

LONG-TERM STABILITY OF PROTECTIVE COATINGS ON LEAD AND LEAD-TIN ALLOY UNDER STORAGE CONDITIONS

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Abstract

Protection of the lead and lead-tin alloys stored in museum and archive depositories under adverse conditions (environment polluted by organic compound, mainly acetic acid) is based on the use of protective coatings (corrosion inhibitors, waxes and varnishes). The aim of this work was to test long-term stability and inhibition efficiency of mainly used protective coatings and final visual appearance of treated lead and lead-tin alloy surface. The monitored parameters were weight gain, color change and change of hydrophobic properties on samples of lead and lead-tin alloys after 2 years in a room environment and after 4 months in an atmosphere polluted with acetic acid.

Keywords: Protective coatings, lead corrosion, corrosion inhibitors

1. INTRODUCTION

Cultural heritage objects are often sensitive to atmospheric conditions, their corrosion damage represents not only financial losses, but especially a loss of historical value [1]. Therefore, it is very important to find a long-term effective system for their protection. One of the possibilities is protective coatings - waxes, varnishes and selected corrosion inhibitors (especially BTA) are used in restoration practice [2]. For the protection of cultural monuments, it is necessary that the chosen protection does not change the appearance of the surface of the treated object, it is reversible, non-toxic and easy to use [1, 2]. Due to lead high corrosion resistance, many of lead and lead-tin alloy artefacts are stored in museums and archives in an inappropriate environment with the presence of organic acids (mainly acetic acid) to which lead is sensitive [3]. In this paper, the long-term stability and anticorrosion effectiveness in an environment contaminated with acetic acid corrosion inhibitors (benzotriazole, cyclohexylamine, thiourea and sodium benzoate), sodium decanoate, microcrystalline wax and Paraloid B48N, which are discussed in literature and used in restoration practice, will be examined.

2. EXPERIMENTAL PART

Lead samples (A = Pb 99.9 %) and lead-tin alloy samples (B = Pb 37 %, Sn 63 %) in dimension 3x8x0.1 cm were used in this work. Samples were grinded with abrasive wadding (3M Scotch-Brite CF-MF), subsequent rinsing with ethanol and then air drying. The coated surface was obtained by:

- immersing the samples into the 0.05 mol·l⁻¹ sodium decanoate (NaC₁₀) aqueous solution for 24 hours, subsequent rinsing by distilled water, ethanol and then air drying for 24 hours,
- immersing the samples into the one from different corrosion inhibitor solutions (0.05 mol·l⁻¹ thiourea aqueous solution, 1.4 mol·l⁻¹ sodium benzoate aqueous solution, 0.03 mol·l⁻¹ ethanol solution of cyclohexylamine (CHA) and 0.03 mol·l⁻¹ ethanol solution of 1,2,3-benzotriazole (BTA)) for 2 hours, subsequent rinsing by distilled water, ethanol and then air drying for 24 hours,

- covering the samples with 10 % solution of Paraloid B48N in xylene, 10 % solution of Paraloid B48N in xylene enriched with 3 wt% of BTA, 15 % solution of microcrystalline wax in benzene (pre-heated for 60 – 70 °C) or 15 % solution of microcrystalline wax in benzene enriched with 3 wt% of BTA (pre-heated for 60 – 70 °C) with a paintbrush and then air drying for 24 hours.

The serial numbers of protective coatings used in this work are mentioned in following **Table 1**:

Table 1 The serial numbers of protective coatings used in this work

no coating	NaC10	thiourea	sodium benzoate	CHA	BTA	Paraloid B48N	Microcryst. wax	Paraloid B48N + BTA	Microcryst. wax + BTA
1	5	8	9	10	11	13	18	21	22

The samples with protective coatings (2 samples of each protective coating) and two samples without coating were exposed in two different environments: a room environment and circulating humid (RH 100 %) corrosive atmosphere provided by acetic acid solution in concentration 0.01 mol·l⁻¹ (AA), the concentration of acetic acid in the atmosphere ranged from 0.6 to 0.3 ppm.

The observation of the hydrophobic properties of the protective coatings was carried out by the contact angles measurement by goniometer SEESystem (Advex Instruments, s.r.o.). The contact angles were measured on 2 samples of each protective coating, 5 measurements were done on each sample.

The color changes on the exposed samples in the CIE L*a*b* color space (CIELAB) were monitored regularly using a portable Konica Minolta CM-700d spectrophotometer (aperture 8 mm, SCI mode) (Konica Minolta GmbH). The color was measured on 2 samples of each protective coating, 5 measurements were done on each sample. The color change (ΔE^*) on exposed samples were calculated according to equation (1):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where ΔL^* , Δa^* and Δb^* represent the difference between the average value of the parameter measured before and after exposure.

The inhibition efficiency of protection coatings was determined from mass increase of exposed samples after exposure in AA.

3. RESULTS AND DISCUSSION

3.1. Mass increas

No sample of lead or lead-tin alloy changed weight during two years of exposure in a room environment. The inhibition efficiency of protection coatings was determined from the difference between the average mass values of exposed samples before (m_{be}) and after (m_{ae}) exposure in AA (**Table 2** and **Table 3**).

Table 2 Average values of weight gain ($\Delta m = m_{ae} - m_{be}$) on lead samples after exposure in AA

Δm (g)	A1	A5	A8	A9	A10	A11	A13	A18	A21	A22
2 years on air + 4 months in AA	0.05	0.07	0.23	0.07	0.08	0.08	0.05	0.07	0.04	0.07
24 hours on air + 4 months in AA	0.06	0.05	0.06	0	0.08	0.07	0.06	0.04	0.02	0.03

According to the values given in **Table 2**, the only one protective coating for lead in an acetic acid polluted atmosphere is BTA-enriched Paraloid B48N (A21), which shows the highest inhibition efficiency (slightly higher

efficiency than for non-treated samples) in both freshly after application and after 2 years exposition in room environment. For non-treated lead samples, a passive layer formed on the air slightly protects the lead in the environment with acetic acid, on the other hand, for all monitored coatings, their anti-corrosion efficiency deteriorates after 2 years from their application. The colored values in **Table 2** show a significant reduction in the effectiveness of the coating after 2 years of its application (especially for the thiourea (A8), also for sodium benzoate (A9) and coatings based on microcrystalline wax (A18, A22) where local corrosion may occur due to insufficient adhesion of the coating to the sample surface).

Table 3 Average values of weight gain ($\Delta m = m_{ae} - m_{be}$) on lead-tin alloy samples after exposure in AA

Δm (g)	B1	B5	B8	B9	B10	B11	B13	B18	B21	B22
2 years on air + 4 months in AA	0.04	0.02	0.03	0.04	0.03	0	0.01	0	0	0
24 hours on air + 4 months in AA	0.02	0.01	0.02	0.02	0.02	0.02	0	0	0	0

For lead-tin alloys, generally more resistant to acetic acid than pure lead, coatings based on BTA (B11), Paraloid B48N (B13), microcrystalline wax (B18) and their combination (B21, B22) can promote acetic acid resistance (**Table 3**). In contrast to pure lead, the corrosion resistance of lead-tin alloys to acetic acid deteriorates after prolonged exposure to air.

3.2. Final visual appearance

Figure 1 shows the condition of lead samples after 2 years of exposure in a room environment. The surface of untreated lead samples (A1), treated with sodium benzoate (A9) and BTA (A11), significantly darkened and turned blue. The surface of the CHA (A10) treated sample turned white. Even under the conversion coatings (A13, A18, A21 and A22) the surface of the lead samples darkened. Only the samples treated with thiourea (A8) did not darken the surface. Treatment of lead and lead-tin alloy samples with NaC_{10} (A5, B5) caused a non-stick whitish soap layer. Microcrystalline wax coatings caused opacity of the sample surface (A13, B13, A21 and B21). Paraloid B48N coatings increased the surface gloss of the samples (A18, B18, A22 and B22). The addition of undissolved BTA in the coating is visible on the surface of samples A21, B21, A22 and B22.

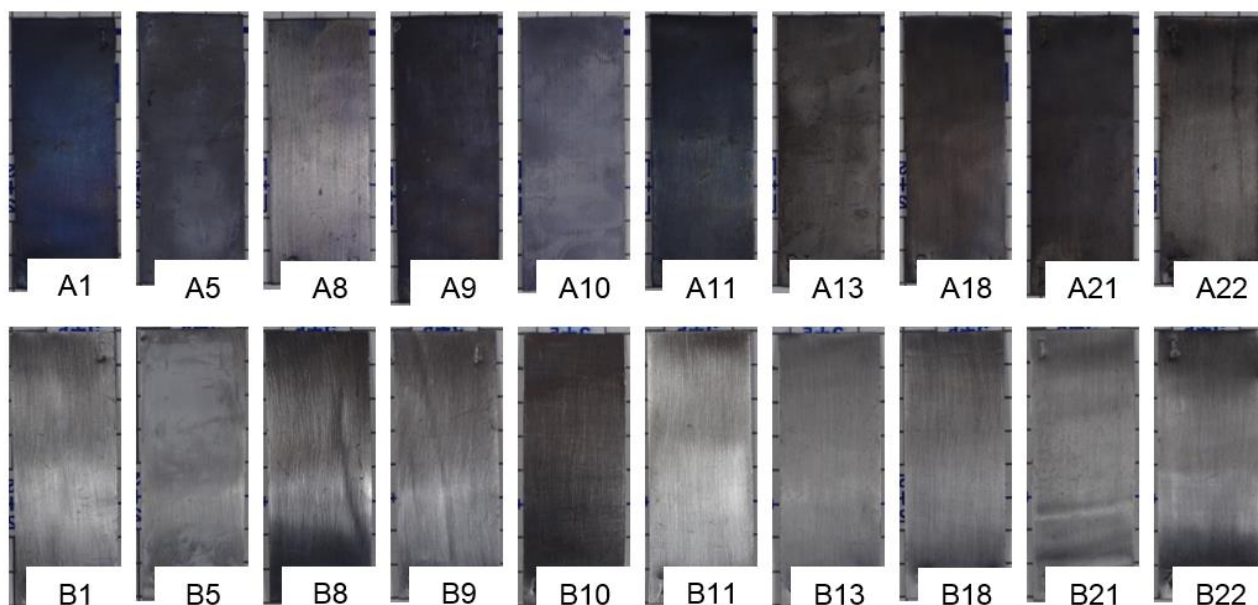


Figure 1 Appearance of lead samples (A, upper row) and lead-tin alloy samples (B, bottom row) after 2 years of exposure in a room environment

The samples of lead and lead-tin alloys, which were placed in an AA environment for 4 months after 2 years in a room environment (**Figure 2**), show the ineffectiveness of inhibitors thiourea (A8, B8), sodium benzoate (A9, B9), CHA (A10, B10) and BTA (A11, B11). The coating formed with NaC₁₀ (A5, B5) proves to be effective against corrosion of lead and lead-tin alloys, but it significantly modifies the metal surface (white soap layer). Lead samples with microcrystalline wax and Paraloid B48N coatings (A13, A18, A21 and A22) show local corrosion attack of samples, red lead oxide (lithargite) even appears under microcrystalline wax coating (A18, A22), indicating high oxygen permeability of the coating. For lead-tin alloy samples, coatings based on BTA, Paraloid B48N and their combination (B11, B18 and B22) prevented corrosion. Lead-tin alloy samples with microcrystalline wax coatings (B13 and B21) show local corrosion attack of samples.

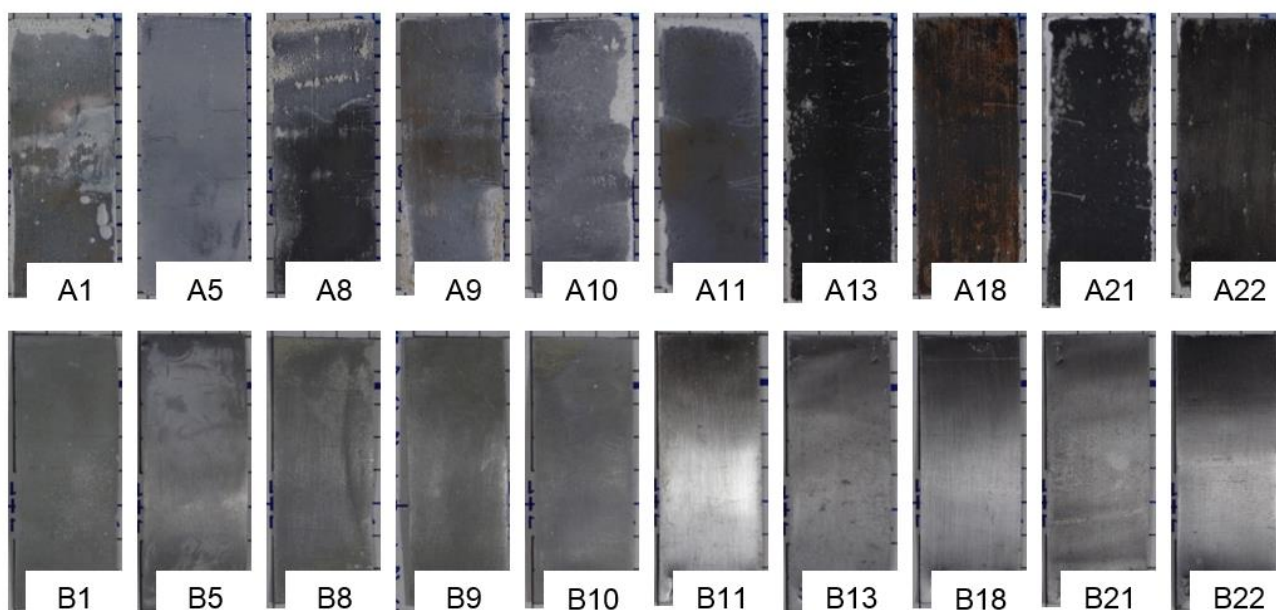


Figure 2 Appearance of lead samples (A, upper row) and lead-tin alloy samples (B, bottom row) after 2 years of exposure in a room environment and 4 months in AA

3.3. Color change

The results of the color measurements are in accordance with the real surface conditions of the lead and lead-tin alloy samples described in the previous chapter (**Figure 1** and **Figure 2**). The color change (ΔE^*) on exposed samples were calculated according to equation (1) from the difference between the average values of the parameter measured of exposed samples before and after exposure (**Table 4** and **Table 5**). The color highlighting of **Table 4** and **Table 5** is explained in **Table 6**.

Table 4 Average values of color change (ΔE^*) of lead samples surface under protective coatings after 1 and 2 years exposure in room environment and 4 months in AA

ΔE^*	A1	A5	A8	A9	A10	A11	A13	A18	A21	A22
1 year on air	31.7	6.6	1.5	15.0	11.4	32.9	8.9	11.0	11.4	5.5
2 years on air	32.6	8.3	2.1	19.1	11.5	29.9	9.6	13.5	10.1	7.1
2 years on air + 4 months in AA	4.3	13.0	8.6	-	8.4	14.5	15.7	15.7	10.7	9.5
24 hours on air + 4 months in AA	7.4	18.4	15.2	-	14.3	20.7	12.5	16.0	12.6	15.5

Table 5 Average values of color change (ΔE^*) of lead-tin alloy samples surface under protective coatings after 1 and 2 years exposure in room environment and 4 months in AA

ΔE^*	B1	B5	B8	B9	B10	B11	B13	B18	B21	B22
1 year on air	1.5	0.7	7.5	6.3	13.1	4.1	2.2	1.7	3.0	6.8
2 years on air	2.1	1.0	7.8	5.7	12.7	3.8	2.8	1.6	3.4	7.2
2 years on air + 4 months in AA	12.1	5.4	4.8	9.4	11.3	8.3	4.6	1.8	5.3	6.9
24 hours on air + 4 months in AA	10.5	1.6	12.1	12.9	13.8	14.3	2.7	0.6	3.5	1.5

Due to the higher corrosion resistance of the lead-tin alloy, the color change values given in **Table 5** are lower than the values for lead in **Table 4**.

Table 6 Verbal explanation of the meaning of color change (ΔE^*) values

ΔE^*	0.2 - 1.0	1.0 - 2.0	2.0 - 4.0	4.0 - 8.0	8.0 - 16.0	16.0 <
characterisation	perceivable	distinguishable	not disturbing yet	slightly disturbing	significant	disturbing

3.4. Hydrophobic properties

Figure 3 and **Figure 4** show the expected result of a small change in the hydrophobic character of conversion coatings (especially microcrystalline wax coatings (A18, B18, A22 and A22)) on both lead and lead-tin alloy samples, both at room exposure and during subsequent exposure in AA. In the case of samples with inhibitor coatings, there is a visible difference in the hydrophobic behavior of the coatings on lead and on lead-tin alloy.

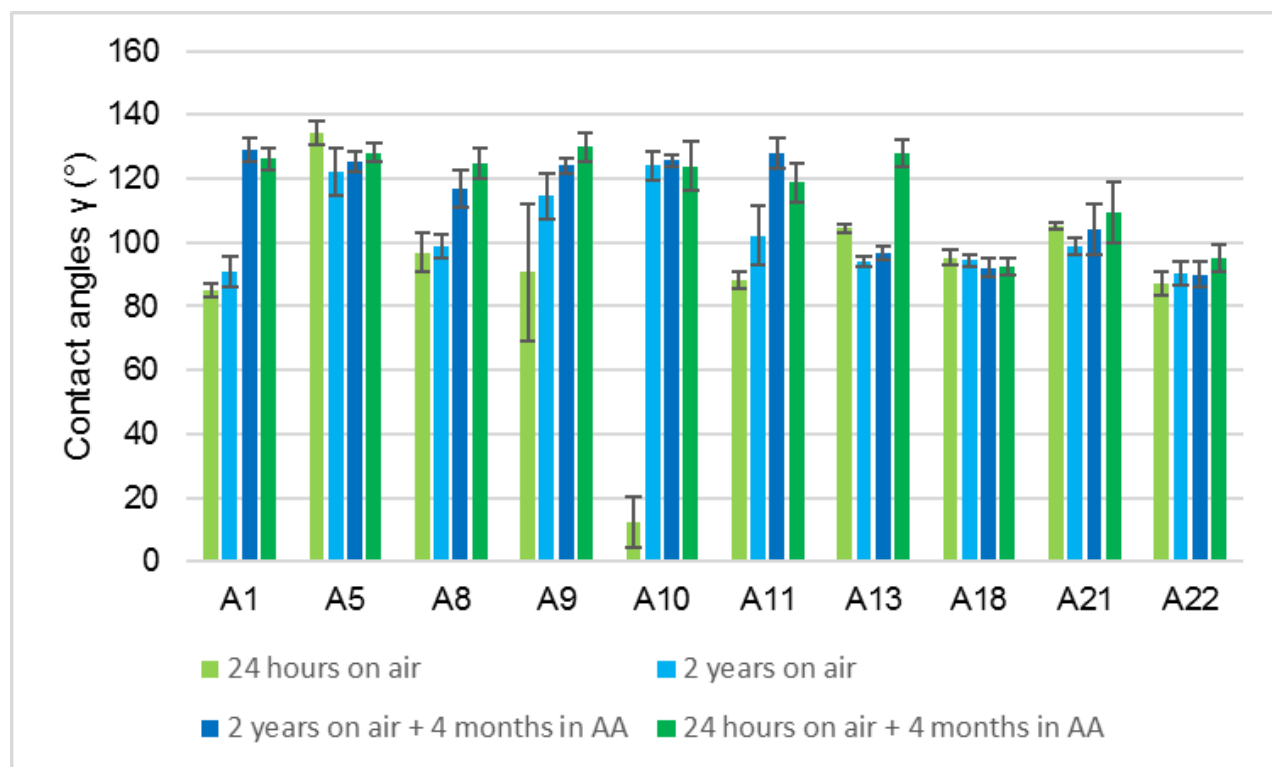


Figure 3 Average values of contact angle (γ) measured on lead samples during indoor exposure and subsequent exposure in AA

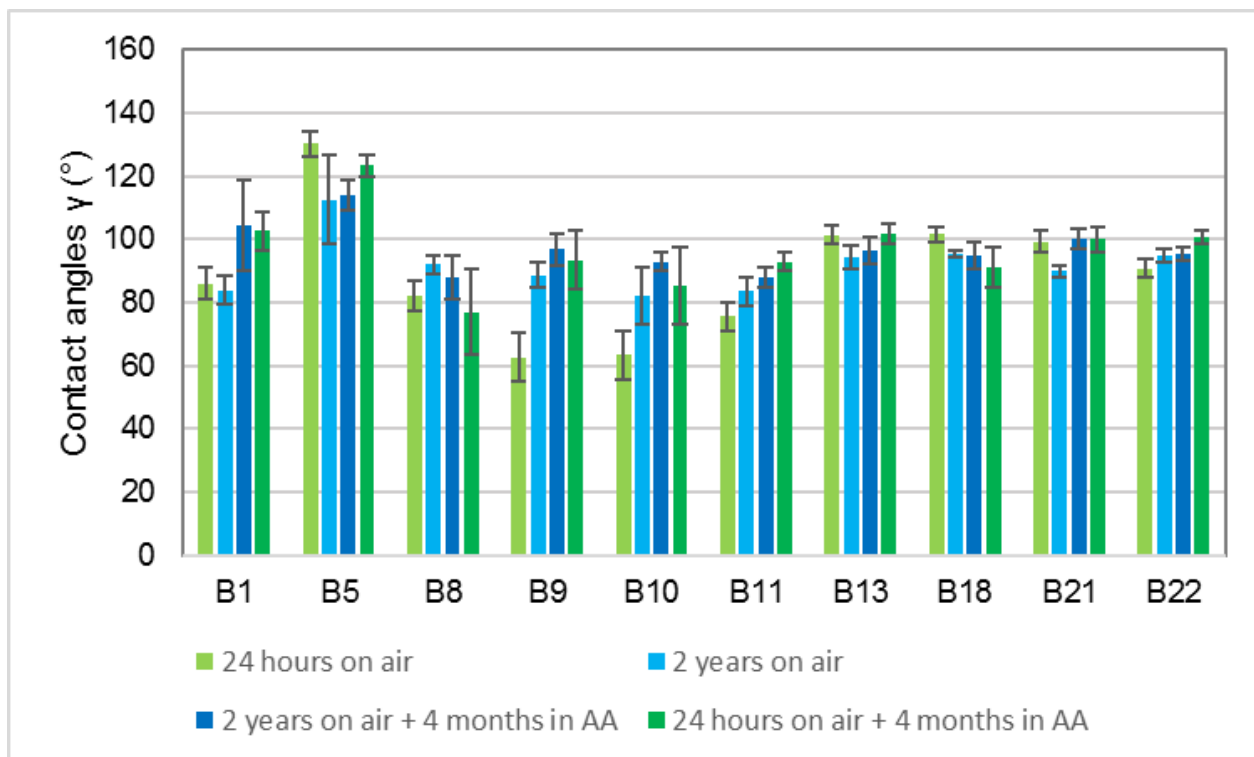


Figure 4 Average values of contact angle (γ) measured on lead samples during indoor exposure and subsequent exposure in AA

4. CONCLUSION

Within the set of protective coatings we monitored, it was not possible to find a coating suitable for lead. None of the monitored coatings was able to effectively protect lead against corrosion in an acetic acid polluted environment (according to weight gain values, the BTA-enriched Paraloid B48N coating was best, but also showed local corrosion of the lead surface) and except for the thiourea treated sample (this coating showed worst corrosion protection of lead in the environment with acetic acid) there were significant visual changes in the lead surface in all monitored samples, which disagrees with the restoration ethics. For lead-tin alloy samples, the Paraloid B48N coating and the BTA inhibitory coating appear as anti-corrosion coatings with an imperceptible change in the sample surface. The disadvantages of these coatings are toxicity and low to zero reversibility.

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