

PRESERVATION OF COPPER ALLOYS BY MEANS OF BTA DOPED VARNISHES AND WAXES AND THEIR OXYGEN PERMEABILITY

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Abstract

The set of five bronze vessels from the Late Bronze Age was found near to the Lidice village in 2014. The copper (I) chloride - nantokite was identified in a mixture of corrosion products. Nantokite is exposed to the surrounding atmosphere after excavation of the bronze vessels from a soil. Nantokite reacts with moisture and oxygen in the air to form basic copper chlorides. Basic copper chlorides have a larger volume than nantokite. The volume change of corrosion products leads to disintegration of metal core along the grain boundaries. Such a type of bronze corrosion damage is called bronze disease. The aim of the study was to suggest preservation coating system with the lowest oxygen permeability. The acrylic based lacquers (Paraloid B72 and Paraloid B48N), waxes (beeswax and microcrystalline wax) and corrosion inhibitor 1,2,3-Benzotriazole (BTA) were tested. Efficiency of monolayer and double layer preservation systems was compared. The double layer preservation system has performed the lowest oxygen permeability compared with the other tested substances. The inner layer is formed of the acrylic lacquer Paraloid B48N with addition of BTA and an outer layer is made of the microcrystalline wax with BTA addition.

Keywords: Copper alloys, preservation, lacquer, wax, oxygen permeability

1. INTRODUCTION

The set of five bronze vessels from the Late Bronze Age was found near Lidice (the village closed to Prague) during archaeological excavations in 2014. Inserted in each other they were stored in a rather shallow pit on the south outskirts of a vast prehistoric settlement area on the left bank of Lidice stream. The vessels are dated to the Late Bronze Age. Particularly, they come from 9th to 8th century BC (Štítary Culture, Ha, B3). Museum of Central Bohemia in Roztoky has owned bronze vessels since 2014 [1].

The vessels were covered in an uneven layer of black-green corrosion products and soil. The biggest vessel was damaged by cracks due to mechanical deformation or specified corrosion process (**Figure 1**).

The vessels are made of bronze - a copper-tin alloy. It is common material in history, it has been used since 3500 B.C. Bronze alloys originating from Late Bronze Age contain up to about 14 wt% tin and belongs to bronze with low tin content [2].

Bronze alloys have a good corrosion resistance in inner and outer atmospheric conditions due to formation of a natural patina. A composition of a natural patina depends, among other, on amount of atmospheric pollutants in the air. Usual bronze natural patina is composed of copper (I) oxide, copper (II) carbonate hydroxide and copper (II) hydroxide sulphate in urban environments. Copper (II) chloride hydroxide is possible to identify in a natural patina of bronze artifacts exposed to marine environments [3]. A natural patina based on copper (I) sulphide can be formed on bronze artifacts due to presence of reduced sulphur compounds especially in inner atmosphere of museums and archives (e.g. hydrogen sulphide and carbonyl sulphide) [3,4].



Figure 1 Damage of the biggest bronze vessel

However, a bronze as well as other copper alloys, suffers from the presence of some pollutants in the air and corrodes. Especially, environment containing volatile organic acids such as acetic or formic acid leads to the corrosion of bronze alloys in activity. Wood, some paints, display cases or degradation of organic materials are common source of volatile organic acids in inner atmosphere of museums and archives [3].

Ozone, hydrogen peroxide, ammonia, nitrogen oxides, or ammonium sulphate could be sources of active corrosion damage of copper and copper alloys in atmospheric and a soil conditions, too [4].

Bronze disease is specific corrosion damage of bronze alloys. This type of corrosion is associated with archaeological bronze finds and their excavation from a soil. The copper (I) chloride (nantokite) is formed in a natural bronze patina of bronze artifacts due to lower concentration of oxygen in a soil electrolyte. A natural bronze patina with nantokite is exposed to atmospheric humidity and higher concentration of oxygen after excavation of bronze artifacts from a soil. It leads to formation of basic copper chlorides (atacamite, paratacamite) from nantokite (1), (2) [3,5].



The forming salts have larger volume than nantokite resulting in an increase of internal stress in a bronze alloy especially along the grain boundaries. It leads to formation of cracks within the material. The cracks could lead up to the disintegration of bronze artifacts.

A large amount of nantokite was identified in corrosion products of the found bronze vessels. Since nantokite oxidation could cause bronze disease and crack formation within the bronze material, the aim of the study was to suggest preservation coating system with the lowest oxygen permeability. The low oxygen permeability of preservation coating system slows down oxidation of nantokite to basic copper chlorides and limits the possibility of formation the other cracks within bronze material.

2. EXPERIMENTAL PROCEDURE

The specimens were compressed from copper powder and nantokite in the ratio 1:2. The specimens were prepared such a model of natural patina of founded bronze vessels (**Figure 2**).

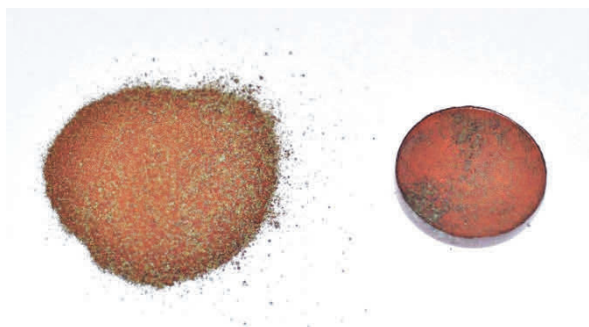


Figure 2 The compressed specimen from copper powder and nantokite

The acrylic based lacquers (Paraloid B72 = B72 and Paraloid B48N = B48N) and waxes (beeswax = BS wax and microcrystalline wax = MC wax) with 3 wt.% addition of corrosion inhibitor 1,2,3-Benzotriazole = BTA and without BTA were used for preparation of the preservation solutions. The concentration of the all preservation solutions were 10 wt.% and all of them were prepared by dissolving in xylene. The preservation solutions were applied on the surface of the specimen by a brush. Monolayer and double layer preservation systems were prepared. The eight types of monolayer preservation system were tested: Paraloid B72, Paraloid B48N, BS wax and MC wax without BTA and with 3 wt.% addition of BTA. Types of double layer preservation system are shown in **Table 1**. The specimens were exposed above a solution of 30 wt.% hydrogen peroxide at RH = 98 wt.% for 24 h.

Table 1 Types of double layer system

	Type 1	Type 2	Type 3	Type 4
The first layer	B72	B48N	B72	B48N
The second layer	BS wax	BS wax	MC wax	MC wax
	Type 5	Type 6	Type 7	Type 8
The first layer	B72 + BTA	B48N + BTA	B72 + BTA	B48N + BTA
The second layer	BS wax	BS wax	MC wax	MC wax
	Type 9	Type 10	Type 11	Type 12
The first layer	B72	B48N	B72	B48N
The second layer	BS wax + BTA	BS wax + BTA	MC wax + BTA	MC wax + BTA
	Type 13	Type 14	Type 15	Type 16
The first layer	B72 + BTA	B48N + BTA	B72 + BTA	B48N + BTA
The second layer	BS wax + BTA	BS wax + BTA	MC wax + BTA	MC wax + BTA

* *The first layer is inner at the metal surface*

Oxidation rate of nantokite to basic copper chlorides was determined with XRD analysis (**XRD diffractometer PANalytical X'Pert PRO**) and digital image analysis (optical microscope EMZ-13TR with Quik Photo Industrial 2.3). Oxygen permeability of monolayer and double layer preservation systems with addition BTA and without BTA was compared.

3. RESULTS AND DISCUSSION

The oxidation rate of nantokite was characterized as a multiple of Increase in basic copper chlorides content on the metal surface after exposure with respect to the content of basic copper chlorides on the metal surface before exposure.

3.1. The specimens without preservation systems

In the case of specimens without preservation systems, the basic copper chlorides content increased after exposure approximately 40.0 times.

3.2. The monolayer preservation systems without addition of BTA

The BS wax was identified as the preservation layer with the lowest oxygen permeability. In the case of BS wax, the basic copper chlorides content increased after exposure by a factor of 7.2. Contrary to that, in the case of the MC wax, the content of basic copper chlorides increased 14.0 times. The acrylic based lacquers (B72 and B48N) showed higher oxygen permeability compared to both the waxes. The content of basic copper chlorides on the metal surface after exposure increased approximately 19.5 times in both cases.

3.3. The monolayer preservation systems with addition of BTA

The addition of 3 wt.% BTA to the preservation layers significantly decreased oxygen permeability even though the wax-free and lacquer-free layer formed only by 3 wt.% BTA deposition showed the highest oxygen permeability of all tested systems. The basic copper chlorides content increased after exposition approximately 38.5 times in this case.

In the case of 3 wt. % BTA addition to preservation systems, both the waxes (BS wax and MC wax) were identified as the preservation layer with the lowest oxygen permeability. The basic copper chlorides content increased after exposure by a factor of 2.0. Contrary to that, the acrylic based lacquers (B72 and B48N) with addition of 3 wt.% BTA showed much higher oxygen permeability. The content of basic copper chlorides on the metal surface after exposure increased approximately 15.5 times in both cases.

3.4. The double layer preservation systems without addition of BTA

The double layer systems Type 2 and 4 (**Table 1**) were identified as the preservation double layer systems with the lowest oxygen permeability. In this case, the basic copper chlorides content increased after exposure approximately by a factor of 2.0. Contrary to that, in the case of the double layer system Type 1 (**Table1**), the content of basic copper chlorides increased 5.8 times. The highest oxygen permeability was shown for the double layer system Type 3 (**Table1**). The content of basic copper chlorides on the metal surface after exposure increased approximately 14.0 times in this case.

3.5. The double layer preservation systems with addition of BTA to the first layer

The double layer systems Type 6 and 8 (**Table 1**) were identified as the preservation double layer systems with the lowest oxygen permeability. In this case, the basic copper chlorides content increased after exposure approximately by a factor of 1.7 for the Type 8 and by a factor of 2.3 for the Type 6. Contrary to that, in the case of the double layer system Type 5 (**Table1**), the content of basic copper chlorides increased 5.0 times. The highest oxygen permeability was shown for the double layer system Type 7 (**Table1**). The content of basic copper chlorides on the metal surface after exposure increased approximately 6.3 times in this case.

3.6. The double layer preservation systems with addition of BTA to the second layer

Similar to the previous results the systems with B48N were identified as better preservation systems with lower oxygen permeability compared to those based on B72. In the case of systems Type 10 and Type 12 (**Table 1**), the basic copper chlorides content increased after exposure approximately 3.0 times and 4.2, respectively. The highest oxygen permeability was shown for the double layer system Type 9 and 11 (**Table1**). The content of basic copper chlorides on the metal surface after exposure increased approximately 5.3 times in both case.

3.7. The double layer preservation systems with addition of BTA to the both layers

The double layer system Type 14 and 16 (Table 1) were identified as the preservation double layer systems with the lowest oxygen permeability. In this case, the basic copper chlorides content increased after exposure approximately by a factor of 2.0. Contrary to that, in the case of the double layer system Type 15 (Table 1), the content of basic copper chlorides increased 3.7 times. The highest oxygen permeability was shown for the double layer system Type 13 (Table 1). The content of basic copper chlorides on the metal surface after exposure increased approximately 4.3 times in this case.

The results of XRD analysis (Chapters 3.1. - 3.7.) were compared with the results of the digital image analysis. The results obtained from both methods correspond to each other (Figure 3).

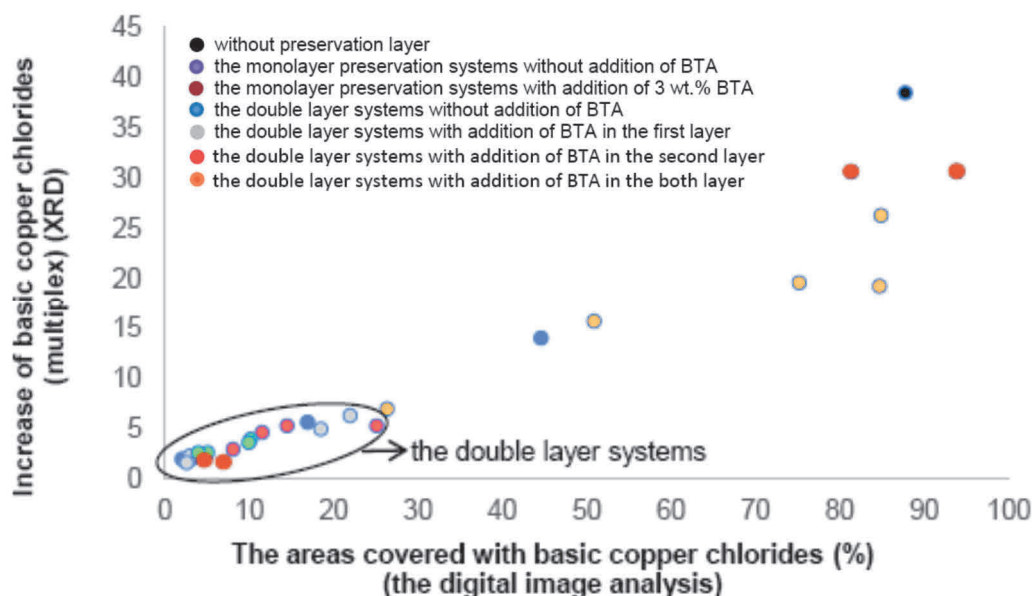


Figure 3 Comparison of the XRD results and digital image analysis results

The tested double layer preservation systems showed lower oxygen permeability compared with the specimens without coatings and with the majority of specimens covered by monolayer preservation systems (Figure 3). In comparison with the acrylic lacquers (B72 and B48N), much lower oxygen permeability was observed on specimens treated with both waxes (BS wax and MC wax).

4. CONCLUSION

The aim of study was to suggest preservation coating system with the lowest oxygen permeability for five bronze vessels from the Late Bronze Age found near Lidice in 2014. For this purpose, the acrylic based lacquers (Paraloid B72 and Paraloid B48N), waxes (beeswax and microcrystalline wax) and corrosion inhibitor 1,2,3-Benzotriazole (BTA) were tested.

The double layer preservation systems with addition of BTA showed the lowest oxygen permeability of all tested preservation systems. Since the oxygen permeability of Paraloid B48N is lower compared to that of Paraloid B72, Paraloid B48N was evaluated as the best first (inner) preservation layer. The microcrystalline wax with addition of BTA is the best option for a second (outside) preservation layer. The oxygen permeability of both the waxes (microcrystalline wax and beeswax) with addition of BTA is comparable. However, the beeswax contains many types of organic and volatile organic compounds which can cause corrosion of copper alloys. Therefore, the beeswax is not suitable as a preservation layer in this case.

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