AMT; A NEW CORROSION INHIBIRTOR?

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Introduction

In both storage and display, the processes of corrosion may threaten the stability of metal artefacts. The theme of this paper is the investigation of the efficacy of a newly cited corrosion inhibitor in the inhibition or prevention of corrosion in copper-tin bronzes. The term inhibitor is derived from the Latin *inhibere*, "to check". Generally, upon excavation most bronzes are covered in a more or less stable corrosion surface, the "patina" in which both the evenness and stability contribute to the aesthetic beauty of the artefact. However, this outer surface has little in common with the original appearance of the artefact.

Adverse burial conditions may cause the accumulation of chlorides within the object and the resultant interaction of chloride with any remaining metal may lead to further deterioration which, in turn, may result, in extreme circumstances, in the complete mineralization and collapse of the artefact.

Many different experiments have been carried out on artefacts to try to prevent further corrosion due to the presence of chlorides but some, for example chemical stripping techniques have caused irreparable damage. In the late fifties and early sixties, certain organic corrosion inhibitors, developed for industry, were tested to try to conserve metal artefacts (Brinch Madsen, 1967). Nowadays, the most widely used is benzotriazole (BTA), Theoretically, this chemical forms a Cu-BTA polymeric complex over the corroded surface which should prevent further corrosion.

More recently, 2-amino-5-mercapto-1,3,4-thiadiazole (AMT) has been proposed as an alternative treatment to that of BTA, (Ganorkar, 1988, 97-101). In practice, it has been found that stabilisation with BTA is not always successful. Furthermore, it has been noted that the treatment may result in darkening of the patina and, in some cases, the development of a slight gloss. A series of experiments were designed to test the effects of AMT however, it was not possible to follow exactly the methodology suggested, by Ganorkar because certain steps e.g. the addition of "a few drops of nitric acid" (Ganorkar, 1988, 98), were considered to be hazardous to the artefacts and may have caused the surface to be etched. Consequently, new methods of treatment with AMT had to be developed.

A search of the literature produced only two articles relating AMT to conservation. Although further information has been requested by personal communication with M.C.Ganorkar in India (personal communication, 1991), it has yet to be received. The Art and Archaeological Technical Abstracts, Chemical Abstracts and Science Citation Index, were consulted as well as chemical suppliers Ciba-Geigy, Merck AG, Imperial Chemical Industries, and Schuchart to reveal only four other publications which relate the complexing behaviour and application of AMT in industrial applications.

As far as could be discerned, it appears that little or no investigative research has been carried out into the conservation properties of AMT. Other conservation laboratories such as the British Museum, the Museum of London, the J.P.Getty Museum, the Metropolitan Museum of Art, and the National Maritime Museum were consulted but to no avail. However, the "Staatliche Akademie der Bildenden Künste" (Sander, 1991) in Stuttgart, Germany, and the "Antikenmuseum Basel und Sammlung Ludwig" in Basel (Faltermeier, 1991), Switzerland were found to have made some investigation and the Akademie provided a short letter describing briefly the details and the results of the experiment (Sander, 3.7.91). Certain chemists, in Imperial College London, UCL Engineering Department, and Birkbeck College were consulted. Unfortunately they were unable to provide any background information as the subject is very specialised.

Since only two articles are directly pertinent to the application of AMT in conservation (Ganorkar, 1988, Rao, 1987), it was decided to test further the usefulness of AMT as a corrosion inhibitor in conservation. A series of experiments was designed to discover the solubility of AMT in various solvents; its effects on corroded surfaces and single corrosion products; and its interaction with pure copper metal. The quantity of copper leached into solution by the AMT was monitored by atomic absorption spectroscopy. Thus the experiments were constructed in such a way so that the effects of AMT might be contrasted under "standard" conditions i.e. uncorroded modern metal in contrast with "non-standard" conditions i.e. archaeological metal. It was anticipated that the latter might provide some insight into the performance of AMT under laboratory conditions.

Chapter 1

1.1 The Chemical Properties of AMT

It appears that the corrosion rate of metals is reduced by the application of, certain compounds and mixed compounds to the surface of the metal. However, in many cases, the way in which these corrosion inhibitors function are not well understood. The mechanism by which AMT interacts with metal to inhibit corrosion is discussed only in three papers and the method of analysis employed is infrared spectroscopy (Ganorkar, 1988, Gajendragad, 1975).

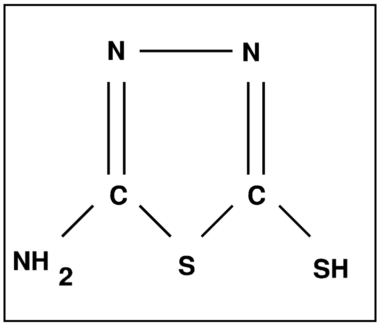


Figure 1 : The structure of AMT

In the literature, AMT, is described under different chemical names because of differences in chemical terminology. However, in order to obtain a fuller understanding of the literature, the various terms are listed below.

AMT stands for 2-amino-5-mercapto-1,3,4-thiadiazole, it is also found under the chemical names of 5-amino-1,3,4-thiadiazole-2-thiol, 1,3,4-thiadiazole-2(3H)-thione-5-amino, 2-amino-1,3,4-thiadiazole-5-thiol, and 2-mercapto-5-amino-1,3,4-thiadiazole. It should be noted that all have the same general chemical formula $C_2H_3N_3S_2$.

Its Chemical Abstract number is RN:2349-67-9 (1991) and, it is listed in the Beilstein Index (1991,674), while specific safety data is given in the Sax Index (1984, 223).

AMT, a heterocyclic compound, is a white-yellowish powdered crystalline solid, with a specific weight of 133.19g/mole. It may be purchased, in a refined form, from chemical suppliers, It does not have to be synthesised further as cited in Ganorkar's article (Ganorkar, 1988, 33). Although Ganorkar mentions its solubility in hot water, it has been found that, in water, the solubility of AMT is 2 g/l at 20^{o}C and in industrial methilated spirits 9 g/l (see experimental details below). In water, it has a pH of 3.9 i.e.acidic and in ethanol its pH is 4.6. This pH is still unsatisfactorily high with regard to the possible etching of the surfaces of artefacts during prolonged treatment. In some cases e.g. where the patina contains a noble metal, a low pH might result in the disintegration of such a patina. Also, basic copper carbonates may be dissolved whilst exposed metallic surfaces may be etched simultaneously.

The melting point of AMT is 238^{O}C, and the thermal decomposition temperature of the compound is ca. 245^{O}C. The decomposition products of the compound may result in possible health hazards, as SOx, and NOx are freed as gases.

Inhalation and ingestion of AMT dust should be avoided there are suspicions that the compound might be carcinogenic. It is recommended strongly that dust mask, goggles, laboratory coat and gloves should be worn and that any treatments should be carried out under an air extraction system or in the fume cupboard, so that any escape of particles is minimised. Also, before work is undertaken, a COSHH Assessment Form must be completed. Merck-Schuchard's DIN-datasheat number 814266, does not give any further indication about toxicity. Merck rules out any possible ecological problems when the chemical is applied and used.

AMT reacts with many metal ions, as do other corrosion inhibitors. It is a by-product of the production of medicinal drugs. In aqueous solution it forms precipitates with Ag, Tl, Hg, Pb, Cu, Cd, Bi, Ni, Co, Zn, and Fe. Some of the precipitates formed by the interaction of these elements with AMT are insoluble in organic solvents. Their solubility constants are as follows:

Cu > Pb > Ag > Ni > Zn
(Domagalina, 1965, 413)

Domagalina proposes 2-amino-1,3,4-thiodiazole-5-thiol as a precipitate in the gravimetric determination of copper, lead, silver, nickel, and zinc ions, because of the slight solubility of the resultant complexes in water. (Domagalina, 1965, 414)

AMT was selected as a corrosion inhibitor in the conservation of bronze because of its ability to form insoluble complexes with copper I and copper II ions in the copper alloy and its corrosion products. It is believed to form a thin polymeric complex layer over the metal surface. The formation of such a complex film has been confirmed on several AMT- treated objects by IR reflectance spectral analysis (Ganorkar, 1988).

1.2 The complexing behaviour of AMT

The complexing behaviour of AMT with metal ions is not as extensively studied as that of BTA. In order to understand the protective behaviour of the AMT, the structure of the AMT-metal complex on the surface of the metal must be understood. The literature search produced three research papers about the ligand formation of AMT and metal ions (Gajendragad,1975a,b , Ganorkar, 1988). Gajendragad's research describes the interaction of AMT with several metal ions and he proposes as its most important feature, that its ligands are capable of existing in four tautomeric forms with different types of metal ions, such as Cu(I) and Cu(II), Ni(II), Rh(I), Pb(II), Pd(I), Pd(0), Pt(I), Pt(0),Ag (I), Au(III), Zn(II), Cd(II), Ti(I) (Gajendragad,1975b,1331)

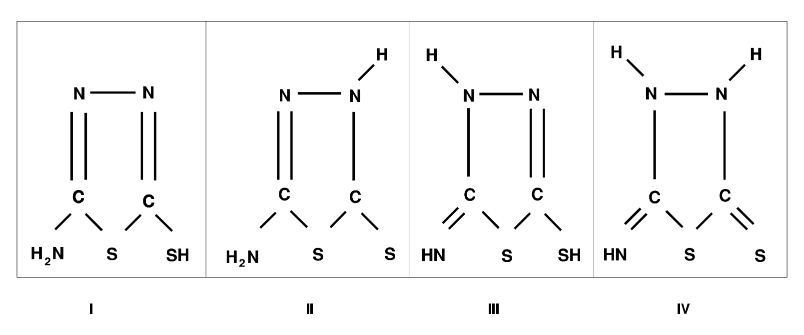


Figure 2 : The four tautomeric forms (Gajendragad,1975b,1331)

The property of AMT to form a polymeric film by complexing with Cu(I) and Cu(II) encourages the belief that it may be useful as a corrosion inhibitor for copper and its alloy but no information has been found which reports the interaction of AMT with copper corrosion products. Furthermore, the formation of complexes with silver, zinc, and lead may widen its use but the full extent of such implications have yet to be studied.

The structural aspects of copper complexes with the AMT ligand were investigated by infrared spectral analysis in which the complexing behaviour of the AMT with metal surface were assessed (Ganorkar 1988, 98; Gajendragad 1975a,b)

Discussion of the infrared spectral data found in the literature (Ganorkar 1988; Gajendragads 1975a,b).

The spectra, of AMT showed a sharp peak at 2520cm^{-1} which Ganorkar assigned to the S-H group but this peak was not present in the spectrum of the coating material, of an AMT-treated bronze (Ganorkar, 1988, 89), which indicated that the deprotonation of the S-H group had occurred and that the sulphur had bonded to the metal ions. The bonding of the sulphur to the metal was confirmed by the presence of a new peak at 345cm^{-1} due to the vibration of the S-Cu group. Other bands at 1620cm^{-1}, 1070cm^{-1}, and 1560cm^{-1} in the spectrum of AMT which where assigned to v C=N, v N=N, and v N-H respectively, had shifted to 1600cm^{-1}, 1045cm^{-1}, and 1510cm^{-1} in the spectrum of complexed form. There were multiple peaks at 2900-3400cm^{-1} in the AMT spectrum, which were assigned to symmetric and asymmetric stretching of the N-H group, which had shifted to 3080-3280cm^{-1} in the complexed spectrum. A peak at 450cm^{-1}, was attributed to a metal-nitrogen bond formed during the complexing reaction, due to the participation of the NH_2 group in active co-ordination (Ganorkar, 1988, 98).

On the other hand, Gajendragads (1975) reports the complexing behaviour in more detail. The interaction of AMT with Cu(I) and Cu(II) was researched using Infrared (IR) spectral data to describe the structures of the proposed AMT-copper ion complexes formed. The results are explained in more detail the mechanism by which AMT functions as a corrosion inhibitor is postulated.

Gajedragad (1975b, 1332) found that the peak due to v(S-H) was not present in the IR spectra of the Cu(I) complex. He assumes, like Ganorkar, that the S-H group in the ligand undergoes ionisation, whereby the sulphur bonds to the metal ion. The band of the v(N-H) group shifts in the direction of the lower wave numbers, indicating that one of the NH groups in the ligand has formed a new bond. The N-H group present in the system, is found to be less basic than an imino group. Which explains the possible formation of a bond through a N atom of the amino group (Gajendragad, 1975b,1332).

A thioamide band-II at around 1365cm^{-1} in the IR spectrum of the complexes shifts in the direction of a higher wave number. This is explained by the bonding through either nitrogen and/or sulphur of the amino groups and the thiocarbonyl group respectively of the ligand and not through the N atom of the ring as that would cause a shift in the position of the thioamide band, due mainly to v(C=N), in direction of the lower wave numbers. The v(C=S)group make a major contribution to the Thioamide band-IV, which shifts towards a lower wave numbers, and confirms that the bond order of the (C=S)group is decreased (Gajendragad, 1975a, 1028).

Confirmation of the formation of new bonds is supported by the appearance of two new peaks in the region of 415-360 cm^{-1} which could be due to the coupled vibrations of v(M-N) and v(M-S) with different bending modes of vibration of the ligand molecule. The Cu(II) complexes are represented in the IR spectra by two bands, at 670cm^{-1} and 530cm^{-1} respectively

(Gajendragad, 1975a, 1027). The proposed mode of linkage of the Cu(I)and Cu(II) ions to the ligand is illustrated in figure 3. (Gajendragad, 1975(b),1333)

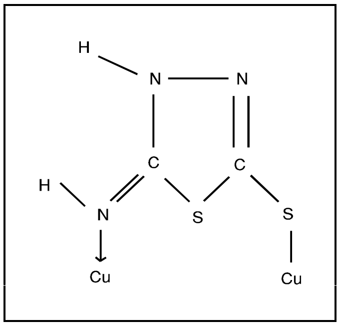


Figure 3: AMT-Metal complex (Gajendragad, 1975(b), 1333)

Gajendragad further proposes a square planar arrangement of the ligand molecules around Cu^{2+} ion. The ligand appears to be a bidentate keeping the preferred geometry's of the metal ions in their complexes. He suggests the following structure of the complex film due to a shoulder at 700cm^{-1}, a weak band at 620cm^{-1}, and a well defined band at 425cm^{-1} in the infrared spectra of Cu(II) complex (Gajendragad,1975a, 1029).

Figure 4: Proposed polymeric structure for Cu(II) (Gajendragad, 1975a, 1029)

When the ligands are in solution, they can be either in thiol and/or thione forms. The Cu(I) bonding scheme during the formation of the complex results from the copper having a great affinity for the highly polarizable sulphur, as compared to nitrogen. Therefore, it would be expected that a Cu(I) sulphur rather than a nitrogen bond would be formed in the complex. This would result in a strong bonding of Cu(I)and the sulphur in the thiocarbonyl group and a weaker bond through the amino nitrogen but a bonding of Cu(I) with thiocarbonyl sulphur cannot be ruled out (Gajedragad, 1975(b), 1333).

Gajendragad suggests that Cu(I) forms a tetrahedral complex since most of Zn(II), Cd(II), Pb(II), Pd(O), and Pt(O) ions have such a geometry. Most of these complexes are insoluble in water and other non co-ordinating organic solvents, further indicating their polymeric structure. (Gajendragad, 1975(b), 1333)

Both Ganorkar and Gajendragad report different wave lengths in the infrared spectra for AMT complexes (Ganorkar, 1988, 98 ; Gajendragas, 1975). This is thought to be due to the analysis of the polymeric layer formed between its $Cu^{+,++}$ ions and the introduced corrosion inhibitor. This is an important property required of a corrosion inhibitor but the thickness and other characteristics of this polymeric film must determined more fully to evaluate its protective properties.

CHAPTER 2

2.1 Solubility of AMT

The data sheet provided by Merck-Schuchart (Din, 814266) describes the solubility of AMT in water at room temperature. Therefore, the maximum solubility of AMT in IMS (industrial methilated spirits) under different temperatures had to be determined, as this data was not available. This data was thought to be necessary as it was proposed to compare AMT directly with BTA which, when used, is often dissolved in a solution of IMS. Generally, the higher the temperature, the greater the dissolution of the corrosion inhibitor. The treatment cited in the literature (Ganorkar, 1988, 98) proposes treatments at temperatures higher than ambient therefore, the effects of temperature require assessment.

The manufacturer, Merck-Schuchart suggests that the maximum solubility of AMT is 2g/l in water at 20^{O}C. This was used as starting point for minimum solubility in ethanol at room temperature. Ethanol was selected as a solvent because water contributes to the corrosion of copper-alloys, in that it interacts with the corrosion products. The hydrolysis of some of the corrosion products, and the slow evaporation rate of water contribute to the risk of the activation of chlorides. The substitution of IMS for water has the advantage of faster evaporation of the solvent after the application of the AMT-solution to the artefact. Also, IMS is less hazardous to health than other solvents often used in conservation, it is relatively cheap to buy and it has a lower surface tension.

The surface tension of the solvent used to dissolve the AMT is important since it relates directly to the penetration rate of the solvent into the corroded, often microfractured, surface. Water has a surface tension of 73.05 at 18^{O}C whilst that of ethyl alcohol at 20^{O}C is 22.75 (Weast, 1981, 235). Thus the latter has better properties of penetration which promotes easier migration of the AMT solution into the micro- fractures of the corroded surface thus allowing the solution to react more efficiently, the penetration can be enhanced further by the application of a vacuum .

To facilitate and maximise the solubility of AMT in IMS, the solution was warmed to 60°C as a result of which, two problems were encountered. Ethanol has a boiling point of 78.5°C. Therefore, it is more highly volatile than water and presents a possible health risk. Its flash point is 15°C which necessitates that precautions are taken when it is warmed to avoid ignition of the solvent. Therefore, the ethanol was warmed in a water bath on a hot plate to ensure that the IMS was not in a direct contact with the hot plate. The bath was maintained at 60°C to minimise the evaporation rate of the solvent. The fumes were drawn off with a fume extraction system. During the heating process, the solutions were stirred by a magnetic follower and the temperature was monitored closely. All tests were carried out in heat resistant glass beakers and small quantities of IMS (100ml) were used.

2.2 Experiments to determine the solubility of AMT in IMS.

By adding AMT in discrete quantities of 0.1g to 100ml of IMS, it was possible to dissolve 0.9g of AMT at room temperature. When the temperature was increased to 35°C, 1.1g AMT dissolved in 10 minutes. It was noted that 1.3g dissolved after 10 minutes at 35°C, but the presence of a very slight precipitate was noted.

1g of AMT was placed in 100ml of IMS and at 35°C, this amount completely dissolved after 15 minutes steady stirring. It had a pH of 4.6 and the AMT did not precipitate upon cooling.

1.5g of AMT was placed in 100ml of IMS at room temperature, without stirring. It did not dissolve completely overnight. and the saturated solution had a pH of 6.

When the temperature was raised to 60°C, and 0.1g of AMT added every 5 minutes it was possible to dissolve completely up too 1.4g of AMT in 5 minutes with no residues upon cooling the solution to room temperature.

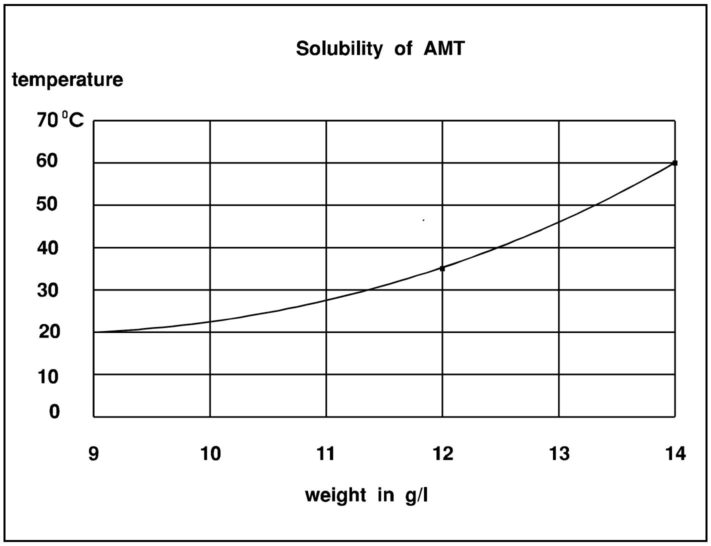


Figure 5: Solubility at different temperatures

The calculated maximum solubility of AMT at room temperature is approximately 9g/l IMS, whilst at 35°C, 12g/l of AMT dissolve, with constant stirring, in 10 minutes. When cooled to room temperature no precipitation of the AMT was visible. The pH of the solution was 4.6.

Chapter 3

3.1 The Treatment of Copper Corrosion Minerals with AMT

In the field of archaeological conservation. benzotriazole (BTA) is the most widely used corrosion inhibitor in the treatment of bronze artefacts. The advantages and disadvantages of its use in such treatments is widely documented and therefore it is a useful standard against which to evaluate the effectiveness of AMT.

Ganorkar observed the formation of a yellow precipitate during his treatment of archaeological artefacts (Ganorkar, 1988, 98). Richey describes, when working with BTA. the formation of a green precipitate resulting from the interaction of BTA and cupric chloride (Richey, 1972, 9) The changes observed during complex formation are not well enough researched. It is not known when or how these changes in structure take place. Therefore it is necessary to design experiments in which it is possible to monitor visual the structural changes which occur during the formation of the complex.

Most of the bronze artefacts encountered in conservation laboratories are of different origin and composition and from different burial environments. These factors contribute to the formation of a variety of corrosion products and differing proportions of corrosion products. and hence make the assessment of a treatment extremely complex.

3.2 Comparison of the inhibitive effects of BTA and AMT

To assess the effects of AMT as a corrosion inhibitor compared with BTA, firstly, an artificial situation was created to reduce the number of variables as the differences and complexities in the chemistry and structure of the corrosion layers in one and the same material can vary greatly thus impeding accurate observation.

The chemical compositions of specific bronze corrosion products are known. Therefore, to simplify matters, reagent grade mineral powders of similar composition to individual corrosion products were substituted. This allowed a weighed amount of the mineral compound to be treated, and ensured that the quantities of impurities which might interfere with the complexing reaction of the corrosion inhibitor were minimised. The mineral powders were supplied by Merck and are available in chemically pure form with only minor traces of impurities.

The mineral names, chemical names and formulae of the bronze corrosion products which were tested are shown in Table 1.

Cuprite	copper(I) oxide	Cu_2O
Malachite	copper(II)basic carbonate	$Cu_2(OH)_2CO_3$
Nantocite	copper(I) chloride	CuCl
Atacamite	basic copper(II) chloride $CuCl_2.3(OH)_2$	
Paratacamite	basic copper(II) chloride $CuCl_2.3(OH)_2$	

Table 1: The minerals treated with AMT and BTA

0.5g of powdered cuprous oxide, basic copper carbonate, cuprous chloride and cupric chloride, were placed in individual vials, each of which contained 10ml of a 3% solution of BTA in IMS, a 1% solution AMT in IMS or 0.2% AMT in distilled water. The individual powders and the corrosion inhibitors were left to react for 48 hours under ambient conditions. The concentration of the benzotriazole and the solvent selected were based on those commonly used in conservation to try to stabilise copper alloys (Brinch Madsen,1967). The AMT was used at a concentration dictated by its maximum solubility in IMS (1%) and distilled water (0.2%) at room temperature to effect maximum complexing during the treatment. The change in colour in each solution was assessed visually during the period of interaction.

3.3 Copper(I) Oxide, CuO, Cuprite

Cuprous oxide is dark red in colour, often it is found as a red layer on archaeological bronzes. After 48 hours treatment, there was no change in the appearance of the solutions containing the copper(I) oxide. Neither treatment formed copper complexes which went into solution, and at the same time, the solutions did not exhibit any noticeable change in colour. Richey made similar observations when Cu_2O was reacted with BTA (Richey, 1972, 7).
From the analysis of all three solutions, by atomic absorption, no noticeable amounts of copper went into solution (see table 2).

3.4 Copper (II) Basic Carbonate, $Cu_2(OH)_2CO_3$, Malachite

3.4.1 BTA in IMS

After mixing into the solution, the green copper carbonate did not appear to undergo an instantaneous change. However, after 10 minutes the copper carbonate settled at the bottom of the beaker and, 15 minutes later there was a separation and a colour change could be observed, when the copper carbonate changed to a dark grey-green colour.

After 24 hours, the solid mixture, at the bottom of the beaker, had separated into two distinct layers. Below the clear solution of BTA dissolved in IMS, the upper brown and cloudy layer was partially suspended in the solution and was thought to be possibly a complex of BTA with copper carbonate while the lower turquoise-green layer appeared to be the unchanged basic copper carbonate. The cloudy brown substance in the upper layer appeared to have increased intensity after a period of 48 hours, and its volume had diminished. No change was observed in any of the other layers.

3.4.2 AMT in IMS/AMT in distilled water

When the mineral was mixed with the solution, no change in colour was observed however, a sediment was deposited at the bottom of the beaker. No changes in colour or structure were discerned after a period of 48 hours.

The results of these experiments illustrate that BTA reacts with copper(II) basic carbonate to form a dark brown complex and reinforce observations about the discoloration of artefacts treated with solutions of BTA. Repetition of such treatments (immersion in a solution of 3% BTA in IMS), may cause the surface of the objects to darken appreciably. In objects treated several times, because of the presence of active chloride corrosion, an almost black surface layer formed .

3.5 Copper(I) Chloride, CuCl, Nantokite

Nantokite is light green in colour, but on bronze artefacts it is light grey, has a waxy "feel" and the extent of its presence may be noted not only on the surface of the object but in the depths of the sub-surface.

3.5.1 BTA in IMS

There was an immediate reaction between the BTA and the cuprous chloride. There was a distinct colour change from the initial light grey-green of the cuprous chloride to a dark olive-green. The olive-green material precipitated partially and started to settle out, at the bottom of the beaker, as a dark green suspension. After 10 minutes, the solution was dark green, and the precipitate on the bottom was dark-olive green. After 24 hours, two layers of solid could be seen: at the bottom there was a light green deposit, which was superimposed by a dark olive-green, almost black substance, which was almost liquid. The liquor above was clear and was assumed to be a solution of BTA in IMS. After 48 hours, the remaining cuprous chloride had collected at the bottom of the beaker, covered by a dark olive-green band, which was, in turn, covered by a turquoise light green cloudy substance, The upper 2/3 of the watery liquid are probably a solution of BTA in IMS.

It appears that the BTA/IMS reacts readily with copper(I) chloride, causing it to oxidise to form copper(II) ions, and, visually the conversion of copper(I) chloride seems not to be complete (Richey, 1972, 8). The colour change from light grey-green to dark olive green, during the treatment of a bronze artefact probably indicates the formation of a polymeric layer which covers the bronze disease, of such chloride bronze artefacts.

3.5.2 AMT in IMS

No instantaneous reaction was observed with the cuprous chloride which settled at the bottom of the beaker. No colour change was noticed. After 15 minutes, a flaky, cloudy precipitate formed in the liquid however, the light green cuprous chloride was evident still at the bottom of the beaker. After 24 hours, the solvent had separated clearly, and the light green deposit at the bottom of the beaker, presumably some of remnants of the cuprous chloride, was covered by a dark olive-green layer. Between the interface of the overlying water-clear solution, and the dark green deposit, floating, light green flakes were observed thus indicating that the light green flakes and the dark green were formed as a result of the interaction of the cuprous chloride with the AMT/IMS.

During the 48 hours a thickening of the dark green layer was observed, indicative of continuing reaction within the solution.

It appears that, in contrast with the BTA-IMS solution, the AMT-IMS solution is not as reactive visually. The visual effects of the reaction are apparent after 24 hours but they are less dramatic than those observed in the BTA-IMS. The presence of unreacted cuprous chloride at the bottom of the AMT-IMS solution, even after 48 hours would suggest that the BTA-IMS has greater powers of complexing.

3.5.3 AMT in distilled water

When the cuprous chloride was mixed with the solution of AMT and distilled water, there was an immediate colour change from the light grey-green of the cuprous chloride to an olive green colour. Immediately, a cloudy substance, probably an AMT-CuCl complex, precipitated and the powdery CuCl settled at the bottom of the beaker. After 5 minutes, no further change was detectable. After 24 hours, the components in the solution were clearly differentiated: a turquoise deposit, at the bottom of the beaker, was covered with a yellow material, which was overlaid by a whitish substance of cloudy appearance. The rest of the solution was clear but was turquoise in colour. After 48 hours, the only change detected was an increase the quantity of the yellow material.

The immediate colour changes are much less apparent than those observed in the CuCl reaction with BTA-IMS. However, the initial reaction of the cuprous chloride powder with the water appears to be more reactive than the reaction with the AMT-IMS solution. The change in colour results in the production of a reactant with a very different turquoise hue from that of the powdery precipitate produced in the AMT-IMS experiment. This would suggest that the AMT-

H_2O is more highly reactive with cuprous chloride than the AMT-IMS solution. The yellow precipitate may be a sulphur-copper complex, similar to that described by Ganorkar (1988, 98) ;

"a yellowish-green crude precipitate was formed on the diseased areas."

A complexing of cuprous chloride was apparent in each of the three solutions, and the atomic absorption analyses of the solutions in the following test revealed that the reaction with the AMT-H_2O results in the highest dissolution of copper. This may imply that a large quantity of chlorides is washed out (Table 2, Sample 21). The greater the initial reactivity of BTA-IMS with cuprous chloride is indicated by a rapid distinctive colour change, possibly caused by the formation of a polymeric film which seals in any remaining chlorides. This may explain the lower quantity of copper determined by atomic absorption when the sample was analysed (Table 2, Sample 1). The initial colour change of CuCl in AMT-distilled water is less apparent but the reaction appears to reach an end point which would suggest that the AMT has complexed with all sites at the surface. The reaction of AMT-distilled water in relation to that of AMT-IMS is more consistent. In AMT-distilled water, after 24 hours, no initial light grey-green coloured cuprous chloride appeared but in the AMT-IMS a small deposit of cuprous chloride remained even after 48 hours. In the case of AMT-IMS, the complexing of AMT with Cu results in a darker coloured complex and therefore, if an object is heavily infested with CuCl, this may result in a discoloration of its surface.

3.6 Copper(II) Basic Chloride, $Cu(OH)_3Cl$, Paratacamite and Atacamite

This mineral is found as both atacamite and paratacamite in corroded bronzes. The pure mineral powder, supplied by Merck, is turquoise in colour.

3.6.1 BTA in IMS:

There is an immediate reaction in which, a green cloudy product is formed between the BTA and the cupric chloride. This was also observed by Richey (Richey, 1972, 9). After 10 minutes, the solution started to precipitate and, 20 minutes later, the resulting reactants separated into bands. The lower 1/5 of the beaker was filled by a cloudy mass whilst the upper 4/5 remained clear, presumably unspent BTA-IMS solution. After 24 hours, 50% of the beaker was filled with a green-turquoise mass, the remaining 50% was filled with clear solution. No changes were noted after 48 hours.

3.6.2 AMT in IMS

There was an immediate reaction and the solution became very dark olive-pine green in colour with a very milky appearance. After 10 minutes, the solution began to separate.

After 20 minutes, a thick olive-green cloudy material filled the beaker, above which was a clear band of liquid. The colour of the olive-green product did not change after its initial appearance. After 24 hours, two bands had separated out. The lower one, a dark grey-green bulk, filled half of the beaker, whilst the upper half was filled with a pine-green clear liquid. After 48 hours, no further changes could be detected.

3.6.3 AMT in distilled water

There was an immediate separation of a light cloudy precipitate which floated in the solution. After the first 10 minutes it started to settle at the bottom of the beaker. 20 minutes later, it had separated completely. The lower part of the beaker was filled with a green-ochre cloudy solution, superimposed by a clear turquoise coloured solution. After 24 hours, two distinct layers were apparent: the lower was cloudy green-yellow in colour, and the upper the clear turquoise solution mentioned above.

After 48 hours little change was noted apart from some compaction of the cloudy layer at the bottom.

All three solutions react readily with the copper(II) basic chloride. They appear to form a partially soluble complex. It may be assumed that copper chlorides, in this form, may be present on the surface of an artefact and that they should readily complex with the corrosion inhibitors and go partially into solution but this has to be confirmed by experiment.

Chapter 4

Atomic Absorption Analysis

Conservation treatments do not always work successfully, sometimes there may be deleterious side effects. In the case of AMT, the extent to which the compound reacts with the various salts has yet to be determined. Some indication of the extent of the reactions was given in the experiments with the copper mineral powders but these must be researched in more detail. However, the reactions occurring within a ancient bronze artefact, infested with chlorides, must be much more complex and provide a natural extension of this research. The corrosion products found in such an artefact are mostly oxides, carbonates and chlorides, and it is to be expected that of these three salts, the carbonates and the oxides, would not be affected adversely by the AMT. An important consequence of treatment by solutions containing AMT is the leaching of surface constituents of a corroded bronze which occurs especially when the object is immersed for any length of time. In the following experiments, the leaching of the copper ions into the solution was monitored by atomic absorption spectrophotometry. In order to determine which copper minerals were more affected by leaching during immersion, the four main copper minerals already described and copper were used as standards. The minerals, copper(I) chloride, copper(II) chloride, cuprous oxide, and basic copper carbonate, while copper turnings were used as a reference. It was thought that the quantity of copper in solution in the cases of copper(I) and copper(II) chloride would give some indication to the amount of chlorides liberated by such a treatment.

The solutions and the conditions under which they were used are listed below:

I. 1% by weight solution of AMT in IMS for 24 hours at room temperature.

II. 0.01M (0.134% by weight) solution of AMT in IMS for 24 hours at room temperature.

III. The treatment, suggested by Ganorkar (1988, 98), in which, the object is heated but, in this case, the minerals were heated for 1 hour at 60°C in a 0.01 M solution of AMT in water.

IV. 3% BTA in IMS for 24 hours at room temperature. The solution of BTA was used as the reference solution and the others were compared with it.

V. For comparison, the minerals were immersed for 24 hours in IMS, and 1 hour in distilled water at 60°C. This was done to try to increase the rate of leaching of the copper ions, and therefore to indicate to what extent, and in what quantities, the solutions caused the metal to lose copper ions. Cu(I) chloride is only slightly soluble in water and It is insoluble in alcohol, In contrast, Cu(II) chloride is soluble both in water and alcohol (Weast, 1981, 98).

Sample preparation for atomic absorption analysis:

Sample No.					Cu count:
1.	3% BTA was dissolved in 50 ml IMS and 0.5g		copper (I) chloride	was added	140ppm
2.	"	"	copper (II) chloride	"	135 ppm
3.	"	"	cuprous oxide	"	1 ppm
4.	"	"	basic copper carbonate	"	2 ppm
5.	"	"	copper turnings	"	0 ppm
6.	1% AMT was dissolved in 50 ml IMS, and 0.5		copper (I) chloride	was added.	147 ppm
7.	"	"	copper (II) chloride	"	210 ppm
8.	"	"	cuprous oxide	"	7 ppm
9.	"	"	basic copper carbonate	"	8 ppm
10.	"	"	copper turnings	"	4 ppm
11.	0.01 AMT was dissolved in 50 ml IMS, 0.5g		copper (I) chloride	was added.	459 ppm
12.	"	"	copper (II) chloride	"	4470 ppm
13.	"	"	cuprous oxide	"	2 ppm
14.	"	"	basic copper carbonate	"	4 ppm
15.	"	"	copper turnings	"	0 ppm
16.	to 50 ml IMS 0.5g		copper (I) chloride	was added.	1160 ppm
17.		"	copper (II) chloride	"	4340 ppm
18.		"	cuprous oxide	"	96 ppm
19.		"	basic copper carbonate	"	1 ppm
20.		"	copper turnings	"	0 ppm
21.	0.01 M AMT in 50 ml destilled water, 0.5g		copper (I) chloride	was added.	615 ppm
22.	(0.134%)	"	copper (II) chloride	"	3330 ppm
23.	"	"	cuprous oxide	"	2 ppm
24.	"	"	basic copper carbonate	"	0 ppm
25.	"	"	copper turnings	"	4 ppm
26.	to 50 ml destilled water, 0.5g		copper (I) chloride	was added.	507 ppm
27.		"	copper (II) chloride	"	3650 ppm
28.		"	cuprous oxide	"	16 ppm
29.		"	basic copper carbonate	"	4 ppm
30.		"	copper turnings	"	0 ppm

Table 2: Sample preparation and Cu count of Atomic Absorption analysis

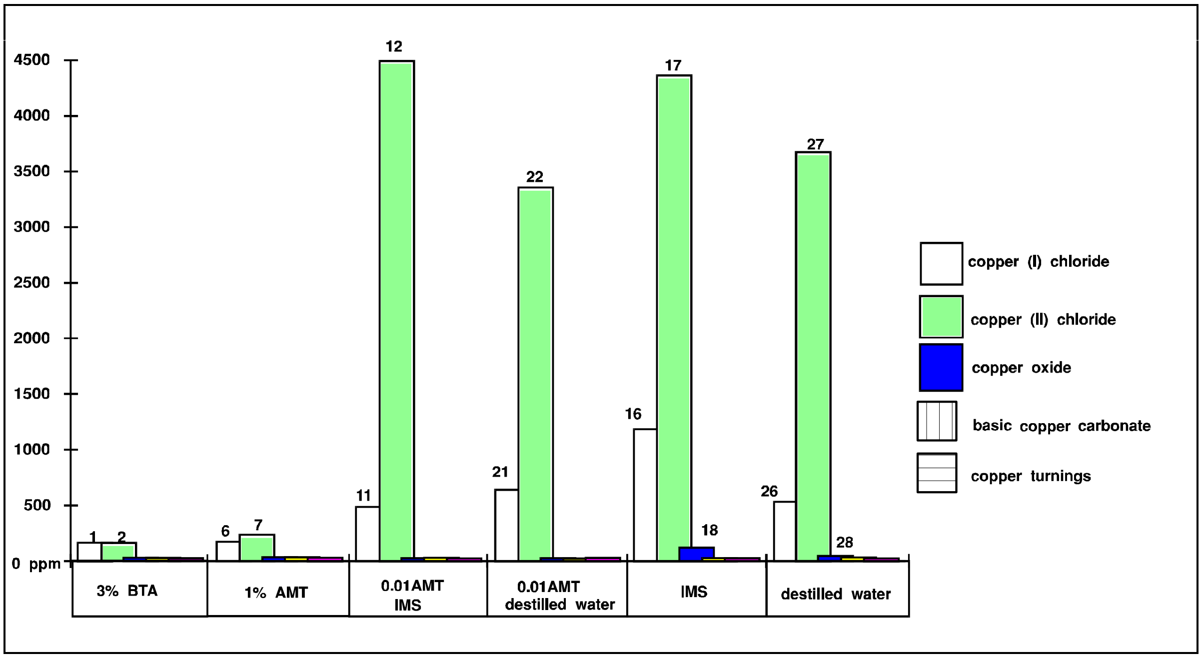


Figure 6: Atomic Absorption analysis of the solutions (copper in ppm) .

After treatment, sample numbers 6, 11 and 21 produced a very strongly coloured yellow precipitate, Ganorkar (1988, 98), also describes such a precipitate, which would appear to show the readiness of the AMT to form complexes with copper(I) chloride.

The samples were than filtered by passing them through Whatman's Grade One Filter Paper. After filtering, some of the solutions were found to be coloured, which is possibly indicative of some complexing of the minerals with the corrosion inhibitors. To measure the quantity of copper in solution, the coloured solutions were diluted by a factor of ten, to prepare the sample for analysis by atomic absorption. In such analysis, the concentration of the copper ions in solution must not exceed 500ppm. At concentrations greater than 500ppm, errors occur caused by the excess copper in the instrument. Five copper standards of 10, 50, 100, 200, and 500ppm were prepared. Two analyses were carried out, one between 10 and 50ppm and the other between 100 and 500ppm. The colour changes which occurred in some samples is described below and relates to the quantity of copper in solution.

Sample No.:		
1.	olive green transparent	140 ppm/Cu(I)
12	light grass-green transparent	4470 ppm/Cu(II)
17.	light grass-green transparent, as no.12	4340 ppm/Cu(II)
22.	light blue	3330 ppm/Cu(II)
26.	milkish transparent slight blue	507 ppm/Cu(I)
27.	light blue transparent, as no.22	3650 ppm/Cu(II)

Table 3: Colour change of solutions and Cu count

The amount of discolouration of the sample solution is directly related to particular copper chloride minerals. The copper(I) chloride does not form visible copper complexes in solution with AMT in IMS. The copper(II) chloride - BTA complex shows up distinctively. The copper(II) complex is seen in all solutions where there is a low amount or no corrosion inhibitor. It is possible that the formation of a polymeric film of copper and corrosion inhibitor bonds the copper to the surface of the object, thus preventing the further dissolution of copper. In this case the polymeric layer has also the effect, during treatment, of trapping the chlorides underlying the polymeric film. It would seem better to allow the chlorides to go first into solution, and then to seel the remaining copper-chlorides into the surface to stop further corrosion. This might be accomplished by the addition of a more concentrated solution containing AMT or BTA at a later stage in the treatment.

When Sample No.18, cuprous oxide in IMS was analysed, it was found to contain 96ppm of copper ions (Table 2). The reasons for the enhanced leaching of the copper ions by the IMS is not understood, especially as the pH of IMS was ca. 5.5 and hence not considered to be very acidic. Unfortunately this analysis could not be repeated due to constraints of time. However, since the quantity of copper in solution, in sample No. 16 was found to be double the amount of that in any of the other copper(I) chloride samples, it is postulated that the IMS used, may be a very good agent for washing copper ions from the chloride salts of copper. The effects of this phenomenon have yet to be confirmed by, for example, analysis of the quantity of chlorides in the solutions of IMS compared with those in solutions of ethanol. It appears that some cuprous oxide dissolves in IMS.

It was found that immersion in IMS for as little as one hour at 60°C causes the dissolution of some copper ions in copper oxide. This is thought to be one of the primary corrosion products to appear on a bronze object. None of the other analyses were found to contain copper ions in solution which derived from any of the copper salts commonly contributing to an artefact's patina.

Chapter 5

5.1 Hydrochloric Acid Corrosion Test

Corrosion tests are usually used to accelerate ageing. Generally, the metal is exposed to a corrosive environment and the effectiveness of the corrosion inhibitor is assessed. A sufficiently large number of samples, a minimum of three but it may be necessary to use 10 or more for reproducible data, must be exposed to determine the effectiveness of the inhibitor (Putilova, 1960, 4).

The following experiment was designed to monitor the stability of AMT treated copper samples in an environment artificially high in chlorides. In most of the corrosion literature the standard chloride environment for a corrosion test cycle, is either produced by an aqueous chloride salt spray, or by direct immersion in a solution of sodium chloride. As these experiments result in the removal of the corrosion products, they were not considered to be suitable as it was thought necessary to gravimetrically assess the stability of the protective layer, by measuring the weight increase, due to the formation of corrosion products; determine visually the quantity of corrosion products produced and their distribution. It was also thought to be of advantage to produce a visual determined serigraphy of the stability of the samples.

Scheiffler (1985, 38) suggests that chloride corrosion may be produced by isolating the samples in a sealed container in hydrochloric acid vapour. After three weeks exposure, the results of analysis of the corrosion products by scanning electron microscope and X-ray powder diffraction showed a variety of chloride corrosion products such as cuprous and cupric chlorides in anhydrous, hydrous and basic forms .

This corrosion test was selected because the standard tests commonly used in industry do not provide for the use of a gravimetric method to measure the weight increase of corrosion products, and visual assessment of the inhibiting effect is not possible. The determination of weight increase and the visual assessment of the quantity and distribution of the corrosion both contribute to the selection of the most efficacious treatment .

In considering the treatment of samples with corrosion inhibitor , four parameter were selected:

1. the amount of AMT used during the treatment
2. the appropriate solvent in which maximum performance is achieved
3. the amount of time in which the sample must be exposed to the corrosion inhibitor
4. the temperature at which the treatment must be undertaken

1. The quantity of AMT selected for the sample material was stated to be 0.01M (0.134%) AMT by weight by Ganorkar (1988, 98). A United States Patent (U.S 4357, 396) states that maximum effectiveness is achieved at 1% by weight AMT (Grunewalder, 1981, 2).

2. The solvent in which the AMT may be used can be either water or any other suitable organic or inorganic solvent, but preferably the compound must be dissolved in an aqueous or alcoholic medium (Grunewalder, 1981, 3). In consideration of hazard to health and expense only water and IMS were thought to be appropriate.

3. The determination of the amount of time for exposure to such corrosion inhibitors is more difficult, as ancient artefacts which have formed a corrosion crust, must have differences in absorption and penetration in comparison with a blank metal sample. Grunewalder (1981, 3) states that the interaction time should be a minimum of 2-5sec for clean copper metal. It was thought necessary to compare this treatment with the one hour treatment as cited by Ganorkar

(1988, 89) and considered in the treatment of corroded copper artefacts, to ascertain the quantity of time needed to provide maximum protection (Ganorkar, 1988, 98).

The standard treatment, immersion in BTA for 24 hours (Brinch Madsen, 1967) was thought to be the most suitable for the assessment of the new treatment, especially as prolonged exposure allows the penetration of corrosion inhibitor into the artefact.

4. The temperature at which the treatment should take place has been stated to be either room temperature (Grunewalder, 1981, 3) or 60^{O}C (Ganorkar, 1988, 98). The advantage of the higher temperature would be less kinetic energy is needed to help the formation of the AMT-copper complex. It is also suggested that the higher temperature allows a better penetration of the inhibitor into the surface due to expansion of the corroded surface, but this effect has yet to be proven.

The AMT treatments were compared with BTA treatment and an untreated copper sample. The experiments were designed to determine if there are any differences in corrosion behaviour due to change in pH during the immersion period. One treatment was repeated to determine any inaccuracy of the data (Table 4, Sample 7 and 8).

5.2 Sample preparation:

The way in which the samples are prepared can result in differences of performance during the corrosion test. It is necessary to remove oily layers and surface protective films to allow free access of the corrosive vapour. Surface cleaning must be carried out in such a way so that the structure of the metal surface is not altered therefore it is important to choose the cleaning agent carefully. Immersion in a cleaning solution my result in a partially clean surface, or in a change of the metal surface because of etching which, in both cases, may result in different amounts of surface attack when the samples are exposed to the corrosive agent.

In the following experiment, 0.01mm thick copper foil was used as the sample material. It was cut into squares of 2cm^2. The surfaces of the copper sheet were degreased in acetone for 10 minutes. The samples were not cleaned by immersion in dilute nitric acid (Pandit, 1987, 37) as this may cause differences in the surface area due to etching, which could, in turn, effect the corrosion behaviour. Also the presence of residual copper nitrates may interfere with the corrosion inhibitor and impair its effectiveness. After cleaning the surface the copper sheets were treated as indicated in Table 4.

Sample preparation in 50 ml of solvent:

Sample No.			
1	0.01M (0.134%) AMT in	water	for 24 hours in vacuum 600 Bar
2	"	IMS	"
3	"	water	for 1 hour at 60^{o}C.
4	"	IMS	"
5	"	water	for 5 sec at 20^{o}C.
6	"	IMS	"
7	"	water	for 5 sec at 60^{o}C.
8	"	"	"
9	"	IMS	"
10	1% by weight AMT in	IMS	for 24 hours in vacuum art 600 Bar
11	"	"	1 hour at 60^{o}C.
12	"	"	5 sec. at 20^{o}C.
13	"	"	5 sec at 60^{o}C.
14	Blank		
15	3% by weight BTA in	IMS	for 24 hours in vacuum.

Table 4: Sample preparation for corrosion test

5.3 Sample corrosion:

Each sample was placed in a glass beaker of volume 1875cm^3 into which a beaker with 10ml of 2 mole Hydrochloric Acid (HCl) was placed. The samples were exposed to the vapour for 10 days. After the first 24 hours no visible corrosion, could be seen therefore, to accelerate the effect, the HCl was replaced by a 36% solution of Hydrochloric Acid. After 10 days the copper sheets were weighed.

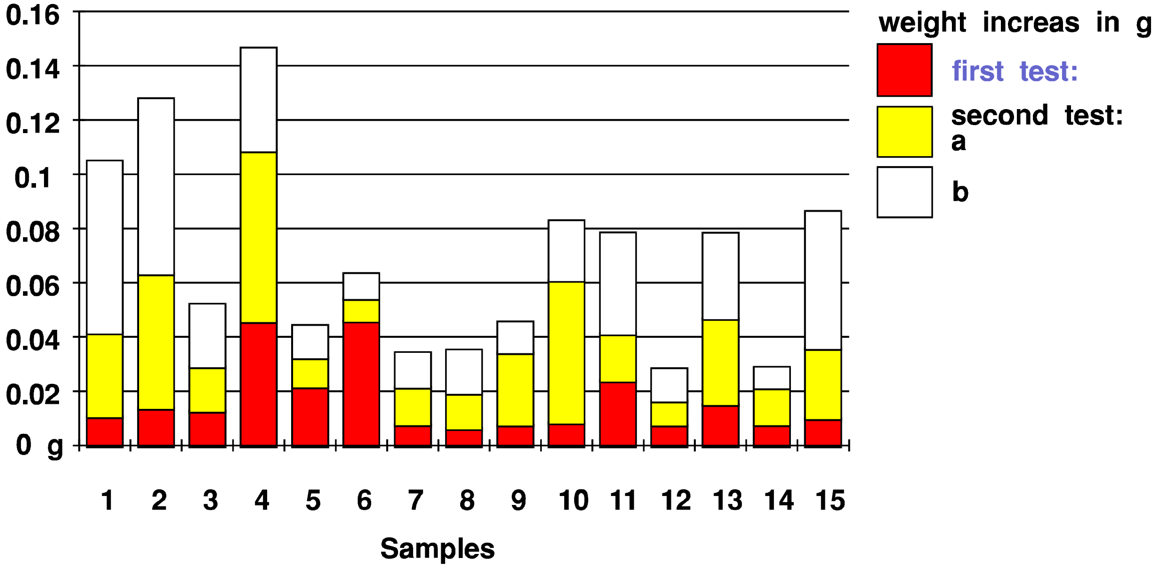
It was found that the lowest weight increase and the smallest amount of visible corrosion occurred with the samples treated with 0.01mole AMT for 5 sec at 60^{o}C in distilled water and therefore brought about the greatest inhibition of corrosion (Figure 7, Appendix 1). However, it is thought that when a corroded bronze is treated, such a short exposure time may result in a partial penetration of corrosion inhibitor into the corroded surface, and therefore, it is suggested that 24 hour immersion in AMT under vacuum is the most suitable way in which to treat such an artefact.

It is not understood why the untreated samples perform as well or better than samples treated with corrosion inhibitor. The high variation in corrosion and the fact that the untreated samples are so little corroded, leads one to the conclusion, that the cleaning of the samples before the treatment in acetone did not result in the complete removal of surface contamination, like for example grease or oxides. Therefore the tests were repeated (Appendix 1 and 2).

The second test was carried out as before (Table 4), the only change was that of sample preparation technique, previous to the treatment with the corrosion inhibitor. Any layers of grease or copper oxides on the surfaces of the sheets were removed by abrading the surface with 5 micron glass spheres using an air abrasive. This ensures even surface cleaning, but it may cause surface hardening which, in turn, may reduce corrosion. The abrasion was followed by immersion for one minute in acetone in a beaker placed in an ultrasonic bath. Two samples were prepared in this way to discover if any differences, as a result of surface hardening, could be discerned. In order to try to correlate the amount of corrosion to the pH of the solution, the pH of the solutions was monitored before, during and after each treatment. A low pH may result in etching, which in turn, would cause the surface area to increases and thus bring about changes in corrosion behaviour (second test samples a,b in appendices).

When all of the samples had been treated, according to table 4, it was found that sample 10 had a heavy brown-black tarnish, sample 4 had a distinct tarnish and samples 1 and 2 had a slight but dark tarnish. The tarnish may be due to the presence of sulphur in the AMT compound.

Theoretically, it would be expected that the most efficacious treatment would involve immersion in the solution containing the corrosion inhibitor under vacuum for 24 hours. However, when the copper sheets had been exposed to the hydrochloric acid fumes, after immersion in a 0.01 mole or 1%, by weight, solution in AMT, for 24 hours under vacuum it was found that the samples had not been protected and this had resulted in the occurrence of more corrosion compared with samples subjected to shorter periods of immersion. The corrosion was not necessarily due to etching caused by acidity as it was found that the low pH of the solution did not correspond with high or low corrosion rates, for example in sample 7, the solution had a pH of 3.6 and the sample was found to have the second lowest rate of corrosion (Figure 7, Appendix 2). Does this infer that in this particular case the presence of a low pH is indicative of protection from corrosion?



(The sample numbers and the described treatments of table 4 correspond)

Figure 7: Hydrochloric acid corrosion test

It would appear from the data gained from the two series of experiments (Figure 7 and Appendix 1) that a treatment which involves a short exposure to the solution of the corrosion inhibitor seems to result in the lowest amount of corrosion. The results, in "ideal" situations indicate that immersion for 5 seconds in water is effective. However, this approach is not necessarily useful in the treatment of artefacts because it is too short a time to allow full penetration of the solution into a corroded surface. Therefore, in the case of artefacts, it would be more efficacious to immerse them in the solution for a longer period of time.

From the data it would appear that the time of exposure seems to be an important factor, the longer the exposure the higher the corrosion rate e.g. immersion for 24 hours under vacuum caused a 9.5% increase in corrosion, immersion for 1 hour caused a 8.4% increase. In contrast, exposure of only 5 seconds caused approximately half of the weight increase due to corrosion, about 4.2%.

The performance of the tests at room temperature resulted in a 6.8% increase in corrosion, while a temperature of 60°C resulted in a 6% increase in corrosion. The concentration of the solution of AMT seems to effect the stability of the copper sheets e.g. 0.01 mole AMT resulted in 6.5%, and 1% AMT in 6% weight increase due to corrosion.

The solvents in which the AMT was dissolved appear to effect stability. After 10 days exposure to hydrochloric acid vapour, samples previously treated in water had a 4.9% weight increase due to corrosion, and samples treated in IMS had a 7.3% increase in weight due to corrosion. The increase of corrosion due to IMS is not surprising since analysis by atomic absorption indicated that the IMS caused leaching out of the copper ions into solution (Table 2), which may suggest that the surface is being etched.

Theoretically, the data extracted from this series of experiments, would lead to the conclusion, that a 1% by weight solution of AMT in water with an exposure time of 5 seconds, at 60°C should give the best protection. However, such a treatment would be impracticable in conservation due to the low solubility of AMT in water (2 g/l) and the short exposure time would not allow good penetration into the corroded surface. Also water may contribute to further corrosion, particularly when the artefact contains chlorides in quantity.

When the quantity of AMT, solvent, time, and temperature, are considered, the most desirable treatment is as follows: 1% AMT in IMS at 60°C for 1 hour. Sample 11 (Table 4) was treated under these conditions and the resultant increase in weight, after exposure to the hydrochloric acid vapours, was 6.6%. In comparison, the standard 24 hour BTA treatment, resulted an average weight increase of 7.8% and therefore was not as effective in corrosion inhibition as the AMT (Figure 7). It was found that if a longer exposure to the corrosion inhibitor was needed, immersion for 24 hours at room temperature in a 1% AMT-IMS solution resulted in 7.4% weight increase after 10 days exposure to the HCl environment, and also the AMT was more effective than BTA as a corrosion inhibitor. The treatment suggested by Ganorkar (1988, 98) immersion in a 0.01M AMT in water for one hour at 60^{o}C resulted in a 4.7% weight increase and therefore would appear to give the best protection from corrosion.

It has to be stated that the conclusion drawn from these corrosion experiments are based on results derived from clean metallic copper samples. These experiments must be performed on corroded artefacts to discover how effective the treatments are in the prevention of further damage by corrosion.

Chapter 6

Treatment of Artefacts

In an ideal situation, each copper alloy artefact has its environmental history wrapped around a perhaps still intact metal core, but this is only partially protective shield against severe conditions of burial. To reveal the "original surface" as accurately as possible is the responsibility of the conservator and depends upon manual skill and knowledge. Mechanical cleaning is normally followed by the introduction of a corrosion inhibitor, e.g. AMT to preserve the exposed surface and deactivate chlorides .

The assessment of the behaviour of AMT, and its performance in a corroding environment, were designed to discover the best possible treatment for an archaeological artefact. Preliminary experiments were carried out on five copper alloy arrowheads in the following way: in each case, the corrosion layer covering the "original surface" was removed by scalpel under a binocular at 20x magnification. The corrosion products removed were tested for chlorides using the silver nitrate test (Vogel,1978, 338). All five arrowheads had chlorides in their corrosion products, and parts of the exposed surfaces were pitted. The pits, typical of such corrosion, were filled with a waxy grey material, probably nantokite. To stabilise the exposed surfaces, four of the arrowheads were treated with AMT and one with the standard BTA treatment. previous to each treatment the arrowheads were degreased in acetone. Table 6 lists the treatment to which each arrowhead was subjected.

arrowhead	amount of inhibitor used	solvent	time	temperature
1	0.01M (0.134g) AMT	100m IMS	24 hours vacuum	room temperature
2	"	"	1 hour	60^{o}C
3	1% AMT	"	24 hours vacuum	room temperature
4	"	"	1 hour	60^{o}C
5	3% BTA	"	24 hours vacuum	room temperature

Table 5: treatments of arrowheads.

The temperature of the solutions kept at 60^{o}C were monitored by thermometer. Before the treatment all solutions were well stirred with an electrical stirrer. After the 24 hour treatment number 5 had a very slight cloudy precipitate in the solution, and the object had darkened in colour.

To monitor the effectiveness of the treatment, the arrowheads were placed in to a humidity chamber in which relative humidity was 100%. After 24 hours exposure to the high humidity, only sample 2 did not show the greenish eruptions typical of active bronze disease, unlike the other four arrowheads. This result contradicts the hydrochloric acid corrosion test, in which sample 4 (Figure 7) had the highest amount of corrosion. But this, in turn, would confirm parts of Ganorkar's (1988, 98) treatment, which suggests 0.01M AMT for one hour at 60^{o}C, would inhibit further corrosion. Sample number 1 was corroded heavily thus suggesting that the 24 hour treatment seems to have no effect at all. Any visible chloride corrosion was removed from the surfaces of all the arrowheads by scalpel, and then the arrowheads were treated a second time by immersion in a 0.01M solution of AMT for 1 hour at 60^{o}C, as this treatment has proven to be effective. During the treatment, sample 1, 3, and 4 had areas in which chloride corrosion occurred, a yellow green precipitate formed and this was removed with a brush it recurred after 5 seconds and was removed by brush. This was done throughout the whole treatment and resulted in a partial removal, of what was thought to be nantokite from the pit corrosion. The precipitate formed a yellowish white material which floated in the solution. The precipitate formed, is mentioned in Ganorkar's article as

"a pale yellowish-green crudy precipitate was formed on the diseased areas" (Ganorkar, 1988, 98). Ganorkar repeated his treatment until no further precipitate formed. In the case of the arrowheads this approach was not thought to be acceptable as it might result in the formation of cavities which could effect the physical stability of the object.

The second treatment was followed by a 24 hour exposure to a RH of 100%, after which only sample 2 was found to be stable.

Since the second treatment resulted in the dissolution of chlorides but did not prevent further corrosion, a new approach was taken. This time samples 2, 3 and 4 were immersed in a 1% solution of AMT in IMS. for 48 hours under a vacuum of 600Bar. In order to deduce whether the formation of a thick polymeric layer of AMT-Cu would entrap the copper chlorides. For comparison, samples 1 and 5 were immersed for 48 hours in a 3% solution of BTA in IMS at 600Bar vacuum. Sample 1 was treated with BTA because Ganorkar suggests a AMT treatment followed by a BTA treatment, is more suitable for heavily corroded objects (Ganorkar, 1988, 100). After the 48 hours of immersion, all of the arrowheads were exposed for 24 hours to a relative humidity of 55%. After this sample 1 had one active CuCl spot, sample 2 had one very small active spot, samples 3, 4 and 5 were stable. This result suggests that a low concentration of AMT in solution results in the dissolution of CuCl and that a high concentration of AMT in solution leads to the formation of an AMT-Cu polymeric film. However, as sample 1 was corroding so badly not even a combined treatment resulted in complete protection.

The application of AMT to heavily chloride-infested objects has been shown to be not immediately successful, and that several treatments were necessary to provide protection. To assess the inhibiting effect of AMT a less corroded object, a high tin bronze mirror, probably Chinese, but from Kota Cina, Sumatra was treated. The corrosion was mechanically removed by scalpel under a binocular microscope at 20x magnification. The corrosion products were ground and tested for chlorides by the silver nitrate test (Vogel, 1978, 338). The test proved positive. The mirror was degreased with acetone, and immersed in 200ml 1% AMT-IMS for one hour at 60^{o}C. The solution had a pH of 4.5. This was followed by a 48 hour exposure to a relative humidity of 100% in a humidity chamber. After this no chloride corrosion was visible. After one month at ambient relative humidity, and without a protective coating, the mirror is still stable.

Conclusion

The initial aim of this project was to find an alternative treatment to benzotriazole particularly as benzotriazole often fails in such cases as bronzes containing a high chloride content. The results of the experiments were not as conclusive as it was hoped for and they leave many more open questions about AMT than were answered. Perhaps the main point learned is that AMT is not the "cure all" of bronze disease. However it proved to be effective, in the removal of large quantities of chlorides, when used at a concentration of 0.01M in alcohol for 1 hour at 60^{o}C or 24 hours in a vacuum chamber at 600 Bar in which the AMT-Cu polymeric film appears to have formed. If necessary, the treatment may be repeated until it is deemed sufficient protection has been provided. In cases of less heavy chloride contamination, inhibition of corrosion should be effected by immersion for 24 hours under vacuum in 1% AMT in alcohol or 1 hour at 60^{o}C in 1% AMT in alcohol. The one hour treatment is to be preferred as it tarnishes the surface of the object less, where metal is exposed. In the case of objects with a patina, the discoloration of copper due to the presence of sulphur in the AMT is negligible in comparison with the advantages of stabilisation.

During the project, ways of measurement of the quantities of chlorides were assessed and it was found that most of the conventional methods of determination involved silver or other metallic elements as well as those involving the use of an electrode. These elements were found to complex readily with the AMT and hence interfere with the readings. It seems that the most promising method in the determination of the quantities of chlorides might be by the oxidation of the sulphur with hydrogen peroxide after which the silver nitrate test could be carried out. Unfortunately, due to restraints of time, this could only be tested in part and the results were not conclusive.

In those cases where BTA tends to form a brown complex with basic copper(II) carbonate and thus causes darkening of the surface of the object, particularly those with a high malachite content, it would be preferable to use AMT in the process of stabilisation as it has the advantage of removing chlorides whilst simultaneously imparting a higher resistance to corrosion.

The result of the experiments described in this paper would imply that more research should be carried out into the effects of corrosion inhibition by AMT not only on copper but also upon its alloys with silver, zinc and lead.

Appendix 1:

The weight increase of the modern metal samples, in grams during the corrosion test after exposure to an environment of hydrochloric acid vapour. First test, second test and average weight increase.

Sample No.:	first test :	second test: a	b	average
1	0.0105	0.0308	0.0634	0.0349
2	0.0135	0.0496	0.0646	0.0425
3	0.0125	0.0163	0.0231	0.0173
4	0.0455	0.063	0.0378	0.0487
5	0.0214	0.0107	0.012	0.0147
6	0.0457	0.0083	0.0092	0.021
7	0.0075	0.0138	0.0128	0.0341
8	0.006	0.0131	0.0159	0.0116
9	0.0073	0.0267	0.0113	0.0151
10	0.0081	0.0526	0.0221	0.0276
11	0.0236	0.0174	0.0372	0.026
12	0.0073	0.0089	0.0119	0.0093
13	0.0149	0.0317	0.0315	0.026
14	0.0075	0.0136	0.0075	0.0095
15	0.0097	0.0259	0.0506	0.0287

Sample preparation for corrosion test for appendix 1 and 2

Sample preparation in 50 ml of solvent:

Sample No.:
1 0.01M (0.134%) AMT in water for 24 hours in vacuum 600 Bar
2 " IMS "
3 " water for 1 hour at 60°C.
4 " IMS "
5 " water for 5 sec at 20°C.
6 " IMS "
7 " water for 5 sec at 60°C.
8 " " "
9 " IMS "
10 1% by weight AMT in IMS for 24 hours in vacuum art 600 Bar
11 " " 1 hour at 60°C.
12 " " 5 sec. at 20°C.
13 " " 5 sec at 60°C.
14 Blank
15 3% by weight BTA in IMS for 24 hours in vacuum.

Appendix 2, Second corrosion test:

The pH values of the immersion solutions before, during and after the treatment; and the weight before and after treatment and the weight increase due to the formation of chloride corrosion, after exposure to hydrochloric acid vapour.

Sample No.:	pH of solution before treatment:	pH after treatment:	weight in g before:	weight in g after:	increase in weight:
1a	4,3	4	0.3787	0.4095	0.0308
b			0.3808	0.4442	0.0634
2a	5,3	5,7	0.3622	0.4118	0.0496
b			0.3935	0.4581	0.0646
3a	3.6	3.1 at 60°C	0.3659	0.3822	0.0163
b		4.2 at 20°C	0.3775	0.4006	0.0231
4a	4.9	5.0 at 60°C	0.3661	0.4291	0.0630
b		5.1 at 20°C	0.3461	0.3839	0.0378
5a	4.5	4.5	0.3909	0.4016	0.0107
b			0.3478	0.3598	0.0120
6a	5.1	5.1	0.3373	0.3456	0.0083
b			0.3738	0.3830	0.0092
7a	3.6	3.6	0.3852	0.3990	0.0138
b			0.3787	0.3915	0.0128
8a	"	"	0.3796	0.3927	0.0131
b			0.3542	0.3701	0.0159
9a	4.9	4.9	0.3918	0.4185	0.0267
b			0.3686	0.3799	0.0113
10a	5.3	4.6	0.3480	0.4006	0.0526
b			0.3788	0.4009	0.0221
11a	3.7	4.3 at 60°C	0.3870	0.4044	0.0174
b		4.9 at 20°C	0.3929	0.4256	0.0372
12a	5.4	5.4	0.3762	0.3851	0.0089
b			0.3742	0.3861	0.0119
13a	3.7	3.7	0.3710	0.4027	0.0317
b			0.3873	0.4188	0.0315
14a			0.3665	0.3801	0.0136
b			0.3536	0.3611	0.0075
15a	4.9	4.8	0.3225	0.3484	0.0259
b			0.3934	0.4440	0.0506

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