after the first application. After two treatments with 0.068M AMT in reagent grade ethanol, the bracelet was still not stable. This was followed by a further treatment with 0.25M BTA. This resulted in a stable artefact.

The discolouration of copper alloys was further investigated by applying BTA, AMT and MBT to naipe fragments from the late Middle Sicán period at Batan Grande, Peru. The naipe fragments were cut into three sections and treated for one or two days with either of the inhibitors.

The sections were then analysed for their colour change, using the Minolta Colorimeter CR-200. AMT and MBT discoloured the surface, giving it an increased yellow colour. The yellowing was much stronger on the AMT treated sections than on the MBT treated sections.

BTA had the least over-all colour change when compared with the two mercapto compounds. However, it darkened the surface of the naipe. There was an increase in overall colour change when an artefact was repeatedly treated with BTA. This supported previous findings when arrowheads were treated several times in BTA solutions.

None of the corrosion inhibitors investigated in this research was able to completely prevent the conversion of cuprous chloride into basic copper chloride, in a high RH environment of 95% RH at 20°C. BTA, AMT and MBT were more protective than AP, DB, MBI, MBO, and MP. BTA is known not to always be effective. AMT has shown to be partially protective. This finding is supported by Brunner's (1993) research. MBT the most promising inhibitor according to the initial findings, also did not immediately inhibit further corrosion when applied to archaeological material.

This work has shown that none of the selected corrosion inhibitors inhibited copper chloride corrosion completely, and that all discoloured. Against this background, the inhibitors with the fewest disadvantages were BTA and AMT. The 24 and 48 hour testing at 95% RH and fluctuating ambient temperature (16-24°C), have indicated AMT to be more protective than BTA. However, long-term tests at high relative humidity have identified BTA as being a better corrosion inhibitor than AMT. BTA clearly caused a smaller overall colour change, but darkened the corrosion surface. Should the darkening be of major importance, then AMT could be used as an alternative. Since, there are no data available, about the long-term application of AMT, it is suggested that BTA would still be judged as superior. After 30 years of application, BTA has shown that there is no major damage caused, when applied carefully.

This work has shown that the experimental treatment of archaeological artefacts with new inhibitor compounds, should not be undertaken without preliminary tests on corroded coupons. Many researchers, such as Ganorkar (1988) and Brunner (1993), have used archaeological material to evaluate new compounds. Their results and the work on archaeological finds in this work, are highly variable, inconclusive and not sufficiently quantitative. Accelerated corrosion testing used in this research was carried out to assess the problems of variability and quantification. Treating an artefact represents the final step in assessing a corrosion inhibitor. The data from various archaeological artefacts cannot be qualified and quantified, since archaeological artefacts have different elemental compositions, different corrosion surfaces, and contain various amounts of copper chlorides.The data resulting from treating an archaeological artefact can only be further assessed, thanks to the data available form the initial standardised corrosion testing, for example, the discolouration of the surface can be predicted, and the preferential dissolution of specific copper corrosion products. In archaeological conservation, the use of archaeological material should only be a last resort when assessing new compounds. Archaeological artefacts are not only unique and irreplaceable, they also contain a complex metallurgical composition and corrosion products on their surface. Corrosion testing on these materials will produce inconclusive data.

9.6 Proposed Further Research

The long-term behaviour of BTA and AMT, in various RH and temperatures, should be further investigated. The surface chemistry of inhibitor films on corrosion layers needs even more extensive research. This is thought necessary to examine why

BTA seems more effective at slowly increasing relative humidity, while AMT is more effective in fluctuating relative humidity. The determination of the observed variation in corrosion inhibition of BTA treated coupons should also be further analysed.

The copper corrosion inhibitors, listed in the appendix should be compared with BTA to evaluate the possibility of better corrosion inhibitors. The proposed corrosion testing procedure for corrosion inhibitors, is a relatively easy corrosion test that can be performed in conservation laboratories with limited equipment, so it would allow further research on a smaller scale.

AP proved to be effective at an RH up to about 90% at 20°C. Its effectiveness should be further investigated, since it was the inhibitor that caused the smallest colour changes. At this point of the research, I would still be reluctant to recommend AP for important artefacts,even where the colour is of major importance. It is not known if AP can form secondary corrosion products. The long-term durability of AP should also be investigated.

The treatment of the arrowheads and the bracelet from the Al Ain Museum have shown that two treatments with AMT and MBT did not completely inhibit further chloride corrosion. These objects were treated with BTA, and were stable after this treatment. This poses the question of combination treatments. It is thought that some inhibitors react preferentially with copper-I and others more with copper-II. In future inhibitor testing, the application of combined treatments should be evaluated.

A final point that should be emphasized is that, during this research much effort was spent standardising corrosion testing procedures. The data collected, however, still show, that the reproducibility of corrosion testing results is not very good for corroded copper coupons. For further research, and testing in archaeological conservation, it is recommended that even more time should be spent assessing the reproducibility of effects. This has presented long-standing problems for the corrosion inhibition of copper archaeological artefacts.

Appendix

Appendix 1: Copper Corrosion Inhibitors in Industrial use.

Compound	Corrosion environment	Toxicity	Commends and Supplier	Reference
(Chlorophenoxybutenyl) ammonium salts				C.A. R180848w Jan. 1987 (C.A.=Chemical Abstracts)
1,3,5-triazine-2,4-dithiol derivs.	water and chloride			C.A. 87:171561j 1977-81
2-(Alkyldithio)-5 mercapto-1,3,4-thiadiazole				C.A.77:48470v 1976-72
2-(Alkyldithio)-5 mercaptothiadiazoles				C.A.80:3528n 1976-72
2-amino-3,4,1-diazoline-1,5-thione	hydrochloric acid and chlorine			C.A. 105:176945q 1982-86
2-aminopyrimidine	sodium chloride		Aldrich A7,860-8, Beil 24.80	C.A. 104:73206x 1982-86
2-aminothiophenol syn. 2-aminobenzenethiol	sodium chloride solutions		Aldrich 12,313-7	C.A.80:77454k 1976-72
2-mercaptobenzoxazole	ammonium chloride			C.A. 86:125623 1977-81
2-methylbenzimidazole syn. methyl-2-benzimidazole	sodium chloride	toxic when heated, irr. skin eye	Aldrich, M2,980-0, Beil 23,145	C.A. 96:110471n 1982-86
3,5-diphenyl-1,2,4-triazole			(Jap.)	C.A.85:147921q 1976-72
3-(5-phenyldithiocarbanyl)propionic acid	hydrochloric acid			C.A.85:196772a 1976-72
4,5-dighydroxyimidiazolinethione-2			(Japn.)	C.A. 100:1778720 1982-86
4-methylbenzotriazole				C.A.82:115145m 1976-72
5,6-dimethylbenzimidazole	sodium chloride		Aldrich D14,720-6, Merck ind. 11,3225	C.A. 88:26477c 1977-81
•	sodium chloride			C.A. 96:110471n 1982-86
5-Me benzimidazole				C.A. 98:220529t 1982-86
5-methylbenzotriazole		toxic when heated	Aldrich 19,630-4, Beil 26.58	C.A.82:115145m 1976-72
Aldehydes	flushed tanks with bleach			C.A. 103:P57873m 1982-86
Alkoxybenzotriazoles	aqueous systems			C.A. 233330v June1991
Alkoxybenzotriazoles	aqueous systems			C.A. P164243e June1991
Alkyl benzotriazoles	aqueous systems			C.A. 148532t June 1991
Alkylimidazole				C.A. 103:74830m 1982-86
Alkyne diol reaction with polyalkilene polyamides	water			C.A. 180984n Jan. 1987
Alluminium comp.-thiourea	sodium hydroxide			C.A. 96:90097w 1982-86
Allylthioureas syn. allylthiocarbamide		toxic when heated		C.A. 96:162274b 1982-86
Amine and Schiff bases	aqueous alcoholic solutions			C.A. 104:158062x 1982-86
Amines				C.A.104:232832s 1982-86
•	steam condenser			C.A. 240627f June 1987
•				C.A. 98:112138f 1982-86
Amino ketones	air			C.A. 99:112138f 1982-86
Aminohethyltriazole	chloride solutions			C.A. 76662f 1991
Aminomethyl-benzotriazole				C.A. 29339w 1991
Aminopyrazole derivates	acid chloride solutions			C.A. 86779b Jan. 1990
Aminothiazole derivs.	chloride			C.A. 103:9493e 1982-86
Aniline derivs.	hydrochloric acid			C.A. 103:44794m 1982-86
Arom triazoles and imine compds	water			C.A. P142532f Jan. 1987
Aromatic amines	water based inks			C.A. P8199u July 1990
Arsenic	sodium chloride solutions			C.A. 100:147360j 1982-86
Arsenite and arsenate	sodium chloride			C.A. 97:204891d 1982-86

Compound	Corrosion environment	Toxicity	Commends and Supplier	Reference
Atadecylamine				Trabanelli, 1970, 189
Azole compounds	air			C.A. 187881w 1991
Azole compounds	humid environments			C.A. 105:160834a 1982-86
Azole-type				C.A. 100:R38099k 1982-86
Azoles				C.A. 100:147366r 1982-86
•				C.A. 102:119358n 1982-86
•				C.A. 99:180108s 1982-86
Azoles and tiaziaes				C.A. 92:P131729r 1977-81
Benzoazo derivs.	water and sea water			C.A. 104: 172676g 1982-86
Benzoisothiazolone and Tolytriazole				C.A. 104:P38568v 1982-86
•	sodium chloride			C.A. 33726m 1991
•	ammonium chloride			C.A. 86:125623 1977-81
•	sodium chloride			C.A. 96:110471n 1982-86
•				C.A. 86:159729s 1977-81
•				C.A. 87:108386 1977-81
•				C.A. 92:155045 1977-81
•				C.A. 78:131227n 1976-72
•	chloride solutions			C.A.79:26401n 1976-72
•	chloride solutions			C.A.83:105295s 1976-72
•	sodium chloride solutions			C.A.78:105247n 1976-72
•				C.A.81:154607 1976-72
•	sodium hydroxide			C.A. 89:10534d 1977-81
•	sodium chloride			C.A.80:40192x 1976-72
•	sea-water			C.A.85:37062c 1976-72
•	sodium chloride solutions			C.A.84:81514e 1976-72
•	aqueous chloride solutions			C.A. 103:78273 1982-86
•				C.A. 105:31849z 1982-86
•				C.A. 102:P30510h 1982-86
2-benzimidazolethiol syns. 2-mercaptobenzimidazole.	sodium chloride		Aldrich M 320-5, Beil 24,119, Merck 11.1092	C.A.79:26420t 1976-72
mercaptobenoimidazole, mercaptobenzimidazole	sodium chloride solutions			C.A.84:81514e 1976-72
•	sodium chloride			C.A.80:40192x 1976-72
•	ammonium chloride			C.A. 86:125623 1977-81
•	sodium hydroxide			C.A. 89:10534d 1977-81
•	ethanol			C.A. 168962g 1991
•				C.A. 92:151619i 1977-81
2-benzothiazolethyol syns. 2mercaptobenzothiazole	sodium chloride	toxic when heated	Merck 261284D Merck ind. 11,5759, Beil 24,119, Aldrich M-330-2	C.A.80:40192x 1976-72
•	sodium chloride solutions			C.A.84:81514e 1976-72
•	sodium hydroxide			C.A. 89:10534d 1977-81
•	ammonium chloride			C.A. 86:125623 1977-81
•				C.A. 92:151619i 1977-81
•				C.A.85:129016u 1976-72
•	cooling water			C.A. P 159849h June 1987

Compound	Corrosion environment	Toxicity	Commends and Supplier	Reference
•	chloride media			105:199123g 1982-86
Benzimidazole syns. 1H-benzimidazole,		toxic when heated	Aldrich 19,412-3, Merck ind. 11.1091	C.A. 27141q Jan. 1990
benzoimidazole, 1,3 benzodiazole				C.A. 160839f Jan. 1987
•	sodium hydroxide			C.A. 89:10534d 1977-81
•	sodium chloride			C.A.80:40192x 1976-72
•	sea-water			C.A.85:37062c 1976-72
•				C.A. 103:13507r 1982-86
•	sodium chloride			C.A. 103:202685h 1982-86
•	hydrochloric acid			C.A. 105:138169e 1982-86
•				C.A. 97:30254f 1982-86
•				C.A.81:15923z 1976-72
Benzimidazole-2-thiol	sea water			C.A. 89:167808u 1977-81
Benzothiazole syn. benzosulfonazole		toxic when heated		C.A. 105:232852u 1982-86
•				C.A. 105:157245t 1982-86
•				C.A. 94:9199r 1977-81
2-benzoxazolethiol syn. 2-mercaptobenzoxazole	sodium chloride	toxic when heated		C.A.80:40192x 1976-72
•	sodium chloride solutions			C.A.84:81514e 1976-72
Benzylfluorenylidene dithiocarbazate				C.A. 239319v June 1991
Bromides and iodides	sea-water			C.A. 88:199818t 1977-81
Carbazide	aqueous solution			C.A. 87:9999m 1977-81
Carboxethyl-N-phenyldithiocabamate	hydrochloric acid			C.A.85:196772a 1976-72
Carboxyl iron chelates	sea water			C.A. P29093v July 1990
•	aqueous solutions			C.A. 101877y July 1990
Cyclohexylammonium benzoate				C.A. 203488r June 1987
Cyclohexilamine chromate				Trabanelli, 1970, p 187
Diazepinones			copper form copper(II) complexes	C.A. 97:144839f 1982-86
Dihydrogen phosphate double salt	chloride solutions			C.A. 96:147532r 1982-86
Dimethylphenylsalfonium	water solutions			C.A. P122749g July 1989
Diphenylcarbazide	chloracetic acids		Sigma D7766	C.A. 92:133630b 1977-81
Dithioxamide syn. rubeanic acid	sodium chloride solutions	toxic when heated	Merck 130613V	C.A.80:77454k 1976-72
Ferrous ion, mercaptobenzothiazole				C.A. P 159846e June 1987
Ferrous salts	sea-water			C.A. 200296v Jan. 1987
Heterocyclic compds.	potassium chloride solutions			C.A. 74869u Jan. 1987
Hexamethylenimine syn. homopiperidine	water		(russ) ICN 157359	C.A.85:132657j 1976-72
•	boiler water system		Aldrich H1,040-1, Beil 20,94	C.A. P82804n July 1989
Hydroxy ethylidene diphosphonic acid	aqueous solutions			C.A. 71095 June 1991
Imidazole and Benzotriazole	chloride		Aldrich 1-20-2, Merck ind. 23,3,568	C.A. 92:151729 1977-81
Imidazoles	air	harmful, toxic when heated	Merck 285466K	C.A. 195965a July 1990
Indazole	Sodium chloride		Aldrich 1-240-1, Beil 23,122, Merck 11,4848	C.A. 96:110471n 1982-86
Indole	sodium hydroxide	toxic when heated		C.A. 89:10534d 1977-81
Inhibitoras	water		copper review	C.A.84:139451a 1976-72
Inhibitoras	water		copper literature survey	C.A 82.6561y 1976-72
Mercapto benzothiazole	aqueous systems			C.A. 181198w Jan.

Compound	**Corrosion environment**	**Toxicity**	**Commends and Supplier**	**Reference**
and tolythiazole				1987
•	chlorinated water			C.A. 23039n Jan. 1987
Mercapto compounds	aqueous chloride solutions			C.A. 101:95998x 1982-86
•	hydrochloric acid			C.A.83:676695 1976-72
Mercaptothiazoline	chlorine derivatives			C.A.80:127344x 1976-72
Methylbenzotraizole		toxic when heated		C.A.81:154607 1976-72
Molybdate				C.A. 97:168462d 1982-86
Na methacrylate, Na acrylate	sodium chloride		(Russ)	C.A. 89:137476s 1977-81
Organic compunds			(important article)	C.A. 97:71866a 1982-86
P-thiocerasol	sodium chloride			C.A.79:26420t 1976-72
Phenylthiourea (1-Phenyl-2-thiourea)	sodium chloride solutions	toxic when heated	Aldrich 22,210-9, Beil 12,388	C.A.80:77454k 1976-72
Polyvinylimidazoles				C.A. 104:169001c 1982-86
•				C.A. 104:211299h 1982-86
Potassiumamoctylhydroxamate	sodium chloride			C.A. 93:122414d 1977-81
Quinoline	sodium chloride, sea-water	harmful, toxic when heated	Merck 300124G	C.A.85:36459a 1976-72
Sodium carbonate	water			C.A. 103:109705e 1982-86
Sodium Sulfide	water		Merck 30244V	C.A. 97:59779s 1982-86
Sulfathiazole syn. N-(2-thiazol)sulfanilamide	sodium chloride		Aldrich 29,290-7, Beil 27(3),4623, Merck ind. 11,8920	C.A.80:40192x 1976-72
•	sodium chloride			C.A.79:26420t 1976-72
•	sodium chloride solutions			C.A.84:81514e 1976-72
•	sea-water			C.A.85:37062c 1976-72
Sulphure containing compounds	Hydrochloric acid			C.A.79:72824a 1976-72
Tetrahydropentamethylquinolinium iodides				C.A. 216659a Jan. 1990
•				C.A. P103540m Jan. 1990
Tetraoctyltnlonate				C.A. 95:191197p 1977-81
Thiabendazole syn.(2-[4-tiazolyl]benzimidazole)	chloride media		Sigma T8904	C.A. 98:94271n 1982-86
Thiadiazole and triazoleamine		toxic when heated		C.A. 98:P18188a 1982-86
•	aqueous solutions			C.A. 119255n July 1989
Thiourea	sodium chloride	toxic when heated	Merck 304234E	C.A. 93:136471g 1977-81
•	sodium chloride solutions			C.A.80:77454k 1976-72
•				Trabanelli, 1970, p187
Phenylthiourea				Trabanelli, 1970, p187
Thiourea and Urea	acid solutions		Urea, Merck 305586G	C.A. 13533u 1991
Thiourea Trichloracetic acid				C.A.79:121180y 1976-72
Tolytriazole	sodium chloride			C.A. 33726m 1991
•				C.A. 104:P38568v 1982-86
•				C.A. 95:R190887b 1977-81
Tolythiazole	aqueous systems			C.A. 181198w Jan. 1987
•	chlorinated water			C.A. 23039n Jan. 1987
Tolytriazole and BTA	sodium chloride solutions			C.A. 96:112209p 1982-86
Triazinedithiols	moist air	toxic when heated		C.A 25883 s 1992
Triazole				C.A. 93:244044d 1977-81
•				C.A. 154848t June 1988
•	water			C.A. P71707d Jan. 1987
Triethanolamine syn.	water	toxic when heated	(russ)	C.A 85:132657j 1976-

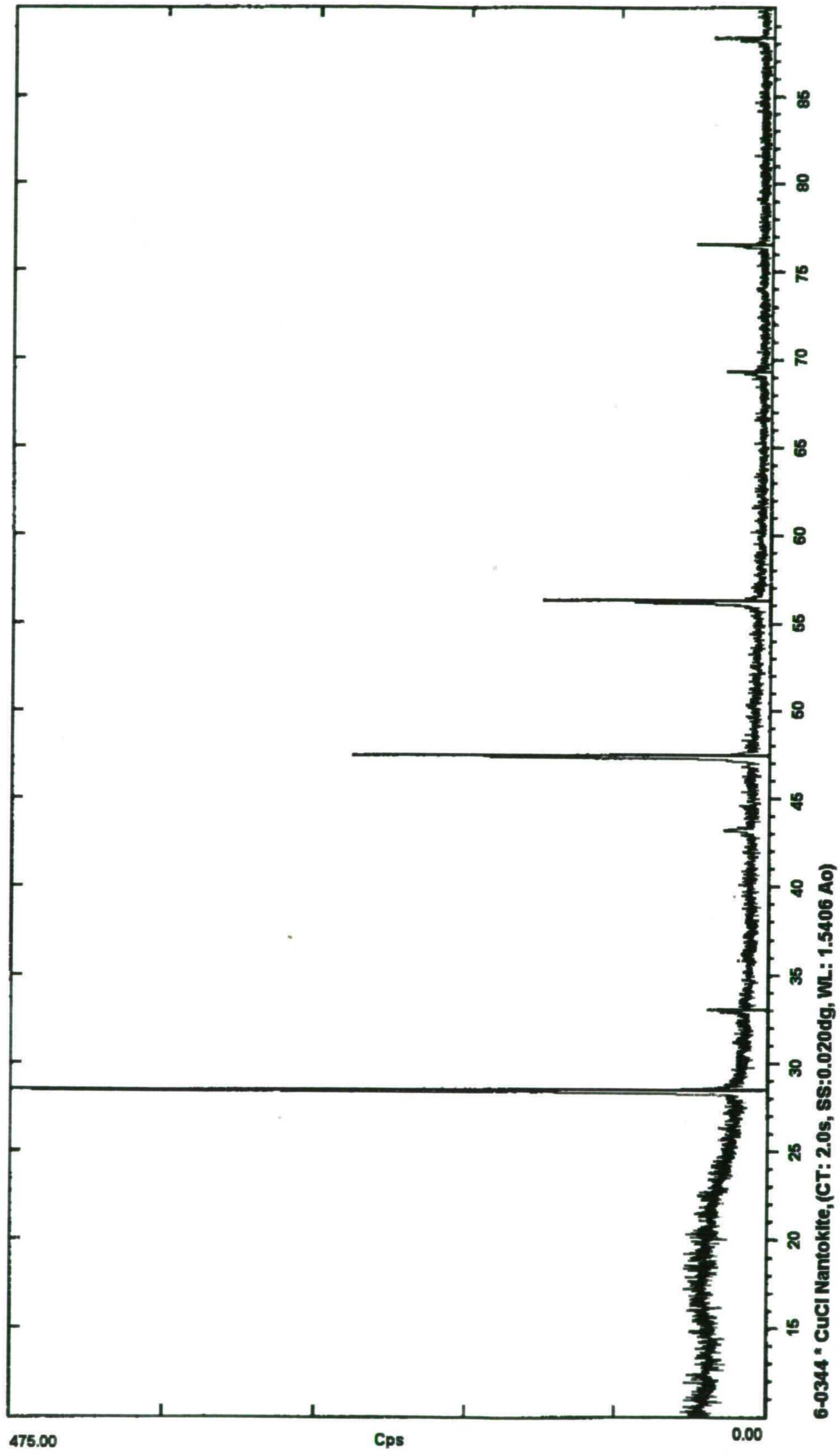
Compound	Corrosion environment	Toxicity	Commends and Supplier	Reference
trihydroxytriethanolamine				72
Triphenylphosphine	acidic-neutral aerated *solutions.*		Harmful, Merck 305373S	C.A. 163005e July 1989
Tris[(N-methyl-N-carboxymethyl)amino]triazine	chloride containing solutions			C.A. 122292q June 1991

Appendix 2: Corrosion Testing Procedures in Industrial use.

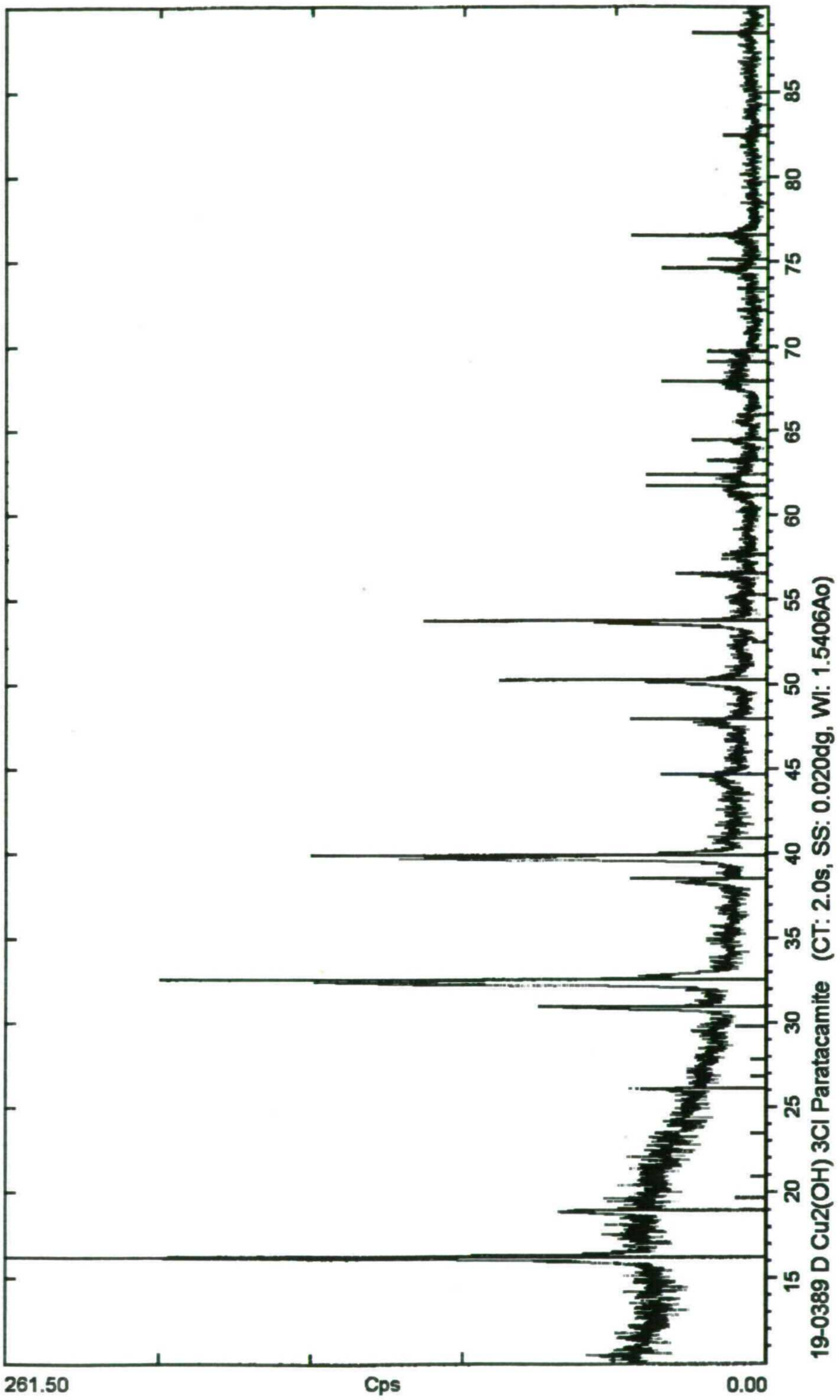
Testing procedures	Number	Scope
Flowers of Sulphur Porosity	ASTM 03.04 - 1984	for coatings on silver, copper, and copper alloys.
Corrodkote procedure	ASTM B380-85	evaluation of corrosion performance of copper/nickel/chromium and nickel/chromium coatings electrodeposited on steel, zinc alloys
Metal and Oxide Coatings thickness by microscopical analysis of crossection	ASTM B-487-73	
Nitric Acid Vapour	ASTM B-735	for gold coatings on copper
Sulphur Dioxide	ASTM B-735	gold coatings on nickel, copper, or copper alloys on flat or nearly flat surfaces
Paper Electrography	ASTM B-741	gold coatings on nickel, copper, or copper alloys on flat or nearly flat surfaces
Evaluation of painted or corroded specimens subjected to corrosive environment.	ASTM D 1654-68	
Rust protection by metal preservatives in the humidity cabinet	ASTM D 1748-70	
Coated metal specimens at 100 % relative humidity	ASTM D 2247-73	
Preparing, Cleaning, and Evaluating Corrosion test Specimens	ASTM G 1-90	procedures for preparing bare, solid metal specimens for tests, for removing corrosion products after testing, and evaluating damage
Abrasion resistance of pipeline coatings	ASTM G 6-72	
Corrosion and corrosion testing,-definition of terms relating to	ASTM G 15-71	
Applying Statistics to Analysis of Corrosion Data	ASTM G 16-88	methods of statistical analyses to interpretation of corrosion test results
Laboratory immersion corrosion testing of metals-recommended practice for	ASTM G 31(31)-72	
Examination and Evaluation of Pitting Corrosion	ASTM G 46-76	guide to identification and examination of pits and evaluation of pitting corrosion
Cyclic Humidity Test	ASTM G 60-86	steels under test to retard protective rust formation
Conducting Moist SO_2 Test	ASTM G 87-84	qualitative assessment test
Determination of resistance to humidity under condensation conditions	BS 3900:Part F2: April 1973	determination of resistance to humidity under condensation condition for paint of related products.
Resistance to artificial weathering	BS 3900:Part F3:1971	test for film failure of paints
Notes for guidance on the operation of artificial weathering apparatus	BS 3900:Part F3: 1971	assistance for setting up apparatus, for natural weathering
Resistance to continuos salt spray	BS 3900:Part F4:1968	procedure to determine resistance of single films or multicoats of paints or allied materials to salt water (artificial sea water)
Determination of light fastness of paints for interior use exposed to artificial light source	BS 3900:Part F5:1972	assessment light fastness of interior paints by exposure to light from artificial source

Testing procedures	Number	Scope
Notes on guidance on the conduct of natural weathering tests	BS 3900:Part F6: 1976	Specification of factors which need to be taken into consideration in the selection of methods for exposure to natural weathering of paint films
Determination of resistance to humid atmospheres containing sulphur dioxide	BS 3900:Part F8:1976	determination of the resistance of paints, and related products to humid atmospheres containing sulphur dioxide.
Determination of resistance to humidity (continuous condensation)	BS 3900:Part F9:1982 ISO 6279-1980	determination of resistance of paints and related materials to conditions of high humidity
Determination of resistance to neutral salt spray	BS 3900:Part F12:1985 ISO 7253-1984	determination of resistance of coatings to neutral salt spray
Filiform corrosion test on steel	BS 3900:Part F13:1986 ISO 4623-84	method for assessing protective action of coatings of paints of varnishes against filiform corrosion
Determination of resistance to liquids	BS 3900:Part G5:1976	three methods to test paint and related coatings to action of liquid
Metallic and related coatings	BS 5411:Part 10 1981	review of methods for testing adhesion of electrodeposit and chemically deposited metallic coatings.
Corrosion testing of metallic coatings	BS 5466:Part 1: 1977	neutral salt spray test to asses quality of coatings
Corrosion testing of metallic coatings	BS 5466:Part 2: 1977	acetic acid salt spray test to asses quality of metal coatings
Corrosion testing in artificial atmospheres: general principles	BS 6917:1987	corrosion test for metals with and with out permanent corrosion protection.
Testing under climatic conditions	DIN 50010-1961	
Corrosion of metals: factors, formula, symbols, units	DIN 50901 8.57	
Corrosion Test: summary	DIN 50905-1959	
Protection against corrosion; testing of derusting agents and inhibitors for iron and steel laboratory tests	DIN 50940 8.52	

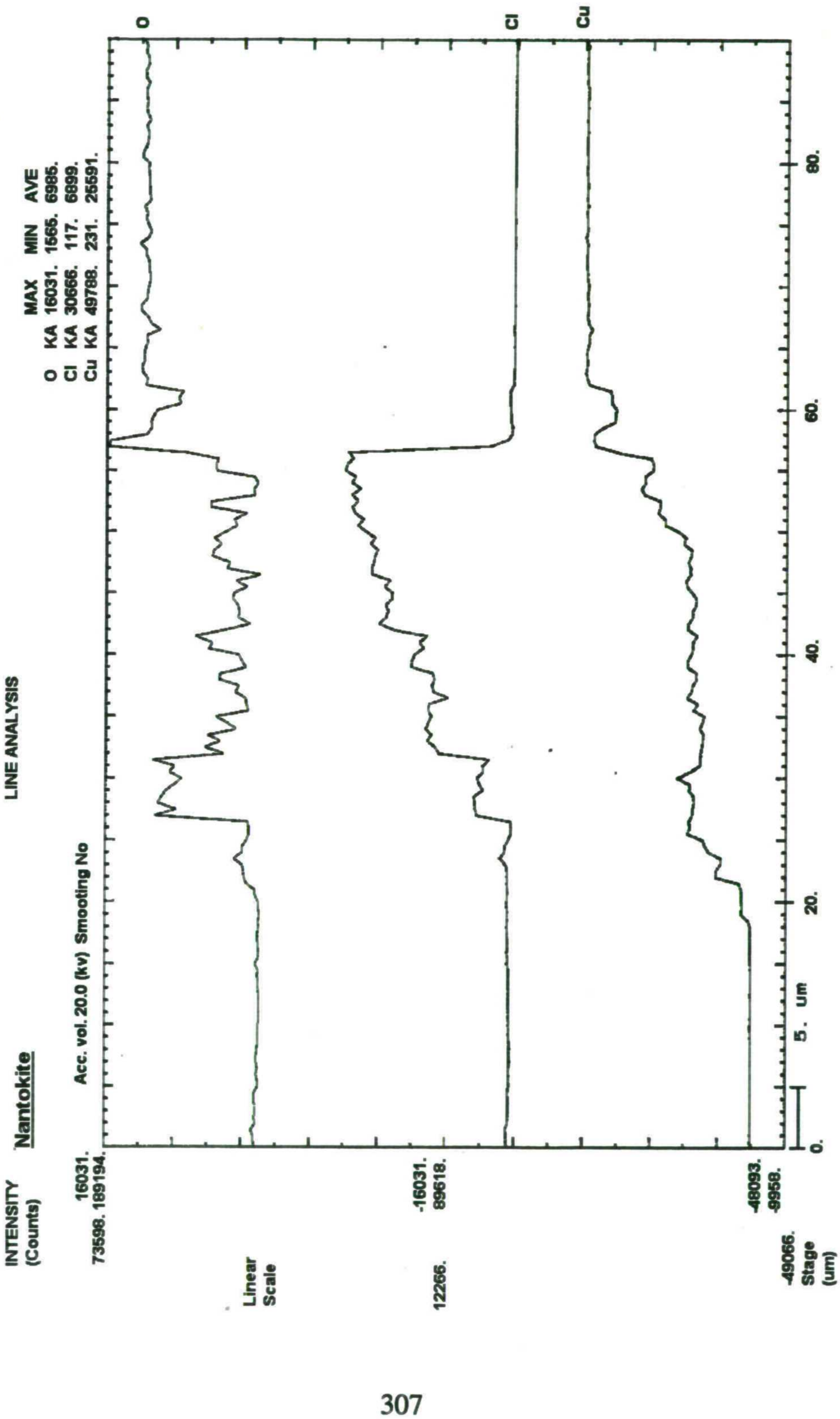
Appendix 3.1: X-ray Powder Diffraction Patern of Nantokite Covered Coupon.



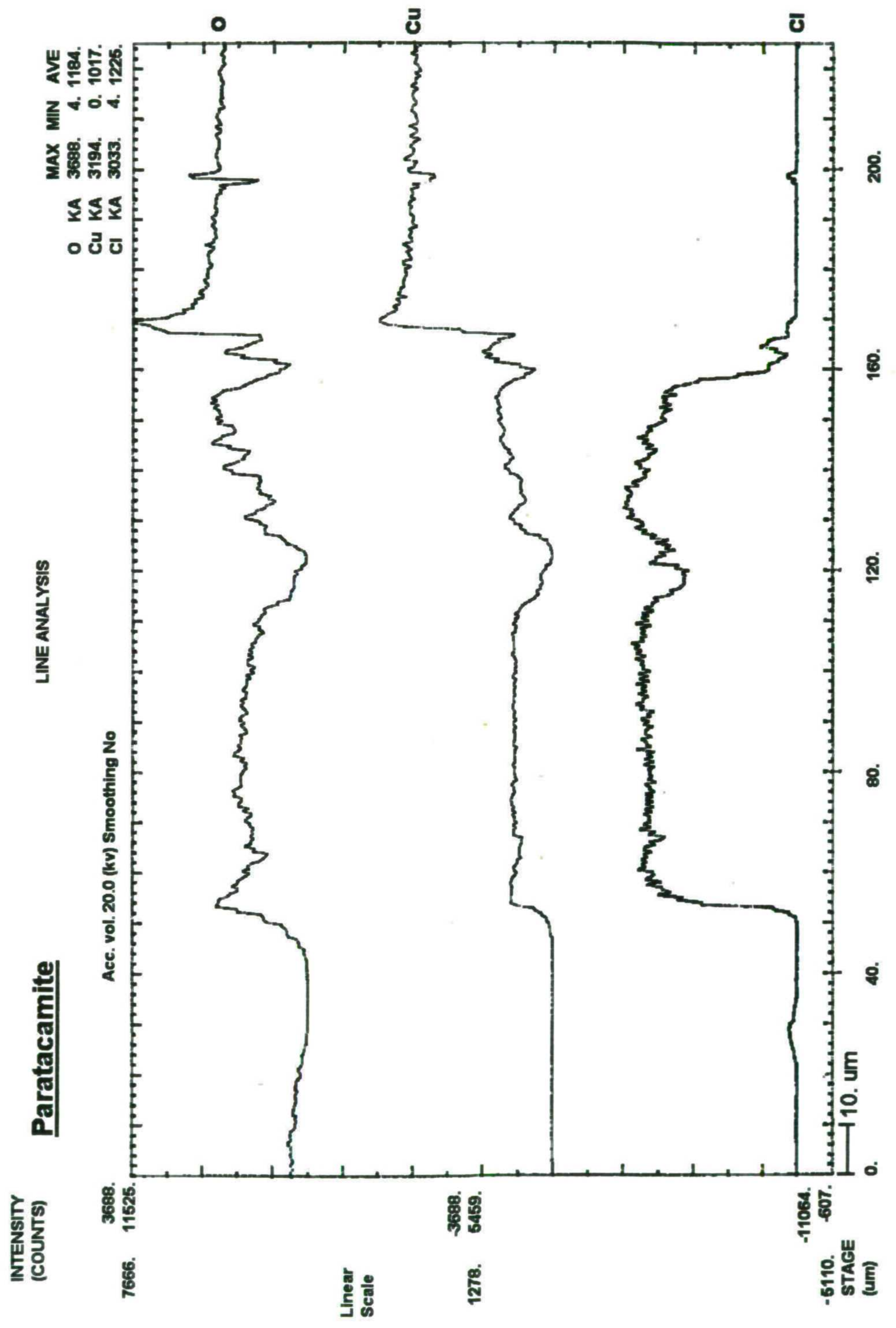
Appendix 3.2: X-ray Powder Diffraction Patern of Paratacamite Covered Coupon.



Appendix 3.3: Electon Probe Microanalysis of Nantokite Covered Coupon.



Appendix 3.4: Electron Probe Microanalysis of Paratacamite Covered Coupon.



Appendix 4: Raw Metric Data

Section 5.2	31.01.94	before	corroded	inhibited	inhibited + dish	24 hours 95% RH	change in mg	mean	s.d.	48 hours 5% RH	change in mg	mean	s.d.
BTA	A1	8.61553	8.62677	8.62596	29.50524	29.56037	55.1			29.56531	60.1		
	A2	8.77829	8.80217	8.80102	29.22016	29.2494	29.2			29.25685	36.7		
	A3	8.62176	8.63153	8.63017	29.51712	29.5316	14.5	33.0	16.8	29.55334	36.2	44.3	11.1
AMT	B1	8.28587	8.27973	8.27971	29.36784	29.38265	14.8			29.38672	18.9		
	B2	8.89817	8.90636	8.90661	29.57724	29.58397	6.7			29.5971	19.9		
	B3	8.97862	9.01406	9.01393	29.63591	29.64835	12.4	11.3	3.4	29.67842	42.5	27.1	10.9
AP	C1	8.94668	8.94651	8.95018	29.27138	29.3401	68.7			29.34347	72.1		
	C2	8.91009	8.9289	8.93005	29.34152	29.41025	68.7			29.40766	66.1		
	C3	8.88853	8.92145	8.92264	29.49269	29.56116	68.5	68.6	0.1	29.56485	72.2	70.1	2.8
DB	D1	8.79658	8.81347	8.77842	29.47789	29.52974	51.9			29.53285	55.0		
	D2	8.67525	8.70938	8.67353	29.88576	29.95491	69.2			29.95654	70.8		
	D3	9.0552	9.08728	9.05057	29.72034	29.78308	62.7	61.2	7.1	29.78692	66.6	64.1	6.7
MBI	E1	8.77091	8.78462	8.81495	28.93162	28.94574	14.1			28.95153	19.9		
	E2	8.96892	8.99066	9.01376	30.09063	30.10524	14.6			30.11292	22.3		
	E3	8.95258	8.98818	9.004	29.30937	29.31809	8.7	12.5	2.7	29.32706	17.7	20.0	1.9
MBO	F1	8.76671	8.77735	8.78049	28.55547	28.57083	15.4			28.58198	26.5		
	F2	8.99079	9.01593	9.02002	28.95428	28.97539	21.1			28.9868	32.5		
	F3	8.67348	8.70505	8.70866	29.50376	29.54568	41.9	26.1	11.4	29.55248	48.7	35.9	9.4
MBT	G1	8.66896	8.68282	8.68532	29.27873	29.28445	5.7			29.2872	8.5		
	G2	8.86245	8.88202	8.87982	28.89395	28.90037	6.4			28.90221	8.3		
	G3	9.07763	9.11202	9.1143	29.42317	29.44718	24.0	12.1	8.5	29.44992	26.8	14.5	8.7
MP	H1	8.75288	8.76411	8.76068	29.53652	29.5406	4.1			29.57565	39.1		
	H2	8.58442	8.583	8.58178	28.89175	28.92312	31.4			28.93274	41.0		
	H3	9.10491	9.12959	9.12451	29.30688	29.36477	57.9	31.1	22.0	29.36658	59.7	46.6	9.3
Blank	BL	9.05813	9.08568		29.89813	29.95103	52.9			29.98218	84.1		

Raw Data in Grams of Corrosion Experiment in Section 5.2.

Appendix 4: Raw Metric Data

Section 5.3	14.02.94	before	corroded	inhibited	inhibited + dish	24hours 95%RH	change in mg	mean	s.d.	48h, 95%RH	change in mg	means	s.d.
BTA	a1	8.94228	8.96735	8.97502	29.85453	29.8589	4.37			29.88757	33.04		
	a2	8.77328	8.79952	8.80639	29.22505	29.23652	11.47			29.26404	38.99		
	a3	8.83932	8.85418	8.8615	29.75035	29.75133	0.98	5.61	4.37	29.76053	10.18	27.40	12.42
AMT	b1	8.83707	8.84879	8.85013	29.93925	29.94773	8.48			29.94918	9.93		
	b2	8.88608	8.90714	8.90863	29.57873	29.58194	3.21			29.59256	13.83		
	b3	8.91604	8.93422	8.92756	29.54993	29.55915	9.22	6.97	2.68	29.57013	20.2	14.65	4.23
AP	c1	8.83737	8.86154	8.8645	29.18516	29.23678	51.62			29.24838	63.22		
	c2	8.92961	8.95263	8.95338	29.36456	29.40858	44.02			29.42324	58.68		
	c3	8.86951	8.89137	8.89228	29.46266	29.51313	50.47	48.70	3.34	29.52748	64.82	62.24	2.60
DB	d1	8.81247	8.8344	8.87604	29.5759	29.5829	7			29.58603	10.13		
	d2	8.85538	8.87355	8.90809	30.12022	30.12593	5.71			30.12859	8.37		
	d3	8.91197	8.93477	8.97348	29.64351	29.64885	5.34	6.02	0.71	29.6536	10.09	9.53	0.82
MBI	e1	8.52983	8.54309	8.62006	28.73656	28.7392	2.64			28.73884	2.28		
	e2	8.93029	8.9426	9.0247	30.10446	30.10633	1.87			30.10594	1.48		
	e3	8.76432	8.78635	8.87923	28.9185	28.9207	2.2	2.24	0.32	28.92042	1.92	1.89	0.33
MBO	f1	8.85281	8.87146	8.87476	28.64956	28.65687	7.31			28.66657	17.01		
	f2	8.86282	8.89377	8.94716	28.88274	28.89288	10.14			28.90357	20.83		
	f3	8.75781	8.78189	8.81595	29.61186	29.63069	18.83	12.09	4.90	29.635	23.14	20.33	2.53
MBT	g1	8.92306	8.93752	8.94934	29.54156	29.54298	1.42			29.54381	2.25		
	g2	8.73134	8.74117	8.75107	28.76502	28.76667	1.65			28.76816	3.14		
	g3	8.79166	8.79848	8.80868	29.11752	29.11866	1.14	1.40	0.21	29.11965	2.13	2.51	0.45
MP	h1	8.85227	8.0945	8.0965	28.87194	28.9001	28.16			28.90621	34.27		
	h2	8.93175	8.85868	8.86015	29.16964	29.17309	3.45			29.1767	7.06		
	h3	8.10419	8.94229	8.94357	29.12584	29.14752	21.68	17.76	10.46	29.15094	25.1	22.14	11.30
Blank	bl1	8.86334	8.87315		29.68509	29.70584	20.75			29.73859	53.5		
	bl2	8.84821	8.85695		29.98063	30.00888	28.25			30.03394	53.31		
	bl3	8.89403	8.90119		29.18468	29.2068	22.12	23.71	3.26	29.23674	52.06	52.96	0.64

Raw Data in Grams of Corrosion Experiment in Section 5.3.

Appendix 4: Raw Metric Data

Section 5.4	21.02.94	before	corroded	inhibited	inhibited + dish	24hours 95%RH	change in mg	mean	s.d.	48hours 95%RH	change in mg	mean	s.d.
BTA	a1	8.83456	8.86057	8.86856	29.7486	29.76626	17.66			29.79535	46.75		
	a2	8.86933	8.91823	8.92512	29.34516	29.35839	13.23			29.39633	51.17		
	a3	9.00269	9.02567	9.03145	29.91917	29.92434	5.17	12.02	5.17	29.94795	28.78	42.23	9.68
AMT	b1	8.57752	8.60654	8.61329	29.69826	29.71316	14.9			29.73054	32.28		
	b2	8.85215	8.88714	8.88884	29.55902	29.56797	8.95			29.58246	23.44		
	b3	9.12176	9.16402	9.16497	29.78724	29.80188	14.64	12.83	2.75	29.81211	24.87	26.86	3.87
AP	c1	8.84817	8.87745	8.87883	29.1996	29.24386	44.26			29.26205	62.45		
	c2	8.83151	8.86652	8.86783	29.27908	29.32565	46.57			29.34241	63.33		
	c3	8.8002	8.84033	8.84246	29.41274	29.44867	35.93	42.25	4.57	29.47174	59	61.59	1.87
DB	d1	8.79418	8.84375	8.8129	29.51235	29.58664	74.29			29.59227	79.92		
	d2	8.82692	8.86002	8.83284	30.04503	30.11254	67.51			30.11841	73.38		
	d3	8.81998	8.85558	8.81819	29.48861	29.55744	68.83	70.21	2.93	29.56288	74.27	75.86	2.90
MBI	e1	8.89167	8.93282	8.96544	29.08113	29.12989	48.76			29.13905	57.92		
	e2	8.53325	8.56267	8.59632	29.67473	29.72481	50.08			29.73448	59.75		
	e3	8.53665	8.55842	8.59277	28.6313	28.68111	49.81	49.55	0.57	28.69215	60.85	59.51	1.21
MBO	f1	8.73053	8.76793	8.76862	28.54383	28.59802	54.19			28.60531	61.48		
	f2	8.83252	8.8758	8.87638	28.81065	28.86312	52.47			28.87359	62.94		
	f3	8.81999	8.86457	8.86514	29.66033	29.71773	57.4	54.69	2.04	29.7253	64.97	63.13	1.43
MBT	g1	8.58746	8.61513	8.63339	29.22612	29.23078	4.66			29.2365	10.38		
	g2	8.85293	8.88687	8.89872	28.91267	28.9144	1.73			28.91675	4.08		
	g3	8.81542	8.8497	8.85922	29.16798	29.16997	1.99	2.79	1.32	29.17278	4.8	6.42	2.82
MP	h1	8.92273	8.95708	8.94723	29.7229	29.77908	56.18			29.78438	61.48		
	h2	8.78346	8.80903	8.80304	29.11267	29.15934	46.67			29.16071	48.04		
	h3	8.73359	8.76323	8.75655	28.93854	28.99516	56.62	53.16	4.59	29.00147	62.93	57.483	6.70
BLANK	bl1	8.87104	8.90504		29.72097	29.78011	59.14			29.7802	59.23		
	bl2	8.51421	8.5365		29.66023	29.71665	56.42			29.72041	60.18		
	bl3	9.12311	9.15239		29.43702	29.5076	70.58	62.05	6.14	29.49892	61.9	60.437	1.11

Raw data in grams of corrosion experiment in section 5.4.

Appendix 4: Raw Metric Data

Section 5.5	28.02.94	before	corroded	inhibited	inhibited + dish	24hours 95%RH	mg	mean	s.d.	48hours 95%RH	mg	mean	s.d.
BTA	a1	8.8178	8.83732	8.73244	29.62543	29.62472	-0.71			29.62484	-0.59		
	a2	8.83703	8.86343	8.75998	29.18536	29.18412	-1.24			29.18507	-0.29		
	a3	8.85204	8.8765	8.77176	29.66517	29.66404	-1.13	-1.03	0.23	29.66428	-0.89	-0.59	0.24
AMT	b1	8.81226	8.83472	8.83672	29.92314	29.9645	41.36			29.9695	46.36		
	b2	8.80954	8.83809	8.83968	29.51248	29.53836	25.88			29.54941	36.93		
	b3	8.80325	8.82278	8.82432	29.44644	29.46951	23.07	30.1	8.04	29.47002	23.58	35.62	9.35
AP	c1	8.84101	8.86587	8.86945	29.19116	29.20405	12.89			29.21275	21.59		
	c2	9.48188	9.52146	9.60214	30.01447	30.03202	17.55			30.02532	10.85		
	c3	8.68694	8.70658	8.80562	29.38527	29.3853	0.03	10.16	7.41	29.34567	-39.6	-2.39	26.68
DB	d1	8.84757	8.88802	8.86505	29.56472	29.58639	21.67			29.57034	5.62		
	d2	8.81776	8.84632	8.85431	30.06591	30.08478	18.87			30.08635	20.44		
	d3	8.83938	8.86193	8.85571	29.52716	29.5473	20.14	20.23	1.14	29.54853	21.37	15.81	7.22
MBI	e1	8.86822	8.88758	8.96999	29.08992	29.0904	0.48			29.09065	0.73		
	e2	8.81267	8.83506	8.91203	29.99376	29.99321	-0.55			29.9935	-0.26		
	e3	8.77745	8.79922	8.87777	28.92104	28.92128	0.24	0.06	0.44	28.92108	0.04	0.17	0.41
MBO	f1	8.81181	8.82823	8.831	28.60643	28.61338	6.95			28.61975	13.32		
	f2	8.93086	8.95978	8.96171	28.89663	28.90143	4.8			28.911	14.37		
	f3	8.84016	8.8596	8.86187	29.6579	29.66243	4.53	5.43	1.08	29.67243	14.53	14.07	0.54
MBT	g1	8.80169	8.82008	8.81806	29.41071	29.47107	60.36			29.47521	64.5		
	g2	8.80768	8.83876	8.83633	28.8506	28.92291	72.31			28.92588	75.28		
	g3	8.67625	8.69719	8.69475	29.00411	29.07005	65.94	66.2	4.88	29.07372	69.61	69.8	4.40
MP	h1	8.72223	8.73715	8.73107	29.50675	29.57996	73.21			29.58066	73.91		
	h2	8.73639	8.75565	8.75028	29.06016	29.12813	67.97			29.12951	69.35		
	h3	9.00346	9.02584	9.02049	29.2035	29.27751	74.01	71.73	2.68	29.27888	75.38	72.88	2.57
BLANK	bl1	8.83318	8.85836		29.6705	29.74485	74.35			29.74563	75.13		
	bl2	8.7404	8.76453		29.88873	29.96407	75.34			29.96525	76.52		
	bl3	8.66479	8.68747		28.97148	29.04521	73.73	74.47	0.66	29.04676	75.28	75.64	0.62

Raw Data in grams of Corrosion Experiment in Section 5.5.

Section 5.6	17.10.94	BEFORE	CUCL2	INHIBITED +GLASS	24 hours 70% RH	48 hours 70% RH	72 hours 70% RH	96 hours 80% RH	120 hrs. 80% RH	144 hrs. 90% RH	168 hrs. 90%	192 hrs. 90%	216 hrs. 100%	change in mg	mean	s.d.
BLANK	1	8.71636	8.73077	29.81308	29.81406	29.83462	29.83547	29.83863	29.84105	29.86532	29.86552	29.86803	29.87575	62.7		
	2	8.83314	8.83779	28.87357	28.87877	28.88997	28.89004	28.91046	28.9132	28.9161	28.91575	28.91804	28.93729	63.7		
	3	8.83202	8.84314	29.41125	29.41152	29.42394	29.44528	29.45407	29.45695	29.45819	29.45796	29.46063	29.4782	67	64.5	1.8
BTA	1	8.27679	8.27482	28.46467	28.46413	28.46394	28.46475	28.46471	28.46475	28.46833	28.46902	28.47084	28.47487	10.2		
	2	8.79977	8.80272	29.10727	29.10669	29.10607	29.10615	29.10649	29.10648	29.10939	29.1094	29.11176	29.11545	8.2		
	3	8.60493	8.6011	29.23295	29.23198	29.23109	29.22951	29.22956	29.22976	29.2334	29.2336	29.23612	29.24	7	8.5	1.3
AMT	1	8.54977	8.55592	28.85116	28.85117	28.85104	28.85112	28.85144	28.85143	28.85168	28.85228	28.85334	28.86135	10.2		
	2	8.61412	8.62172	28.93256	28.93269	28.93233	28.93267	28.93345	28.93357	28.93449	28.93431	28.93573	28.93927	6.7		
	3	8.74668	8.75287	29.07465	29.07508	29.07503	29.07504	29.0753	29.07539	29.07586	29.07562	29.07653	29.0796	5	7.3	2.2
AP	1	8.65994	8.66086	27.32305	27.31736	27.31733	27.31735	27.31763	27.31772	27.32544	27.32978	27.33211	27.35733	34.3		
	2	8.67099	8.6725	29.01449	29.01124	29.01107	29.01115	29.01155	29.01166	29.05385	29.05935	29.06101	29.06914	54.7		
	3	8.7611	8.75982	29.54165	29.53926	29.53915	29.53921	29.53937	29.53998	29.54488	29.55053	29.5596	29.59157	49.9	46.3	8.7
DB	1	8.38204	8.37463	29.07974	29.08409	29.08628	29.08667	29.0939	29.09565	29.09909	29.1002	29.10247	29.10558	25.8		
	2	8.76737	8.7701	29.9288	29.92985	29.93361	29.93514	29.93887	29.94048	29.94407	29.94504	29.9474	29.9493	20.5		
	3	8.93215	8.93878	29.63458	29.63296	29.64153	29.64372	29.64892	29.65026	29.65297	29.65358	29.65604	29.65851	23.9	23.4	2.2
MBI	1	8.83	8.83362	29.42415	29.42398	29.42468	29.42475	29.42531	29.42538	29.42697	29.42654	29.4279	29.43352	9.4		
	2	8.8199	8.82486	29.67307	29.67349	29.67427	29.67459	29.675	29.67498	29.67551	29.67535	29.67652	29.69024	17.2		
	3	8.78798	8.78248	28.72707	28.72747	28.72817	28.72848	28.7287	28.72877	28.72911	28.72944	28.73014	28.74043	13.4	13.3	3.2
MBO	1	8.75209	8.75777	28.14417	28.14442	28.14436	28.14413	28.14436	28.14443	28.14535	28.14528	28.14585	28.14797	3.8		
	2	8.93116	8.93257	28.87013	28.87038	28.87045	28.87049	28.87071	28.87122	28.87236	28.87281	28.87345	28.87719	7.1		
	3	8.8581	8.85111	21.42286	21.4229	21.42307	21.42324	21.42341	21.42394	21.42469	21.4253	21.42581	21.42835	5.5	5.5	1.3
MBT	1	8.75291	8.76165	21.41152	21.41185	21.41176	21.4116	21.4116	21.41171	21.41185	21.41175	21.412	21.41249	1		
	2	8.87439	8.89544	29.61079	29.61161	29.61266	29.61325	29.61512	29.61602	29.61774	29.61892	29.61998	29.62484	14		
	3	8.75143	8.75664	21.77934	21.77967	21.77994	21.78005	21.78035	21.78052	21.78062	21.78087	21.78115	21.7823	3	6.0	5.7
MP	1	8.82533	8.82841	29.39365	29.39409	29.39419	29.39421	29.39466	29.39497	29.39917	29.40082	29.40161	29.40873	15.1		
	2	8.84135	8.84436	20.66864	20.66937	20.66957	20.66969	20.67263	20.67502	20.69494	20.69989	20.70425	20.72671	58.1		
	3	8.49493	8.48575	28.93931	28.93983	28.93986	28.93996	28.94162	28.94238	28.95578	28.96027	28.96366	28.97888	39.6	37.6	17.6

Appendix 4: Raw Data in Grams of Corrosion Experiment in Section 5.6.

Section 5.7	1.11.94	before	cucl2	inhibited with glass	dish	24 hours 70% RH	48 hours 80% RH	second inhibition	24 hours 80% RH	48 hours 90% RH	72 hours 90% RH	96 hours 90% RH	change in mg	mean	s.d.
blank	1	8.82274	8.85778	30.94303	22.08696	30.94444	30.99560	30.99695	30.99789	30.99896	30.99932	30.9999	56.9		
	2	8.76796	8.80765	31.31575	22.50984	31.31579	31.36302	31.36469	31.36745	31.36681	31.36702	31.3677	51.9		
	3	8.77753	8.81758	31.40335	22.58753	31.40342	31.45108	31.45310	31.45476	31.45937	31.46212	31.4625	59.1		
	4	8.80236	8.83752	31.97128	23.13544	31.97114	32.02405	32.02577	32.03036	32.03194	32.03422	32.0348	63.5		
	5	8.95341	9.00167	30.87616	21.87609	30.87629	30.94032	30.94027	30.94491	30.94587	30.94618	30.9463	70.1	60.3	6.2
BTA	1	8.74261	8.79347	31.21737	22.41635	31.21695	31.21616	31.21457	31.21444	31.21480	31.21493	31.2152	-2.2		
	2	8.73052	8.77921	30.78293	21.99537	30.78242	30.78117	30.78021	30.77987	30.77957	30.77893	30.7792	-3.7		
	3	8.81228	8.86279	31.40250	22.53241	31.40219	31.40010	31.40129	31.40095	31.40063	31.40027	31.3999	-2.6		
	4	8.80855	8.85529	31.44944	22.58645	31.44904	31.44760	31.44806	31.44770	31.44734	31.44705	31.4467	-2.7		
	5	8.75730	8.79131	31.49195	22.69146	31.49159	31.49095	31.48987	31.48954	31.48949	31.48952	31.4897	-2.3	-2.7	0.5
AMT	1	8.78875	8.83025	30.90546	22.07399	30.90536	30.90543	30.90616	30.90640	30.90787	30.90780	30.9080	2.5		
	2	8.71610	8.76488	31.45951	22.69427	31.45932	31.45902	31.46002	31.46005	31.46067	31.46093	31.4616	2.1		
	3	8.17984	8.22177	30.68313	22.46086	30.68292	30.68240	30.68320	30.68314	30.68328	30.68343	30.6837	0.6		
	4	8.82756	8.87954	31.80134	22.92150	31.80125	31.80072	31.80157	31.80154	31.80160	31.80153	31.8019	0.6		
	5	8.82283	8.85567	31.91138	23.05529	31.91102	31.91086	31.91143	31.91136	31.91152	31.91152	31.9116	0.2	1.2	0.9
MBO	1	8.82445	8.87103	31.46677	22.59440	31.46678	31.46733	31.49460	31.49460	31.49465	31.49435	31.4944	27.6		
	2	8.73617	8.78383	31.43714	22.65197	31.43705	31.43698	31.47175	31.47157	31.47145	31.47133	31.4713	34.2		
	3	8.80636	8.86378	31.53308	22.66751	31.53307	31.53600	31.58499	31.58462	31.58453	31.58476	31.5850	51.9		
	4	8.77267	8.81766	31.57098	22.75206	31.57071	31.57107	31.80153	31.60550	31.60535	31.60526	31.6052	34.2		
	5	8.59772	8.62924	32.28596	23.65551	32.28592	32.28640	31.91142	32.32188	32.32181	32.32173	32.3218	35.8	36.7	8.1
MBT	1	8.92222	8.96304	29.94030	20.96926	29.93988	29.94027	29.94096	29.94091	29.94096	29.94109	29.9411	0.8		
	2	8.79856	8.84284	29.70786	20.85680	29.70793	29.70770	29.70895	29.70889	29.70912	29.70917	29.7092	1.3		
	3	8.80267	8.84441	30.23815	21.38482	30.23808	30.23777	30.23824	30.23807	30.23825	30.23821	30.2383	0.1		
	4	8.77189	8.81701	29.78791	20.96056	29.78775	29.78769	29.78783	29.78782	29.78795	29.78793	29.7879	0		
	5	8.74844	8.78728	30.05207	21.25564	30.05185	30.05192	30.05247	30.05252	30.05268	30.05268	30.0526	0.5	0.5	0.5
MP	1	8.77949	8.82226	30.84016	22.01846	30.84119	30.85757	30.84541	30.85513	30.87507	30.87954	30.8818	41.6		
	2	8.12299	8.14372	31.55980	23.41573	31.55975	31.56627	31.56060	31.56397	31.58638	31.59746	31.6009	41.1		
	3	8.85824	8.89005	32.25836	23.37026	32.25830	32.26518	32.26067	32.26284	32.28558	32.29835	32.3020	43.6		
	4	8.84149	8.88305	30.98976	22.10984	30.98989	31.00236	30.99409	30.99798	31.02071	31.02804	31.0312	41.4		
	5	8.78699	8.81527	32.31514	23.50128	32.31535	32.32498	32.31835	32.32118	32.34810	32.35657	32.3595	44.4	42.4	1.3

Appendix 4: Raw Data in Grams of Corrosion Experiment in Section 5.7.

Section 5.9	21'11'94	Before	CuCl2	Glass	Inhibited	Day 1 10% RH	Day 2 10% RH	Day 3 10% RH	Day 6 10% RH	Day 7 10% RH	Day 8 10% RH	Day 9 10% RH	Day 10 80% RH	Day 11 80% RH	Day 12 80% RH	Day 13 80% RH
BLANK	1	8.7760	8.79725	22.0870	30.88333	30.88324	30.88338	30.88316	30.88312	30.88324	30.88316	30.88332	30.91076	30.91499	30.91562	30.91633
	2	8.7732	8.79666	22.5099	31.30503	31.30506	31.30512	31.30503	31.30489	31.30492	31.30501	31.30515	31.34898	31.35202	31.35284	31.35408
	3	8.8212	8.85267	22.5886	31.43989	31.43998	31.44008	31.43974	31.43963	31.43959	31.43973	31.43991	31.47396	31.48591	31.48662	31.48948
	4	8.7573	8.78468	23.1359	31.91873	31.91854	31.91854	31.91850	31.91840	31.91837	31.91852	31.91866	31.96023	31.96636	31.96731	31.96750
	5	8.8243	8.86588	21.8765	30.74050	30.74035	30.74031	30.74025	30.74017	30.74010	30.74032	30.74028	30.78613	30.78913	30.78961	30.78947
BTA	1	8.7887	8.81525	22.4167	31.23990	31.23976	31.23962	31.23940	31.23932	31.23923	31.23941	31.23939	31.23954	31.23917	31.23916	31.23918
	2	8.7651	8.79350	21.9952	30.79226	30.79193	30.79213	30.79195	30.79194	30.79180	30.79205	30.79202	30.79182	30.79146	30.79114	30.79170
	3	8.8213	8.85013	22.5323	31.38726	31.38710	31.38703	31.38685	31.38694	31.38680	31.38708	31.38702	31.38633	31.38640	31.38611	31.38647
	4	8.7733	8.80136	22.5867	31.39463	31.39436	31.39434	31.39425	31.39408	31.39411	31.39430	31.39426	31.39350	31.39367	31.39350	31.39335
	5	8.7491	8.77679	22.6916	31.47966	31.47936	31.47933	31.47922	31.47924	31.47926	31.47932	31.47923	31.47920	31.47983	31.47965	31.47924
AMT	1	8.8240	8.84694	22.0740	30.92212	30.92192	30.92190	30.92185	30.92175	30.92172	30.92192	30.92194	30.92215	30.92236	30.92254	30.92196
	2	8.7420	8.77213	22.6944	31.46727	31.46718	31.46711	31.46709	31.46697	31.46705	31.46716	31.46721	31.46734	31.46731	31.46758	31.46750
	3	8.7741	8.80243	22.4618	31.26484	31.26466	31.26460	31.26452	31.26440	31.26451	31.26471	31.26461	31.26474	31.26496	31.26494	31.26472
	4	8.7960	8.82539	22.9214	31.74735	31.74724	31.74726	31.74719	31.74702	31.74708	31.74734	31.74723	31.74735	31.74796	31.74790	31.74760
	5	8.7553	8.77799	23.0547	31.83325	31.83302	31.83299	31.83291	31.83290	31.83284	31.83315	31.83308	31.83314	31.83361	31.83391	31.83384
MBT	1	8.7800	8.80125	20.9697	29.78030	29.77990	29.77995	29.77989	29.77978	29.77986	29.77996	29.77980	29.78002	29.78022	29.78044	29.78021
	2	8.8004	8.82723	20.8578	29.69550	29.69539	29.69522	29.69509	29.69500	29.69504	29.69515	29.69521	29.69532	29.69572	29.69580	29.69561
	3	8.7992	8.82798	21.3851	30.22322	30.22314	30.22298	30.22298	30.22281	30.22280	30.22306	30.22293	30.22296	30.22321	30.22339	30.22288
	4	8.7655	8.79006	20.9610	29.76162	29.76152	29.76144	29.76133	29.76114	29.76127	29.76148	29.76128	29.76166	29.76220	29.76212	29.76200
	5	8.7473	8.77240	21.2557	30.03822	30.03794	30.03796	30.03794	30.03771	30.03784	30.03808	30.03798	30.03799	30.03852	30.03863	30.03814

Appendix 4: Raw Data in Grams of Corrosion Experiment in Section 5.9.

Section 5.9		Day 14 80% RH	Day 15 80% RH	Day 16 80% RH	Day 17 80% RH	Day 18 80% RH	Day 19 80% RH	Day 20 85% RH	Day 21 85% RH	Day 22 85% RH	Day 23 85% RH	Day 24 90% RH	Day 25 90% RH	Day 26 90% RH	Day 27 90% RH	Day 28 90% RH
BLANK	1	30.91716	30.91775	30.91788	30.92403	30.92428	30.92470	30.92625	30.92690	30.92757	30.92771	30.92870	30.92901	30.93055	30.93111	30.93191
	2	31.35651	31.35735	31.35637	31.35679	31.35591	31.35635	31.35684	31.35783	31.35862	31.35872	31.36088	31.36005	31.36232	31.36276	31.36297
	3	31.49284	31.49287	31.49177	31.49257	31.49187	31.49189	31.49279	31.49413	31.49511	31.49525	31.50216	31.50122	31.50390	31.50435	31.50471
	4	31.97033	31.97010	31.96872	31.96925	31.96947	31.97060	31.97191	31.97252	31.97329	31.97330	31.97729	31.97707	31.97933	31.97971	31.98019
	5	30.79070	30.79116	30.79062	30.79083	30.79094	30.79117	30.79248	30.79158	30.79214	30.79234	30.80166	30.80225	30.80406	30.80468	30.80514
BTA	1	31.23932	31.23915	31.23879	31.23898	31.23862	31.23845	31.23874	31.23868	31.23881	31.23865	31.23868	31.23821	31.23899	31.23902	31.23928
	2	30.79201	30.79183	30.79060	30.79099	30.79072	30.79070	30.79108	30.79104	30.79136	30.79128	30.79268	30.79206	30.79355	30.79348	30.79366
	3	31.38678	31.38675	31.38601	31.38603	31.38591	31.38588	31.38618	31.38638	31.38673	31.38663	31.38896	31.38835	31.38995	31.39004	31.38998
	4	31.39390	31.39390	31.39335	31.39327	31.39247	31.39275	31.39332	31.39326	31.39363	31.39363	31.39336	31.39273	31.39412	31.39420	31.39410
	5	31.47934	31.47938	31.47893	31.47892	31.47880	31.47860	31.47907	31.47896	31.47903	31.47902	31.47880	31.47839	31.47936	31.47928	31.47922
AMT	1	30.92221	30.92222	30.92217	30.92248	30.92249	30.92264	30.92300	30.92301	30.92318	30.92321	30.92539	30.92595	30.92685	30.92706	30.92720
	2	31.46764	31.46767	31.46768	31.46798	31.46769	31.46818	31.46870	31.46870	31.46888	31.46884	31.47249	31.47349	31.47538	31.47570	31.47600
	3	31.26504	31.26483	31.26470	31.26490	31.26451	31.26480	31.26529	31.26520	31.26544	31.26531	31.26550	31.26563	31.26665	31.26674	31.26677
	4	31.74781	31.74783	31.74765	31.74799	31.74790	31.74796	31.74844	31.74838	31.74866	31.74860	31.75147	31.75283	31.75402	31.75432	31.75467
	5	31.83360	31.83368	31.83344	31.83359	31.83369	31.83364	31.83411	31.83389	31.83413	31.83390	31.83503	31.83545	31.83623	31.83637	31.83644
MBT	1	29.78022	29.78007	29.77996	29.78033	29.78045	29.78036	29.78059	29.78038	29.78064	29.78054	29.78035	29.78049	29.78141	29.78133	29.78126
	2	29.69556	29.69553	29.69536	29.69565	29.69566	29.69573	29.69586	29.69576	29.69594	29.69582	29.69568	29.69563	29.69631	29.69630	29.69641
	3	30.22320	30.22316	30.22286	30.22314	30.22327	30.22319	30.22354	30.22342	30.22354	30.22337	30.22336	30.22320	30.22381	30.22394	30.22388
	4	29.76195	29.76208	29.76185	29.76203	29.76192	29.76209	29.76238	29.76233	29.76249	29.76231	29.76230	29.76225	29.76287	29.76295	29.76293
	5	30.03831	30.03853	30.03818	30.03847	30.03848	30.03849	30.03872	30.03872	30.03881	30.03866	30.03887	30.03901	30.03939	30.03949	30.03956

Appendix 4: Raw Data in Grams of Corrosion Experiment in Section 5.9.

Section 5.9		Day 29 90% RH	Day 30 90% RH	Day 31 90% RH	Day 32 90% RH	Day 33 90% RH	Day 34 90% RH	Day 35 95% RH	Day 36 95% RH	Day 37 95% RH	Day 38 95% RH	Day 39 95% RH	Day 40 95% RH	Day 41 95% RH	Day 42 95% RH	Day 43 95%/25
BLANK	1	30.93314	30.93364	30.93407	30.93472	30.93540	30.93593	30.93722	30.93782	30.93913	30.94002	30.94128	30.94194	30.94266	30.94351	30.94434
	2	31.36421	31.36480	31.36517	31.36564	31.36637	31.36667	31.36788	31.36820	31.36942	31.37021	31.37075	31.37155	31.37229	31.37243	31.37355
	3	31.50607	31.50683	31.50724	31.50759	31.50842	31.50871	31.50999	31.51032	31.51170	31.51222	31.51274	31.51332	31.51387	31.51420	31.51512
	4	31.98140	31.98192	31.98246	31.98286	31.98374	31.98430	31.98572	31.98589	31.98740	31.98802	31.98902	31.98909	31.98950	31.99025	31.99112
	5	30.80702	30.80770	30.80823	30.80890	30.80962	30.81030	30.81138	30.81183	30.81322	30.81394	30.81481	30.81537	30.81610	30.81625	30.81729
BTA	1	31.23824	31.23835	31.23810	31.23818	31.23850	31.23846	31.23879	31.23885	31.23918	31.23924	31.23965	31.23921	31.23950	31.23941	31.23946
	2	30.79362	30.79426	30.79427	30.79433	30.79482	30.79487	30.79542	30.79555	30.79620	30.79642	30.79677	30.79856	30.79936	30.79947	30.80035
	3	31.39020	31.39041	31.39035	31.39037	31.39087	31.39109	31.39147	31.39157	31.39208	31.39229	31.39262	31.39245	31.39276	31.39297	31.39374
	4	31.39420	31.39427	31.39433	31.39436	31.39475	31.39508	31.39578	31.39600	31.39677	31.39753	31.39772	31.39766	31.39814	31.39829	31.39888
	5	31.47920	31.47957	31.47953	31.47946	31.47982	31.48006	31.48062	31.48057	31.48111	31.48140	31.48121	31.48123	31.48139	31.48148	31.48176
AMT	1	30.92750	30.92768	30.92751	30.92760	30.92808	30.92818	30.92923	30.92989	30.93086	30.93217	30.93272	30.93279	30.93344	30.93377	30.93488
	2	31.47660	31.47702	31.47736	31.47734	31.47821	31.47830	31.48115	31.48242	31.48390	31.48534	31.48565	31.48639	31.48684	31.48717	31.48834
	3	31.26773	31.26766	31.26765	31.26763	31.26814	31.26826	31.26881	31.26896	31.26972	31.26998	31.27048	31.27064	31.27108	31.27117	31.27196
	4	31.75515	31.75524	31.75543	31.75554	31.75637	31.75681	31.75959	31.76051	31.76141	31.76223	31.76274	31.76295	31.76347	31.76367	31.76443
	5	31.83663	31.83665	31.83650	31.83665	31.83698	31.83735	31.83860	31.83895	31.83994	31.84071	31.84120	31.84142	31.84187	31.84207	31.84294
MBT	1	29.78139	29.78140	29.78126	29.78122	29.78144	29.78137	29.78180	29.78158	29.78183	29.78192	29.78191	29.78173	29.78193	29.78207	29.78207
	2	29.69647	29.69636	29.69621	29.69616	29.69641	29.69661	29.69668	29.69667	29.69683	29.69685	29.69687	29.69665	29.69687	29.69686	29.69681
	3	30.22387	30.22378	30.22354	30.22352	30.22378	30.22396	30.22405	30.22405	30.22417	30.22420	30.22417	30.22405	30.22425	30.22412	30.22418
	4	29.76286	29.76298	29.76288	29.76280	29.76310	29.76323	29.76325	29.76329	29.76350	29.76359	29.76396	29.76362	29.76385	29.76386	29.76386
	5	30.03931	30.03972	30.03942	30.03965	30.03971	30.03996	30.04009	30.03986	30.04035	30.04024	30.04049	30.04024	30.04038	30.04045	30.04073

Appendix 4: Raw Data in Grams of Corrosion Experiment in Section 5.9.

Section 5.9		Day 44 95%/25°C	Day 45 95%/25°C	Day 46 95%/30°C	Day 47 95%/30	Day 48 95%/30°C	Day 49 95%/30°C	Day 50 100%/30°C	Day 51 100%/30°C	Day 52 100%/30°C	change in mg	mean	s.d.
BLANK	1	30.94551	30.94586	30.94792	30.94878	30.94954	30.95073	30.95244	30.95415	30.95486	71.6		
	2	31.37430	31.37473	31.37650	31.37690	31.37752	31.37833	31.37914	31.38057	31.38036	75.4		
	3	31.51616	31.51630	31.51765	31.51786	31.51829	31.51902	31.51984	31.52129	31.52175	81.9		
	4	31.99200	31.99325	31.99447	31.99505	31.99579	31.99656	31.99759	31.99853	31.99864	79.9		
	5	30.81825	30.81871	30.81992	30.82046	30.82112	30.82159	30.82249	30.82344	30.82383	83.3	78.4	4.3
BTA	1	31.23988	31.23948	31.23992	31.23976	31.23985	31.23979	31.23999	31.24002	31.23971	-0.2		
	2	30.80096	30.80252	30.80373	30.80407	30.80475	30.80554	30.80622	30.80803	30.80891	16.6		
	3	31.39436	31.39625	31.39728	31.39732	31.39779	31.39837	31.39871	31.39973	31.40001	12.7		
	4	31.39952	31.39965	31.40025	31.40018	31.40057	31.40080	31.40101	31.40151	31.40175	7.1		
	5	31.48187	31.48195	31.48199	31.48183	31.48213	31.48202	31.48211	31.48228	31.48229	2.6	7.8	6.2
AMT	1	30.93724	30.93913	30.94384	30.94615	30.94774	30.95035	30.95452	30.95932	30.96398	41.9		
	2	31.48976	31.49166	31.49549	31.49849	31.49998	31.50206	31.50666	31.51030	31.51478	47.5		
	3	31.27302	31.27516	31.28509	31.28808	31.28930	31.29039	31.29286	31.29595	31.29995	35.1		
	4	31.76543	31.76707	31.77015	31.77183	31.77345	31.77723	31.78178	31.78631	31.79078	43.4		
	5	31.84468	31.84639	31.85353	31.85677	31.85895	31.86320	31.87061	31.87615	31.88083	47.5	43.1	4.6
MBT	1	29.78220	29.78262	29.78303	29.78296	29.78336	29.78375	29.78483	29.78533	29.78566	5.4		
	2	29.69722	29.69714	29.69762	29.69747	29.69758	29.69790	29.69814	29.69849	29.69847	3		
	3	30.22453	30.22447	30.22496	30.22495	30.22505	30.22521	30.22564	30.22609	30.22609	2.9		
	4	29.76424	29.76426	29.76453	29.76451	29.76469	29.76471	29.76501	29.76575	29.76549	3.9		
	5	30.04096	30.04131	30.04182	30.04196	30.04227	30.04261	30.04334	30.04392	30.04397	5.8	4.2	1.2

Appendix 4: Raw Data in Grams of Corrosion Experiment in Section 5.9.

5.10	24.4. 1994	before	cucl$_2$ corroded	inhibited	inhibited+ dish	Day 1 10% RH amb.tmp.	Day 2 10% RH amb.tmp.	Day 5 10% RH amb.tmp.	Day 7 10% RH amb.tmp.	Day 9 10% RH amb.tmp.	Day 13 10% RH amb.tmp.	Day 15 10% RH amb.tmp.	Day 16 10% RH amb.tmp.	Day 19 10% RH	Day 20 10% RH amb.tmp.	24 hours 95% RH 20°C	48 hours 95% RH 20°C	72 hours 95% RH amb.tmp.
BTA	a1	8.7875	8.82068	8.82774	32.1988	32.19917	32.19921	32.19908	32.19905	32.19917	32.19899	32.19921	32.19906	32.19961	32.19989	32.19472	32.20057	32.20187
	a2	8.74358	8.78208	8.76408	31.46202	31.46226	31.46242	31.46219	31.46224	31.46242	31.46192	31.46225	31.46207	31.46205	31.46229	31.46159	31.46301	31.46450
	a3	8.71557	8.75454	8.79242	30.86427	30.86456	30.86452	30.8646	30.8646	30.86475	30.8643	30.86447	30.86453	30.86441	30.86474	30.8635	30.86485	30.86725
	a4	8.74541	8.78034	8.79231	31.44686	31.44715	31.44716	31.44691	31.4469	31.44685	31.44665	31.44676	31.44675	31.44673	31.44713	31.44654	31.44787	31.45002
	a5	8.79811	8.83248	8.84086	32.49776	32.49804	32.49804	32.49781	32.49782	32.49799	32.49751	32.49772	32.4981	32.49784	32.49812	32.49784	32.49819	32.49832
		before	cucl2	inhibited	inhibited+ glass	Day 1 10% RH amb.tmp.	Day 4 10% RH amb.tmp.	Day 6 10% RH amb.tmp.										
BTA	b1	8.72708	8.75885	8.77195	32.18965	32.1895	32.18955	32.18996								32.18977	32.19029	32.19094
	b2	8.90944	8.94235	8.95759	29.57901	29.57897	29.57885	29.57927								29.5781	29.57926	29.57969
	b3	8.75969	8.79191	8.80942	31.56184	31.56187	31.56157	31.56199								31.56025	31.56127	31.56154
	b4	8.82167	8.84945	8.86473	30.8835	30.88331	30.88306	30.88361								30.88204	30.88349	30.88415
	b5	8.70822	8.74395	8.75783	32.25933	32.25928	32.25916	32.25963								32.25919	32.261	32.26368
BTA	c1	8.82313	8.85637	8.8658	28.77861											28.77819	28.77865	28.77988
	c2	8.79255	8.82501	8.82965	29.42226											29.42166	29.42244	29.42449
	c3	8.79479	8.82044	8.82592	29.90427											29.90289	29.90359	29.90497
	c4	8.49897	8.52146	8.52766	28.82181											28.82082	28.82124	28.82139
	c5	8.75569	8.78565	8.79178	29.60395											29.60353	29.60411	29.60522
Blank	Bl1	8.84766	8.87728		29.18714											29.27127	29.27434	29.27474
	Bl2	8.76991	8.79457		28.83357											28.91734	28.91861	28.91659
	Bl3	8.91875	8.95159		30.03686											30.1246	30.1243	30.12621
	Bl4	8.70803	8.73197		29.03036											29.11171	29.11405	29.11610
	Bl5	8.7598	8.7918		28.97438											29.06267	29.06507	29.06548

Appendix 4: Raw Data in Grams of Corrosion Experiment in Section 5.10.

in ppm	BTA	AMT	AP	DB	MBI	MBO	MBT	MP	Blank
Copper	0	0	0	26	15	11	0	0	1
	0	0	0	18	15	15	0	0	1
	0	0	0	14	16	10	0	8	1
	0	0	0	14	16	9	0	0	0
	0	0	0	15	18	7	0	0	0
mean	**0**	**0**	**0**	**17**	**16**	**10**	**0**	**2**	**1**
Cuprite	1	0	42	21	156	102	0	2	15
	0	0	68	20	170	95	1	3	17
	1	1	35	21	164	95	1	4	14
	2	0	24	20	174	94	2	0	12
	1	1	12	20	167	89	1	1	16
mean	**1**	**0**	**36**	**20**	**166**	**95**	**1**	**2**	**15**
Malachite	0	1	1	31	329	269	0	4	1
	0	1	0	26	289	256	0	4	2
	1	1	0	27	324	236	0	0	2
	1	0	0	33	275	335	1	3	2
	0	1	0	35	257	307	0	1	2
mean	**0**	**1**	**0**	**30**	**295**	**281**	**0**	**2**	**2**
Nantokite	120	200	3	485	28	167	10	984	1300
	187	242	8	369	895	237	630	860	1300
	119	251	7	358	24	103	5887	990	1400
	115	243	0	359	667	122	3673	928	1200
	103	221	1	478	145	62	2303	999	1300
mean	**129**	**231**	**4**	**410**	**352**	**138**	**2501**	**952**	**1300**

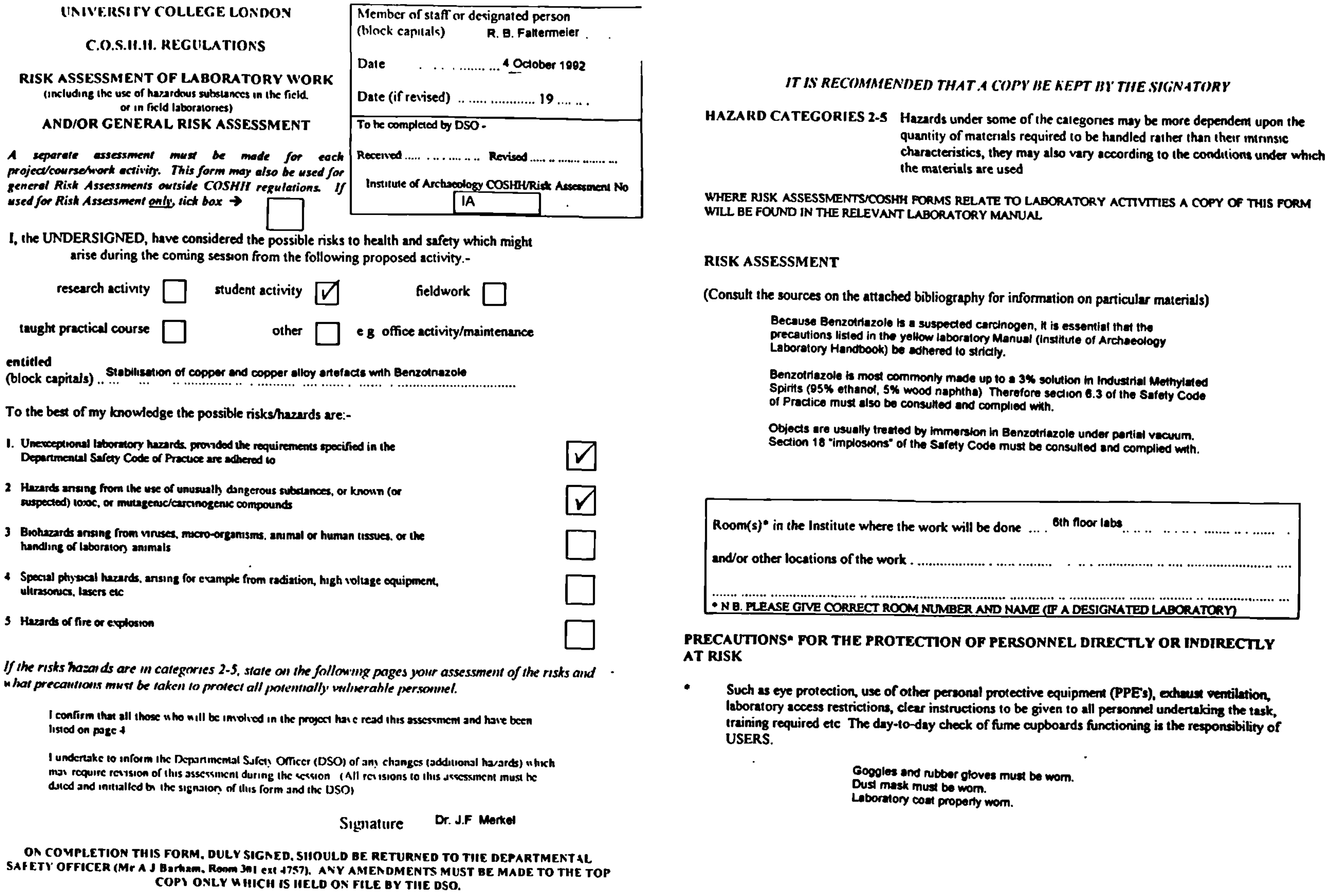
Appendix 5: Atomic Absorption Spectroscopy Data of Chapter 6, in ppm.

24 hours								48 hours							
Cuprite	L*	a*	b*	Δ L*	Δ a*	Δ b*	Δ E*		L*	a*	b*	Δ L*	Δ a*	Δ b*	Δ E*
Mineral	42.7	39.7	20.4	ref	ref	ref	ref		42.7	39.7	20.4	ref	ref	ref	ref
Blank	41.8	39.9	20.7	-0.9	0.2	0.3	1.0		41.7	39.9	21.1	-1.0	0.2	0.7	1.2
BTA/IMS	-	-	-	-	-	-	-		38.4	36.1	21.7	-4.3	-3.6	1.3	5.8
BTA	38.8	36.9	21.8	-3.9	-2.8	1.4	5.0		38.7	35.9	21.6	-4.0	-3.8	1.2	5.6
AMT	38.0	33.8	21.0	-4.7	-5.9	0.6	7.6		38.5	38.3	23.3	-4.2	-1.4	2.9	5.3
AP	42.5	39.7	20.9	-0.2	0.0	0.5	0.5		42.3	39.4	20.5	-0.4	-0.3	0.1	0.5
DB	32.0	34.5	25.2	-10.7	-5.2	4.8	12.8		33.9	34.3	25.9	-8.8	-5.4	5.5	11.7
MBI	39.4	36.1	21.8	-3.3	-3.6	1.4	5.1		35.3	28.9	24.5	-7.4	-10.8	4.1	13.7
MBO	38.8	39.0	23.7	-3.9	-0.7	3.3	5.2		43.8	41.2	22.7	1.1	1.5	2.3	3.0
MBT	38.3	39.5	22.9	-4.4	-0.2	2.5	5.1		40.1	38.8	25.8	-2.6	-0.9	5.4	6.1
MP	41.7	40.0	21.4	-1.0	0.3	1.0	1.4		42.9	40.3	22.3	0.2	0.6	1.9	2.0
Malachite	L*	a*	b*	Δ L*	Δ a*	Δ b*	Δ E*		L*	a*	b*	Δ L*	Δ a*	Δ b*	Δ E*
Mineral	55.5	-34.4	4.6	ref	ref	ref	ref		55.5	-34.4	4.6	ref	ref	ref	ref
Blank	55.3	-34.6	4.8	-0.2	-0.2	0.2	0.3		54.6	-34.4	5.0	-0.9	0.0	0.4	1.0
BTA/IMS	-	-	-	-	-	-	-		53.4	-33.6	5.9	-2.1	0.8	1.3	2.6
BTA	53.2	-33.1	5.3	-2.3	1.3	0.7	2.7		53.2	-33.4	5.8	-2.3	1.0	1.2	2.8
AMT	53.1	-31.7	6.5	-2.4	2.7	1.9	4.1		53.5	-31.9	8.1	-2.0	2.5	3.5	4.7
AP	55.3	-34.8	5.0	-0.2	-0.4	0.4	0.6		54.3	-34.1	4.8	-1.2	0.3	0.2	1.3
DB	50.1	-27.6	6.9	-5.4	6.8	2.3	9.0		52.3	-30.2	5.8	-3.2	4.2	1.2	5.4
MBI	55.1	-33.3	5.0	-0.4	1.1	0.4	1.2		53.6	-31.7	5.4	-1.9	2.7	0.8	3.4
MBO	53.2	-31.1	6.6	-2.3	3.3	2.0	4.5		56.5	-29.2	5.3	1.0	5.2	0.7	5.3
MBT	55.2	-31.4	15.7	-0.3	3.0	11.1	11.5		55.2	-23.6	27.0	-0.3	10.8	22.4	24.9
MP	55.7	-34.6	6.2	0.2	-0.2	1.6	1.6		55.2	-34.6	7.6	-0.3	-0.2	3.0	3.0
Nantokite	L*	a*	b*	Δ L*	Δ a*	Δ b*	Δ E*		L*	a*	b*	Δ L*	Δ a*	Δ b*	Δ E*
Mineral	75.9	-17.0	38.5	ref	ref	ref	ref		75.9	-17.0	38.5	ref	ref	ref	ref
Blank	65.8	-25.3	19.5	-10.1	-8.3	-19.0	23.1		78.5	-14.7	22.5	2.6	2.3	-16.0	16.4
BTA/IMS	-	-	-	-	-	-	-		53.5	-8.7	13.1	-22.4	8.3	-25.4	34.9
BTA	49.3	-11.8	22.1	-26.6	5.2	-16.4	31.7		57.0	-11.8	14.5	-18.9	5.2	-24.0	31.0
AMT	61.1	-22.0	30.3	-14.8	-5.0	-8.2	17.6		45.8	-3.0	10.7	-30.1	14.0	-27.8	43.3
AP	60.6	-20.3	41.3	-15.3	-3.3	2.8	15.9		73.5	-8.4	29.8	-2.4	8.6	-8.7	12.5
DB	68.8	-17.7	15.2	-7.1	-0.7	-23.3	24.4		49.7	1.6	19.7	-26.2	18.6	-18.8	37.2
MBI	66.3	-19.3	21.8	-9.6	-2.3	-16.7	19.4		59.0	-4.1	7.4	-16.9	12.9	-31.1	37.7
MBO	61.6	-17.9	22.7	-14.3	-0.9	-15.8	21.3		59.0	1.3	7.9	-16.9	18.3	-30.6	39.5
MBT	62.1	-19.8	24.6	-13.8	-2.8	-13.9	19.8		56.9	-5.5	17.0	-19.0	11.5	-21.5	30.9
MP	65.5	-28.7	15.0	-10.4	-11.7	-23.5	28.2		58.3	-5.2	15.8	-17.6	11.8	-22.7	31.1

Appendix 6: Colorimetric Raw data of Chapter 7.

BTA	L*	a*	b*		AMT	L*	a*	b*		MBT	L*	a*	b*
untreated1	50.47	-12.32	4.97		untreated1	51.56	-15.69	5.29		untreated1	44.59	-4.45	7.42
2	51.9	-17.69	6.72		2	49.1	-10.33	3.57		2	45.43	-5.56	8.47
3	50.98	-14.15	5.55		3	47.48	-9.48	3.77		3	40.56	-4.47	8.79
4	51.19	-13.99	5.46		4	47.16	-12.57	4.81		4	42.81	-4.67	9.07
5	51.27	-14.01	5.5		5	48.27	-9.36	3.62		5	45.96	-4.58	7.65
6	51.07	-12.57	5.71		6	45.54	-8.33	3.74		6	45.36	-5.29	8.81
7	49.75	-12.6	5.84		7	50.72	-14.38	5.17		7	39.44	-4.92	8.94
8	51.07	-13.81	5.65		8	52.71	-14.27	4.72		8	43.23	-5	8.98
9	50.18	-14.98	4.64		9	49.93	-10.96	3.58		9	44.91	-4.95	8.75
10	48.89	-12.86	4.48		10	46.74	-11.71	4.64		10	39.33	-6.06	8.18
mean	**50.68**	**-13.90**	**5.45**		mean	**48.92**	**-11.7**	**4.291**		mean	**43.16**	**-5.00**	**8.51**
24 hrs. 1	57.21	-19.58	1.66		**24 hrs. 1**	53.33	-16.89	7.39		**24 hrs. 1**	40.45	-5.14	12.3
2	53.1	-18.34	2.66		2	52.62	-18.01	7.88		2	44.66	-5.76	15.61
3	50.48	-17.7	3.59		3	51.81	-15.82	8.17		3	46.11	-8.2	15.32
4	49.95	-15.92	4.83		4	49.57	-15.76	9.07		4	41.57	-6.69	13.07
5	48.65	-15.44	6.05		5	48.74	-15.93	9.37		5	45.31	-7.57	15.47
6	51.65	-16.53	3.4		6	53.66	-18.16	7.73		6	45.31	-6.9	16.41
7	50.84	-16.95	3.69		7	51.66	-15.57	7.16		7	40.7	-6.01	12.38
8	60.29	-20.61	2.2		8	52.8	-19.23	7.4		8	44.47	-5.85	15.02
9	49.83	-15.52	4.74		9	48.61	-14.41	8.5		9	42.07	-8.09	14.33
10	54.48	-18.55	2.58		10	49.27	-16.26	9.49		10	42.93	-6.74	13.32
mean	**52.65**	**-17.51**	**3.54**		mean	**51.21**	**-16.6**	**8.216**		mean	**43.36**	**-6.70**	**14.32**
48 hrs. 1	45.22	-13.52	3.75		**48 hrs. 1**	47.27	-10.46	10.8		**48 hrs. 1**	46.06	-7.45	15.51
2	47.05	-13.5	4.91		2	44.7	-10.42	8.41		2	42.33	-6.11	14.35
3	45.83	-15.58	3.83		3	44.17	-9.16	8.6		3	40.01	-5.92	11.69
4	44.53	-13.26	4.92		4	48.24	-13.61	11.47		4	46.13	-7.17	15.98
5	45.41	-13.55	5.54		5	49.28	-17.81	11.12		5	44.09	-6.74	14.3
6	47.39	-14.13	5.2		6	49.17	-13.35	11.52		6	46.28	-7.35	16.12
7	44.43	-10.01	4.21		7	47.59	-10.8	10.83		7	43.63	-6.33	14.01
8	48.33	-14.19	3.79		8	47.76	-11.12	10.16		8	39.04	-5.58	10.77
9	46.15	-15.72	3.94		9	48.72	-13.5	11.49		9	41.41	-5.78	13.27
10	45.78	-13.19	5.43		10	46.18	-11.13	9.25		10	45.75	-7.52	15.81
mean	**46.01**	**-13.7**	**4.552**		mean	**47.31**	**-12.14**	**10.37**		mean	**43.47**	**-6.60**	**14.18**

Appendix 7: Colorimetric Raw Data of Naipes Treated with BTA, AMT and MBT.



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Member of staff or designated person (block capitals)	R. B. Faltermeier
Date	4 October 1992
Date (if revised)	19
To be completed by DSO -	
Received	Revised
Institute of Archaeology COSHH/Risk Assessment No	IA

I, the UNDERSIGNED, have considered the possible risks to health and safety which might arise during the coming session from the following proposed activity.-

research activity ☐ student activity ☑ fieldwork ☐

taught practical course ☐ other ☐ e g office activity/maintenance

entitled
(block capitals) Stabilisation of copper and copper alloy artefacts with Benzotriazole

To the best of my knowledge the possible risks/hazards are:-

1. Unexceptional laboratory hazards, provided the requirements specified in the Departmental Safety Code of Practice are adhered to ☑
2. Hazards arising from the use of unusually dangerous substances, or known (or suspected) toxic, or mutagenic/carcinogenic compounds ☑
3. Biohazards arising from viruses, micro-organisms, animal or human tissues, or the handling of laboratory animals ☐
4. Special physical hazards, arising for example from radiation, high voltage equipment, ultrasonics, lasers etc ☐
5. Hazards of fire or explosion ☐

If the risks/hazards are in categories 2-5, state on the following pages your assessment of the risks and what precautions must be taken to protect all potentially vulnerable personnel.

I confirm that all those who will be involved in the project have read this assessment and have been listed on page 4

I undertake to inform the Departmental Safety Officer (DSO) of any changes (additional hazards) which may require revision of this assessment during the session (All revisions to this assessment must be dated and initialled by the signatory of this form and the DSO)

Signature Dr. J.F Merkel

ON COMPLETION THIS FORM, DULY SIGNED, SHOULD BE RETURNED TO THE DEPARTMENTAL SAFETY OFFICER (Mr A J Barham, Room 301 ext 4757). ANY AMENDMENTS MUST BE MADE TO THE TOP COPY ONLY WHICH IS HELD ON FILE BY THE DSO.

IT IS RECOMMENDED THAT A COPY BE KEPT BY THE SIGNATORY

HAZARD CATEGORIES 2-5 Hazards under some of the categories may be more dependent upon the quantity of materials required to be handled rather than their intrinsic characteristics, they may also vary according to the conditions under which the materials are used

WHERE RISK ASSESSMENTS/COSHH FORMS RELATE TO LABORATORY ACTIVITIES A COPY OF THIS FORM WILL BE FOUND IN THE RELEVANT LABORATORY MANUAL

RISK ASSESSMENT

(Consult the sources on the attached bibliography for information on particular materials)

Because Benzotriazole is a suspected carcinogen, it is essential that the precautions listed in the yellow laboratory Manual (Institute of Archaeology Laboratory Handbook) be adhered to strictly.

Benzotriazole is most commonly made up to a 3% solution in Industrial Methylated Spirits (95% ethanol, 5% wood naphtha) Therefore section 6.3 of the Safety Code of Practice must also be consulted and complied with.

Objects are usually treated by immersion in Benzotriazole under partial vacuum. Section 18 "implosions" of the Safety Code must be consulted and complied with.

Room(s)* in the Institute where the work will be done 6th floor labs

and/or other locations of the work

* N B. PLEASE GIVE CORRECT ROOM NUMBER AND NAME (IF A DESIGNATED LABORATORY)

PRECAUTIONS* FOR THE PROTECTION OF PERSONNEL DIRECTLY OR INDIRECTLY AT RISK

- Such as eye protection, use of other personal protective equipment (PPE's), exhaust ventilation, laboratory access restrictions, clear instructions to be given to all personnel undertaking the task, training required etc The day-to-day check of fume cupboards functioning is the responsibility of USERS.

Goggles and rubber gloves must be worn.
Dust mask must be worn.
Laboratory coat properly worn.

Appendix 8: example of COSHH assessment for corrosion inhibitor used in this research (BTA)

Material	Number	Supplier
Benzotriazole	12748	Fluka Chemie AG, CH-9470 Buchs
2-Aminopyrimidine	09380	Fluka Chemie AG, CH-9470 Buchs
2-Amino-5-mercapto-1,3,4-thiadiazole	08380	Fluka Chemie AG, CH-9470 Buchs
5,6-Dimethylbenzimidazole	39580	Fluka Chemie AG, CH-9470 Buchs
2-Mercaptobenzimidazole	63710	Fluka Chemie AG, CH-9470 Buchs
2-Mercaptobenzoxazole	63750	Fluka Chemie AG, CH-9470 Buchs
2-Mercaptobenzothiazole	63720	Fluka Chemie AG, CH-9470 Buchs
2-Mercaptopyrimidine	63851	Fluka Chemie AG, CH-9470 Buchs
Copper turnings	27812	BDH Pool, BH15 1TD, England
Copper I oxide	20882-5	BDH Pool, BH15 1TD, England
Copper II carbonate	20789-6	BDH Pool, BH15 1TD, England
Copper I chloride	10092	BDH Pool, BH15 1TD, England
Copper II chloride	278353j	BDH Pool, BH15 1TD, England
Copper II chloride hydrate	1008822	BDH Pool, BH15 1TD, England
pH10 buffer solution	19240	BDH Pool, BH15 1TD, England
Ethanol 99.7-100%	10107	BDH Pool, BH15 1TD, England
Aceton	10003 7t	BDH, Poole, BH 15 1TD, England
Polishing fluid	Ilocut 430	Castrol Ltd, SWIN DON, England
Sandpaper		Buehler, Lake Bluff, IL 600444, USA
Epoxy mounting resin	Epo-kwick	Buehler, Lake Bluff, IL 600444, USA
Photo film	AGFA Ultra ISO 50	AGFA-AG, D-51301 Leverkusen
Incralac	LA1	Conservation Resources (U.K.), Unit 1, Horspath Industrial Estate, Cowley, Oxford, OX4 2RD, England
Paraloid	B72	"
Silica Gel	300624U	BDH Pool, BH15 1TD, England
Glass beads 47 micron		Croxton and Garry
Instruments		
Abrasive unit		R.S. Jackson
Atomic absorption spectrophotometer	SP9	Pye Unicam
Balance	AT261 delta range	Mettler
Camera	OM-2n	Olympus
Colorimeter	CR200	Minolta
Deionised water	SD2800	Seradest
Electron probe microanalyser	Superprobe JXA 8600	Jeol
Humidity chamber	812417	Fisons
IR lamp	300CH	Philips
Metal polisher	universal polisher	Metaserv
Microscope	BH2	Olympus
Polishing fluid	Ilocut 400	Castrol
Thermohygrometer		Rotronic
X-ray powder diffraction	D5000	Siemens

Appendix 9: List of Suppliers

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