

PROTECTION OF LEAD BY PRESERVATION ACRYLIC COATINGS IN ACETIC VAPORS ENVIRONMENT

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<https://doi.org/10.37904/metal.2020.3553>

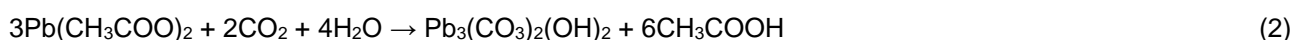
Abstract

A lead was used in the past in a variety of applications for example for roofs of churches, garden ornaments, lead seals, and organ pipes. Lead alloys are susceptible to a corrosion attack in an environment containing volatile organic compounds especially acetic acid vapors. The source of acetic acid vapors is mainly wood, glued joints, some varnishes, plastics, and paints. In the acetic acid vapors environment, the corrosion rate of Pb alloys rapidly increases. The study of protective properties of acrylic coatings of lead (Paraloid 72, B48N a B44) in an environment containing acetic acid vapors was the aim of this work. The acrylic coatings were prepared with or without 1,2,3, - Benzotriazole (BTA). Painted lead samples were exposed in an environment containing acetic acid vapors for 8 weeks. The color change of lead surfaces was observed by a spectrophotometer during the exposition. The preservation effect of acrylic coatings were evaluated by the mass gain of lead samples during the exposition. The surface of the lead samples after exposition was observed by optical microscopy, and X-ray diffraction analysis. The research proved that the Paraloid B44 with BTA has the best protective properties of lead in an environment containing acetic acid vapors from all tested coatings.

Keywords: Lead, corrosion, acrylic varnish, acetic acid, gain mass

1. INTRODUCTION

Historical museum collections contain a big amount of historical objects, which were made from lead or lead alloys. These objects are stored in museum depositaries with other historical objects. Many historical objects are a source of volatile organic compounds. Other sources of these volatile organic compounds in depositaries are unsuitable packaging materials, wood, unsuitable coatings, and adhesives and etc. [1]. Lead is an amphoteric metal and has good corrosion resistance given by the formation of a passive layer on the lead surface. The passive layer is formed predominantly of α -PbO [2,3]. Active lead corrosion takes place in the presence of volatile organic acids in the atmosphere. Non-cohesive and soluble corrosion products are formed on the lead surface (e.g. lead formate or lead acetate etc.) [3,4]. The mechanism of lead corrosion in acetic acid vapor environment is described by the following equations [5]:



Elimination of the lead active corrosion requires the elimination of volatile organic acid source from the environment [6] or protection of lead surfaces by the preservation layer. The aim of this work was to compare preservation layers resistance of acrylic varnishes Paraloid B72, B48N and B44 and to consider their use as lead corrosion protection of lead in acetic acid vapor environment.

2. EXPERIMENTAL

10%, 7%, and 5% solutions of acrylic varnishes Paraloid B72, B 48N, and B 44 were prepared. The acrylic varnishes were dissolved in acetone with the addition of a corrosion inhibitor 1,2,3 – Benzotriazole (BTA) and without BTA. BTA was dissolved in ethanol and the solution was added into the solutions of acrylic varnishes. The concentration of BTA in the solutions of acrylic varnishes was 3 %. The viscosity of all preservation solutions was measured by dynamic vibrational viscometer AD SV-10 with the measuring range 0.3 – 10 000 mPa.s. The lead samples 70x50x5 mm were used for the experiment. The chemical composition of used lead alloy corresponded to DIN 1719. The lead samples were grinded by sandpapers P80 – P800 and weighted. Then, the surface of the samples was coated by preservation solutions. The drying of preservation layers was 48 hours at ambient temperature and then they were weighted again. The approximate thicknesses of preservation layers were calculated from weight differences. The lead samples were exposed in an acetic acid vapor environment for 8 weeks at room temperature and RH = 100 %. The source of acetic acid vapor was a solution of 0.01 mol.l⁻¹ acetic acid. Ventilators ensured the homogenous environment in the experimental boxes. The color change of lead surface was observed only for 10% solutions of acrylic varnishes before and after application of the preservation layers coating and after exposition. The color change of lead surface was measured after the exposition on the selected places of samples without visible corrosion products. The color change was observed by spectrophotometer Minolta CM 700d with CIELAB color space. The corrosion rate of lead samples was observed by the weight gain of corrosion products on the lead surface. The weight gain was measured after the exposition. All presented results are the average value of four measurements except for solution viscosity determination. The value of viscosity of all preservation solutions was measured only one time.

3. RESULTS AND DISCUSSION

3.1. Viscosity

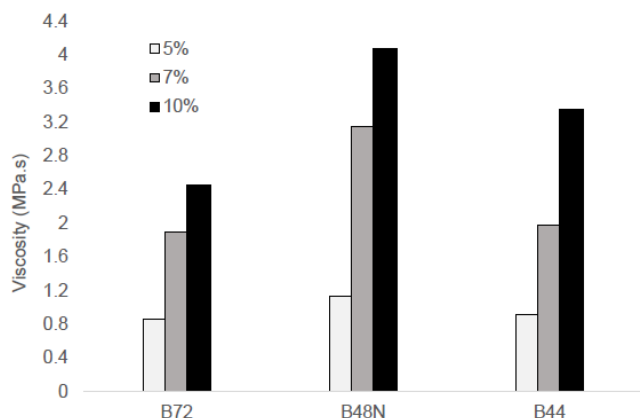


Figure 1 The viscosity of acrylic varnishes without BTA

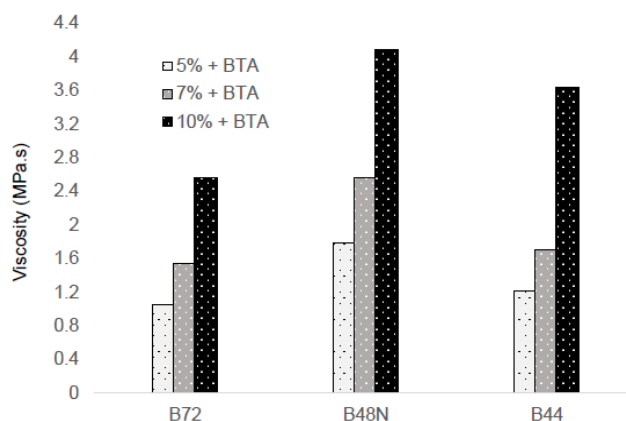


Figure 2 The viscosity of acrylic varnishes with 3 % BTA

The highest viscosity has the acrylic varnish B48N and the smallest viscosity has the acrylic varnish B72 at all observed concentrations. The comparable values of viscosity with acrylic varnish B72 has also acrylic varnish B48N at 5% and 7% concentration (Figure 1). The addition of BTA hasn't a significant influence on the viscosity of the acrylic varnishes solutions (Figure 1, 2).

3.2. The thicknesses of preservation layers

The thicknesses of preservation layers on the lead samples increase with the increasing viscosity of acrylic varnishes solutions and the addition of BTA hasn't significant influence on it (Figures 3, 4).

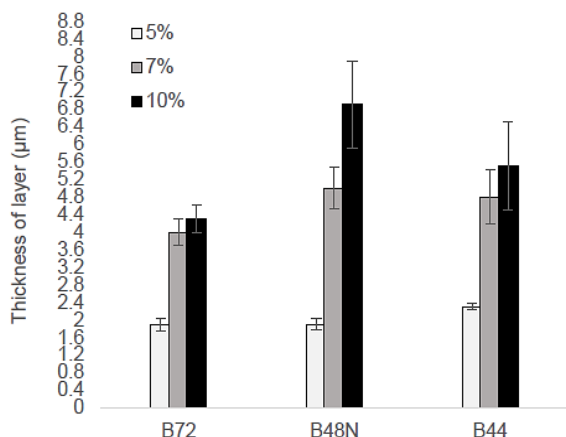


Figure 3 The thickness of layer of acrylic varnishes without BTA

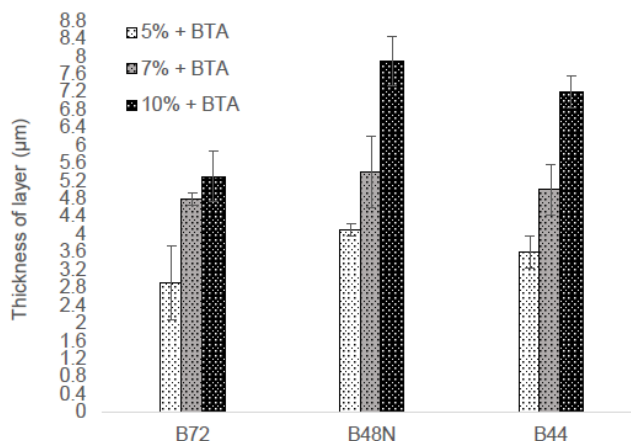


Figure 4 The thickness of layer of acrylic varnishes with 3% BTA

3.3. The corrosion resistance of lead samples in an acetic acid vapor environment

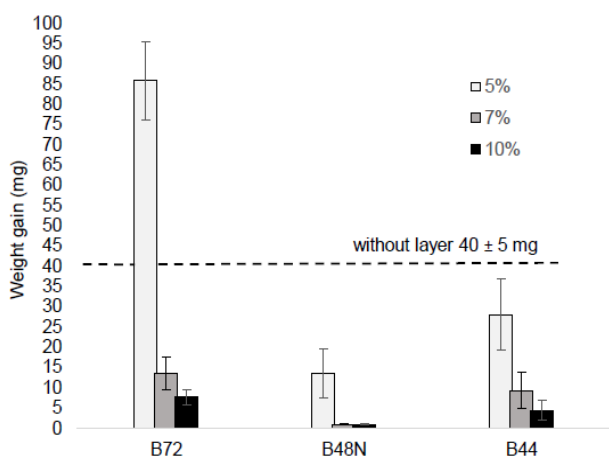


Figure 5 The weight gain of lead samples without BTA after 8 weeks exposition

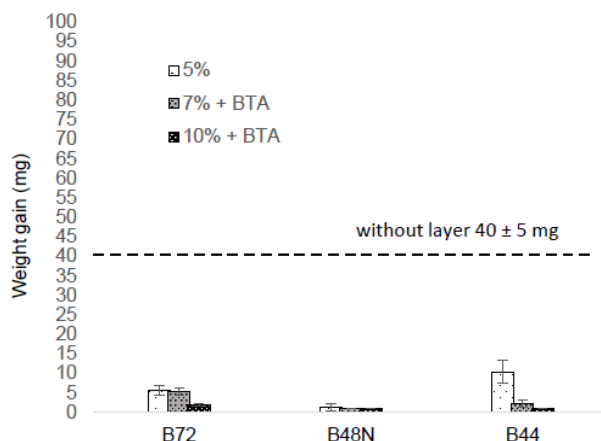


Figure 6 The weight gain of lead samples with BTA after 8 weeks exposition

The smallest resistance of preservation layers formed by acrylic varnish B72 was observed at all tested concentrations (Figure 5). The copolymer of Methyl acrylate (MA) and Ethyl methacrylate (EMA) in 30 (MA): 70 (EMA) ratio is the main component of the acrylic varnish B72. EMA is insoluble in water but on the other hand, solubility of MA is 5 g/ 100ml H₂O at 20 °C [7]. The acrylic varnish B72 viscosity is the lowest at all three tested concentrations (Figures 1, 2) and the thicknesses of preservation layers of B72 are the smallest of all tested acrylic varnishes (Figures 3, 4). Therefore, the acrylic varnish B72 has probably the smallest resistance in an acetic acid vapor environment with high humidity comparing with the other tested varnishes (Figure 5).

The reason for the two times higher weight gain of lead samples with the 5% B72 preservation layer comparing with the lead samples without preservation layer is probably the high number of defects in the 5% B72 preservation layer, high humidity, and an acetic acid vapor environment containing oxygen. This combination probably leads to faster damaging of lead passive layer with the 5% B72 preservation layer comparing with the lead samples without the 5% B72 preservation layer (Figure 5).

The copolymer of Butyl acrylate (BuA) and Methyl methacrylate (MMA) in 25 (BuA): 75 (MMA) ratio is the main component of the acrylic varnish B48N. The solubility of BuA is 0.14 g/100 ml H₂O [7] and MMA is 1.5 g/100

ml H₂O at 20 °C [7]. The acrylic varnish B48N viscosity is the highest at all three tested concentrations (**Figures 1, 2**) and the thicknesses of preservation layers of B48N are the greatest of all tested acrylic varnishes (**Figures 3, 4**). Therefore, the acrylic varnish B48N has probably the highest resistance in an acetic acid vapor environment with high humidity comparing with the other tested varnishes (**Figure 5**).

Methyl methacrylate (MMA) is the main component of acrylic varnish B44. The solubility of MMA is 1.5g/100ml H₂O at 20 °C [7]. The viscosity and thickness of B44 preservation layers are comparable with the viscosity and thickness of B72 preservation layers at 5% and 7% concentration (**Figures 1 – 4**). Higher viscosity and thickness were observed only at the 10% B44 preservation layer (**Figures 1 – 4**).

The weight gain of lead samples with the 7% and 10% B44 preservation layer is comparable with the weight gain of lead samples with the 7% and 10% B72 preservation layer (**Figure 5**). However, the weight gain of lead samples with the 5% B44 preservation layer is three times lower than the weight gain of lead samples with the 5% B72 preservation layer. The main reason is probably the less number of defects in the 5% B44 preservation layer and the smaller solubility of MMA in water comparing with the solubility of MA, which is one of the main components of B72 acrylic varnish (**Figure 5**).

The addition of BTA in all tested acrylic varnishes significantly decreased the weight gain of all lead samples (**Figure 6**). The corrosion inhibitor BTA formed the adsorbed molecular layer on the lead surface [8]. This layer was a barrier between the experimental environment and the lead surface and significantly protected the lead surface in the places of defects of all tested acrylic varnishes (**Figure 6**).

3.4. The color differences of lead surfaces

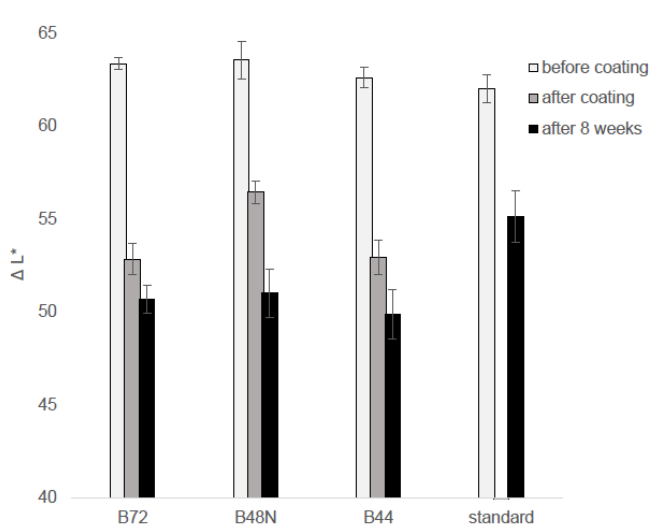


Figure 7 The color change of lead samples without BTA after 8 weeks exposition

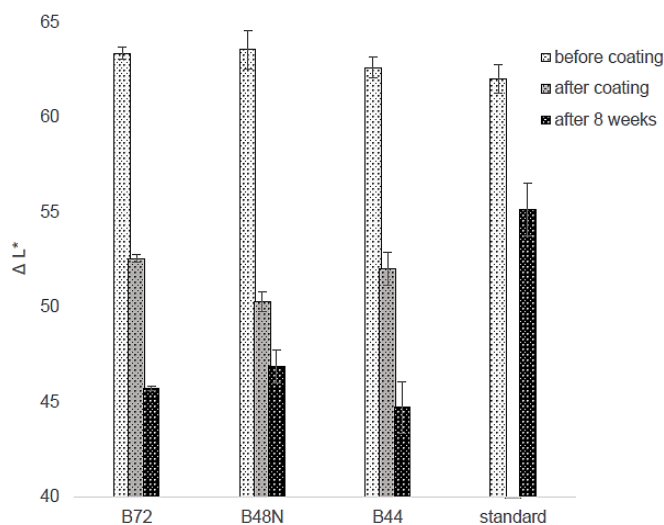


Figure 8 The color change of lead samples with BTA after 8 weeks exposition

The conservation layer of all tested acrylic varnishes led to the significant darkening of the lead samples after coating and the smallest darkening was observed after using B48N preservation layer (**Figure 7**). The lead surfaces were 5 - 10 % darker after exposition comparing with the coated lead surfaces before exposition (**Figure 7**). After the exposition, the all coated lead samples were 7 - 11 % darker compared with the standard without a preservation layer (**Figure 7**).

The addition of BTA in all tested acrylic varnishes significantly increased darkening of the lead samples 6 - 12 % after the exposition comparing with the lead samples, which were coated only by acrylic varnishes without BTA (**Figure 7, 8**). After the exposition, all preservation layers with the addition of BTA led to 15 - 19 % darkening of the lead surfaces compared with the standard without a preservation layer (**Figure 8**).

4. CONCLUSION

The resistance of the three types of acrylic varnishes (B72, B48N, and B44), which was used as lead preservation layers, were tested in the acetic acid vapor environment.

The acrylic varnish B48N has the highest resistance in the acetic acid vapor environment. The smallest darkening of the lead surface was observed after using the preservation layers B48N comparing with the other tested varnishes. On the other hand, the viscosity of B48N preservation layers is the highest of all. It means that the acrylic varnish B48N is applicable for a smooth lead surface without narrow and deep relief details.

The 7% and 10% solution of acrylic varnish B44 has also high resistance in the acetic acid vapor environment. But, the higher darkening of the lead surface was observed after using the preservation layers B44 comparing with the acrylic varnish B48N. On the other hand, the viscosity of B44 preservation layers is lower than the viscosity of B48N preservation layers. It means that the acrylic varnish B44 is more applicable for a lead surface with narrow and deep relief details.

The addition of corrosion inhibitor BTA to all tested solutions of acrylic varnishes significantly increased corrosion resistance of lead in an acetic acid vapor environment. However, the surface of lead samples was much more tarnished after exposition comparing with lead surfaces, which were coated with acrylic varnishes without BTA.

The acrylic varnish B72 with the addition or without the addition of corrosion inhibitor BTA has the worst resistance in an acetic acid vapor environment at all tested concentrations.

ACKNOWLEDGEMENTS

Financial support from specific university research (MSMT No 20-SVV/2020).

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