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The role of benzotriazole (BTA) in bronze protection

Abstract

In a first set of experiments, copper-benzotriazole (CuBTA) complexes were made under varying conditions from solutions of benzotriazole (BTA) with copper mineral powders commonly associated with bronze corrosion, as well as by immersion of simulated copper corrosion surfaces in BTA solutions. Complexes were characterized as polymeric cuprous (Cu(I)) and/or cupric (Cu(II)) BTA complexes in all systems investigated. It was found that the CuBTA complexes vary in terms of bonding, composition, physical structure, thickness and uniformity, depending upon the reactants and the conditions of reaction. In a separate series of experiments, CuBTA film growth on rolled bronze was investigated by ellipsometry and external reflection, also known as reflection-absorption infrared spectroscopy. Results indicated that CuBTA film growth in near-neutral conditions is dependent on time, BTA concentration, and solvent. Evidence related to film thickness also suggested that Cu(I)BTA films develop in a step-wise manner. Some properties of the Cu(I)BTA films, including heat stability, oxidative stability, and ability to form on unclean surfaces or under the coating Inralac, were also investigated. These results are discussed within the context of BTA as a pretreatment for coated outdoor bronzes.

6.1. Introduction

1H-benzotriazole (BTAH or, generally, BTA) has been in use as a corrosion inhibitor for the conservation treatment of bronzes since the late 1960s [1]. Despite the search for improved inhibitors, BTA remains one of the most effective and acceptable anti-corrosion treatments available for copper alloys today [2]. Although there has been concern to the contrary, recent articles have asserted that BTA is safe for use in conservation [3], and conservators in the fields of archaeological and outdoor sculpture conservation continue to rely on BTA for treatment of archaeological and outdoor copper alloys and bronze art and ornamentation. However, the uneven success of this agent in treatments for bronze disease and bronze corrosion in outdoor exposures remains an important subject of

scrutiny and scientific research. In particular, a scientific basis for the choice of treatment parameters has been lacking.

As a result of this discrepancy in research and application, there is a gap in knowledge between the theoretical usefulness of BTA as a corrosion inhibitor for bronze in general, and the observed inconsistency of its success. The first set of experiments presented in this chapter investigates the interaction of BTA with typical copper oxide and chloride corrosion products associated with bronzes, as well as with model copper corrosion surfaces. Results shed light on several factors which influence the corrosion protection properties of CuBTA films as formed on heterogeneous, corroded copper alloy surfaces during typical treatment conditions.

In the context of coatings for outdoor bronzes, the role of CuBTA films under thicker protective coatings was also probed. As outlined in Chapters 2 and 3, samples of cast bronze and 50-year-old, naturally corroded copper samples were given various surface preparations, including brush-coating with 1.5% BTA/ethanol before applying the protective coatings; the samples were then exposed to either accelerated indoor or natural outdoor weathering. As discussed, visual inspection and x-ray diffraction (XRD) measurements of corrosion on the uncoated substrates treated with BTA showed that this treatment by itself has little inhibiting effect on the formation of chlorides and black corrosion in accelerated, simulated outdoor weathering and natural outdoor weathering. Furthermore, BTA treatment prior to the application of a coating did not show any clear performance benefit in these testing regimes. These observations are supported by reports in the literature that air-dried Cu(I)BTA films have vastly decreased corrosion protection in NaCl solutions compared to films that form and remain in a NaCl/BTA solution [4,5]. It is also known that CuBTA protection in sulfate solutions is superior to that in chloride solutions [6]. It is thus unclear whether it is possible to optimize BTA pretreatment of outdoor bronzes and, in so doing, unambiguously boost the protection of a coating system.

In order to gain a better understanding of these observations, a further set of experiments was designed in which CuBTA film formation on rolled bronze was studied by external reflection, also known as reflection-absorption infrared spectroscopy (RAIR). RAIR was used to investigate the thickness of CuBTA films formed on rolled bronze under various conditions of BTA concentration and solvent, as well as to gather chemical information about the films themselves. The formation of a CuBTA film from contact with an organic coating such as Inralac, which contains BTA, was also investigated. Chemical aspects of the coatings were discussed in Chapter 5. Ellipsometry and electrochemical impedance spectroscopy (EIS) were also utilized to confirm trends observed by RAIR.

6.2. Background

It is well established that BTA complexes with copper, copper alloys, and cuprous oxide surfaces to form a cuprous film $(\text{Cu(I)BTA})^*$. The complex is usually identified as polymeric $[\text{Cu(I)BTA}]$ (Figure 1) [7,8,9,10,11,12,13,14,15]. In this structure, BTA acts as a unidentate bridging ligand in a linear chain of alternating Cu^{1+} and resonance-stabilized BTA molecules. $[\text{Cu(I)BTA}]$ is reported to be amorphous, insoluble, and to be stable up to about 200°C , depending on the atmosphere [7,9,16]. A related cuprous film complex, consisting of the polymeric linear chain $[\text{Cu}_2\text{BTACl}]$, has been proposed for complexes prepared with high concentrations of chlorides [17].

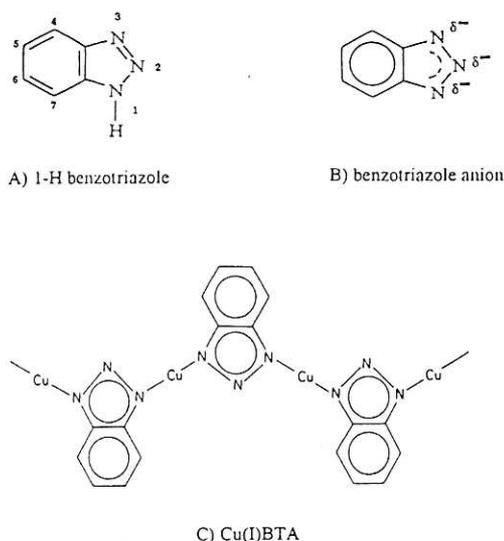


Figure 1 Proposed structures for A) 1-H benzotriazole (BTA); B) BTA anion; and C) Cu(I)BTA .

BTA may also form cupric complexes $(\text{Cu(II)BTA})^*$, the structures of which are less well defined, partly because they have received less attention. Cotton [7] proposed the polymeric network structure of $[\text{Cu(II)(BTA)}_2]$ as shown in Figure 2. In this structure, the Cu^{2+} ions act as crosslinking sites between BTA

*The complexes are referred to without specific compositions unless otherwise noted.

ligands in a square planar geometry. The inordinately long Cu-N bonds drawn in Cotton's structure suggest a fundamentally different, weaker type of metal-ligand interaction than that described for [Cu(I)BTA]. Based on evidence of non-ideal stoichiometry in some cases, Cotton proposed the existence of another, undefined cupric BTA derivative whose composition is influenced by preparation in the presence of chlorides. Roberts [18] also proposed an alternative structure of Cu(II)BTA with distorted octahedral geometry for the cupric complexes, with the inclusion of oxide and/or water ligands. In addition, Caramazza et al. [19] reported a non-polymeric, cupric chloride-BTA derivative with the composition of $\text{Cu}_2(\text{BTA})_2\text{BTAHCl}_2$, although it is unclear what the structure of such a complex would be. Cupric complexes have also been reported to be insoluble, to have slightly lower thermal stability than [Cu(I)BTA], and to be crystalline when prepared with excess chlorides [7].

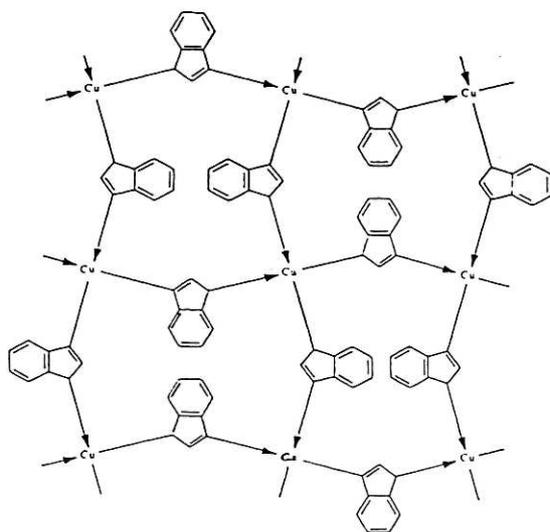


Figure 2 Proposed structure for Cu(II)BTA (Cotton [7]).

It is not known whether Cu(II)BTA derivatives inherently impart corrosion protection equal to that of thin, highly polymerized films of [Cu(I)BTA] formed on clean copper surfaces. However, the effectiveness of any film in corrosion protection depends largely on a combination of its adhesive and film properties. The corrosion control which BTA treatments have often been observed to impart to archaeological bronze objects may lie to some extent in the excellent coverage and

adhesion of CuBTA films, which form primary chemical bonds to underlying copper mineral surfaces.

Other important protective properties of CuBTA films are largely determined by the chemical and physical structure of CuBTA films, as well as their growth mechanism. The majority of investigations into the inhibition effect of BTA on copper and copper alloys advance the theory that CuBTA films protect the metal from corrosion by means of a highly impermeable physical barrier layer to chloride and sulfate ions, rather than by chemical or electrochemical means. Good barrier protection in films generally arises from high ionic resistance, crosslink density, and degree of polymerization. On the other hand, permeability should be low; the effect of crystallinity on protective properties may be variable. Film uniformity itself is also an important property in order to avoid the creation or aggravation of electrochemical potential differences or osmotic pressure gradients, which are driving forces for corrosion [20].

There is overwhelming evidence in the literature that the method of preparation, including condition and oxidation state of the reacting surface, pH, temperature, and chloride and oxygen concentration, strongly influence Cu-BTA reactions. These variables have been implicated in reported differences in key film properties, such as thickness, oxygen permeability, degree of polymerization, crystallinity, resistance, and thermal stability. For example, film formation under non-corrosive conditions has been found to be self-limiting, leveling off as the thickness effectively reinforces the underlying oxide and blocks the metal surface. Under acidic conditions, i.e., $\text{pH} \leq 4.0$, the underlying oxide or patina tends to dissolve and be replaced by thick CuBTA films, reported to grow up to 5000 Å. In this case, the CuBTA film formation is accompanied by simultaneous corrosion beneath the CuBTA film, so that the combined processes result in nearly unlimited growth. However, these CuBTA films are known to be much less protective [4,9,14,20,21,22].

In this light, CuBTA inhibition should be highly dependent on thickness, as well as properties such as porosity, uniformity and degree of polymerization. Investigations into the dependence of CuBTA thickness on BTA concentration and exposure time are not unanimous and have typically examined copper maintained in BTA solutions at concentrations much lower than are used in conservation applications [9,23]. Optimization of these film properties for conservation applications, as well as an understanding of corresponding chemical and physical structure, are thus of key importance in the field and have remained a subject of speculation and trial and error.

The purpose of the experiments described in this chapter is to gain an understanding of the structure of CuBTA films produced by typical BTA treatments of bronze, as well as the effect of some treatment parameters on film properties. This research focused primarily on the parameters of BTA concentration, time of immersion, pH and solvent. Evidence presented in this paper concurs with the literature in that different methods of CuBTA film preparation, such as found in typical conservation treatments, may have significant influence on the CuBTA films, especially in terms of thickness and uniformity.

6.3. Experimental methods

6.3.1. BTA-copper mineral reaction products

Model systems that mimic natural bronze reaction products were made for study. CuBTA complexes were formed by reacting solutions of 1-H BTA (Aldrich, 99.99%) and Cu₂O (cuprite), CuO (tenorite), CuCl (nantokite), CuCl₂, Cu₂(OH)₃Cl (paratacamite), Cu₂(OH)₂CO₃ (malachite), or copper powders, under varying conditions of solvent, pH, and molar ratio of BTA to Cu. Commercially available mineral powders were reagent grade. Paratacamite was synthesized according to the method of Tennent and Antonio [24] and its identity was confirmed by x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The additional presence of lower hydroxy chlorides and/or hydroxides of copper was suggested by non-ideal stoichiometry found in x-ray photoelectron spectroscopy (XPS) elemental analysis. The XPS O(1s) spectrum of the paratacamite also indicated that a minor amount of cuprous oxide was present.

All CuBTA reaction products were gravity filtered, rinsed repeatedly with reagent alcohol to remove excess BTA, and dried at room temperature under vacuum. Solvents were double distilled deionized water, HPLC grade reagent alcohol, and acetone. Aqueous solutions below pH 5.0 were adjusted by the addition of HCl, while basic solutions above pH 7 were adjusted by the addition of NaOH. Reaction products were analyzed by FTIR as ground powders in oven-dried KBr pellets with a Digilab FTS-40 spectrometer equipped with a DTGS detector, and by XRD on a Philips 1710 open-architecture diffractometer, and, in one case, a Philips 1840 powder camera diffractometer. The x-ray sources were Cu K α , and spectra were acquired at instrumental settings of 30 mA, 40 kV, and 0.02 °/sec. Peaks were recorded by Sietronic Software and transferred to the Fein-Marquart software program for analysis. Several of these reaction products were analyzed by XPS on a V.G. ESCA III Mark II spectrometer, using Mg K α radiation with a photon energy of 1253.6 eV (400 W), ambient temperature, chamber pressure below 10⁻⁸ Torr, and a take-off angle of 45°.

CuBTA films were formed on simulated copper corrosion surfaces by immersion in 3% (wt/vol) solutions of BTA in alcohol or water, followed by rinsing. Three types of substrates were used: 1) mechanically polished, 2 mm thick copper coupons (Aldrich, 99.999%), on which selective corrosion films were formed either in air (cuprous oxide), electrochemically, or by adsorption of mineral solids on the surface; 2) pellets of compressed mineral powders; and 3) rolled, oxidized copper sheet coupons which had been used for paratacamite synthesis and had corrosion patinas formed during this process. CuBTA films were analyzed mainly by FTIR microreflection spectroscopy, using a UMA-300 FTIR microscope attachment equipped with an MCT detector, and by XRD. All FTIR spectra were recorded in absorbance. Three mineral pellets immersed 17 hours in BTA/alcohol were examined by XPS using a Perkin-Elmer 5300 XPS spectrometer, using MgK α radiation, with a photon energy of 1253.6 eV (400 W), ambient temperature, chamber pressure below 10⁻⁸ Torr, and a take-off angle of 45°.

6.3.2. CuBTA films on bronze

RAIR of thin Cu(I)BTA films formed on rolled bronze by immersion in a) 1.5 wt.% BTA/ethanol, b) 3.0 wt.% BTA/ethanol, or c) 1.5 wt.% BTA/water was performed with a Bio-Rad Digilab FTS-60A Fourier transform infrared spectrometer fitted with a Harrick versatile reflection attachment for center-focused beam and a retro-mirror accessory, plus a wire-grid polarizer set for parallel beam polarization. The angle of incidence in all cases was 78 degrees. Samples were purged with dry air for 10-20 minutes to minimize the presence of atmospheric moisture. The final reflection spectra were obtained by digitally subtracting the cleaned bronze spectrum, placing each sample with the same geometry in the accessory before and after treatment. In some cases of very long immersion in BTA solutions, sample spectra were produced by subtracting that of a new, freshly scanned, untreated rolled bronze coupon. Absorbance at 745 cm^{-1} was calculated with the WIN-IR software from the maximum height of this peak to a baseline drawn between 835 to 729 cm^{-1} .

Solutions of BTAH (Aldrich, 99%) were made with HPLC-grade ethanol or millipore, distilled and deionized water. The pH of aqueous BTAH solutions was 5.30. The rolled bronze (Lubaloy Co.) was spring-tempered, 425 bronze, 0.016 gauge, with an alloy composition of 88.5% Cu, 9.5% Zn, 2% Tin. Rolled bronze samples were polished with a series of Micro-mesh cloths from either 2400 or 6000, to 12000 mesh. The polished samples were solvent cleaned by wiping and rinsing with alternating polar and non-polar solvents until they passed the water-break test [25], immersed into the appropriate BTA solution, rinsed thoroughly with ethanol, and air dried.

Ellipsometry was performed with a Rudolph Research Inc. thin film ellipsometer, type 43603-200E at the University of Cincinnati. Film thickness was calculated from measurements of the delta and psi parameters using a film refractive index of 1.6 [9,26]. An uncoated bronze coupon served as the background, so that the thickness of the natural cuprous oxide layer was subtracted from CuBTA thickness measurements.

Electrochemical impedance spectroscopy (EIS) was conducted at North Dakota State University on a set of polished rolled bronze samples that had been immersed in 3% BTA/ethanol solutions for 4 minutes, 1046 minutes, or 10,047 minutes. EIS measurements were taken with a Gamry Instruments PC-3 Potentiostat, using a removable 1.5 inch (outer diameter) glass tube clamped to the bronze coupon by an o-ring. The glass tube was filled with the dilute Harrison's solution (0.35 wt. % $(\text{NH}_4)_2\text{SO}_4$ and 0.05 wt. % NaCl in H_2O). A saturated calomel reference electrode and a platinum counter electrode were also immersed in the solution. The amplitude applied to the system was 5 mV, and the frequency range was from 0.1 Hz to 10,000 Hz. Impedance modulus is reported as an average of three spots on each sample.

TABLE I: Frequencies and Tentative Assignments of Infrared Absorption Bands in Benzotriazole and CuBTA Complexes

Benzotriazole ¹ (cm ⁻¹)	Cu(I)BTA ² (cm ⁻¹)	Cu(II)BTA (cm ⁻¹)	Tentative Assignment
3346/3259 (broad)		3420-3435 (broad)	HOH stretching (adsorbed water; water of crystallization)
3500-3200 (m)			N ⁻ -HOH; NH ⁻ -OH ₂ stretching
3146			free N-H stretching
3076/3036 (w)	3076/3059/3040 (w)	3057-3097(w)	aryl C-H stretching
2991/2958/2908; 2850-2400 (m)			NH ⁻ -N stretching (intermolecular)
1640 (w)			liquid H ₂ O
1621	1612 (vw)	1612-1619 (m)	aryl ring stretching
1595 (w)	1580 (w)	1577 (m)	
1506 (w)			
1460 (m)	1490-1492 (m)	1490-1492 (w-m)	aryl + triazo (?) stretching
1419 (m)	1445 (m)	1445 (m)	aryl + triazo (?) stretching
1382 (m)	1388-1390 (m)	1385/1395 (vw)	aryl + triazo (?) stretching
1305 (w)	1299 (w)	1298 (w)	
1265	1270 (w)	1271-1275 (m)	
1207 (s)		1211-1223 (m)	triazole ring stretching
	1195 (w-m)		
	1149-1152 (m-s)	(1150-1152) (w)	triazole ring stretching
1143 (w)		1132 (vw)	
	1119 (w-m)		
1075 (w)			aryl ring mode (?)
	1046	1028-1030 (w)	
1006			N-H in-plane bending (?)
982 (m)	991 (w-m)	996 (w)	
876 (w-m)			
776 (m)	787-789 (m)	788-789 (m)	aryl out-of-plane 4 adjacent C-H wag
743-745 (s)	741 (s)	745 (s)	
707 (m)			N-H wagging (?)
		682 (w)	
		641-643 (w-m)	
607			triazole ring torsion
		561-564 (w-m)	
		435 (w-m)	

¹based on assignments for benzimidazole by Colthup [19] and Cordes and Walter [20].

²based on assignments by Poling [4] and Suetaka and Morito [7].