EVALUATION OF THE INHIBITION EFFICIENCY OF BTA DEPENDING ON THE METHOD OF APPLICATION

[1]Kristýna Charlotte STRACHOTOVÁ, [2]Milan KOUŘIL, [2]MSALLAMOVÁ Šárka

[1]*Museum of Prague, Prague, Czech Republic, EU, strachotova@muzeumprahy.cz*

[2]*UCT - University of Chemistry and Technology Prague, Prague, Czech Republic, EU*

https://doi.org/10.37904/metal.2025.5139

Abstract

The effectiveness of the protection of the base metal by the popular corrosion inhibitor BTA (1,2,3-benzotriazole) depending on the method of application of the inhibitor was verified on lead coupons in an environment contaminated with acetic acid. The BTA inhibitor was applied alone or in combination with a protective wax and/or varnish coating: a multi-layer system (BTA-single-layer wax/varnish, BTA-double-layer wax+varnish) or a BTA additive to the wax/varnish coating. As part of a long-term experiment (almost 2 years), the effect of the length of immersion of the metal in the BTA solution and the effect of aging of the protective coating on its anti-corrosion effectiveness and visual changes of the base metal were monitored.

Keywords: BTA, protective coatings, lead corrosion, corrosion inhibitors

1. INTRODUCTION

1,2,3-benzotriazole (BTA) is still the most popular corrosion inhibitor for use on cultural objects. The formation of a metal-BTA complex film has been observed not only with copper [1-4], but also with lead [3], zinc [3] and silver [4]. Its high anti-corrosion efficiency has been repeatedly confirmed in various laboratory and outdoor tests [3-6]. Compared to inhibitors of the same anti-corrosion efficiency, the color shift when using BTA is not so pronounced [3]. However, it should be emphasized that when using it, the color change (darkening) of the metal surface occurs. The way in which BTA effectively protects the metal (is it the inhibitory effect of BTA or the barrier effect of the surface film?) and the way it binds to the metal surface are not yet 100% clear [1, 3]. Likewise, it is not clear how to apply BTA to objects. Currently, both direct application of BTA by immersing the object in its 3% alcohol solution [3], addition of BTA to wax (Revax 30, Soter 201 LC [6]) or varnish (Incralac [6]) coating and use as a vapor inhibitor in a closed package are used [3]. The combination of barrier coatings (wax, varnish) with BTA increases and prolongs the anti-corrosion effect, especially in outdoor exposures [3]. This work aims to find the most suitable method of applying BTA to objects, so that the caused color change and the resulting anti-corrosion protection are most balanced, the application procedure is as less demanding as possible, but effective and at the same time the protective effect is long-lasting.

2. EXPERIMENTAL PART

2.1. Samples

In this work, lead samples (Pb 99.9%) with dimensions of 3x8x0.1 cm were used. The samples were abraded with abrasive wool (3M Scotch-Brite CF-MF) followed by rinsing with ethanol and air drying. After cleaning, the samples surface was coated:

- **BTA inhibitor alone** (single-layer of BTA) - immersing the samples in a corrosion inhibitor solution (0.03 mol·l^{-1} ethanol solution of 1,2,3-benzotriazole (***BTA***)) for 2 and 24 and 48 hours, followed by rinsing the sample with distilled water and ethanol and then air drying for 24 hours,

- **combination of BTA inhibitor with barrier coatings** (Paraloid B48N, microcrystalline wax):

a) **single-layer system** - covering the samples with 10 % solution of Paraloid B48N in xylene enriched with 3 wt.% of BTA or 15 % solution of microcrystalline wax in benzine enriched with 3 wt.% of BTA (pre-heated for 60 – 70 °C) with a paintbrush and then air drying for 24 hours, addition of 3 wt.% BTA to wax/varnish in solid form (***3 wt.% BTA***) or dissolved in ethanol (***3 wt.% BTA (Et-OH)***),

b) **multi-layer system** - samples with single-layer of BTA (***2h immersion in 0.03M BTA***) coated with a 10% solution of Paraloid B48N in xylene or 15% solution of microcrystalline wax in gasoline (preheated to 60 – 70 °C) with a paintbrush and then air drying for 24 hours or with a combination of both (bottom layer of Paraloid B48N (air drying for 48 hours) and after that top layer of microcrystalline wax (air drying for 24 hours)

- samples with single-layer of Paraloid B48N enriched with 3 wt.% of BTA (solid form or dissolved in ethanol) coated with 15% solution of microcrystalline wax in gasoline (preheated to 60 – 70 °C) with a paintbrush and then air drying for 24 hours

- **reference** - coating the samples with a 10% solution of Paraloid B48N in xylene or 15% solution of microcrystalline wax in gasoline (preheated to 60 – 70 °C) with a paintbrush and then air drying for 24 hours or a combination of both (bottom layer of Paraloid B48N (air drying for 48 hours) and after that top layer of microcrystalline wax (air drying for 24 hours)) and samples without coating (only cleaning).

2.2. Procedure

For each method of application of the BTA inhibitor and for reference, 2 samples were prepared and exposed for 2 years in the open air - during this exposure, the change in the weight of the samples and the change in the color of the surface of the samples were monitored. Subsequently, 2 samples were prepared again in the same way for each method of application of the BTA inhibitor and for reference and together with the original samples (exposed to air for 2 years) were exposed to an aggressive environment - 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 – for 4 months. The change in the weight of the samples and the change in the color of the surface of the samples were monitored again.

2.3. Experimental techniques

The change in the color of the surface of the 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, D65) (Konica Minolta GmbH). 5 measurements were done on each sample. The graphs show the average value of the parameter L*, a*, b* or gloss of both samples, the standard deviations are negligible and are omitted from the graphs.

The change in the weight of the samples during exposure was determined using an analytical balance. The mass increase (r_{mi}) was then calculated according to the equation (1). Standard deviations in the graphs correspond to values of 2 samples.

$$r_{mi} = \frac{m_{ae}-m_{be}}{A\cdot t} \qquad (1)$$

where:

m_{ae}/ m_{be} - mass of the sample after/ before exposition (g), A - surface area of sample (m^2), t - time of exposure (year).

3. RESULTS AND DISCUSSION

3.1. Effect of immersion time in BTA solution

In the monitored period of 2 years in a non-aggressive environment, the change in the surface color of the lead sample treated with the BTA inhibitor corresponds to the natural change in the surface color of the lead (**Figure 1- Figure 3**) regardless of the length of immersion (application) in the BTA solution. The significant factor that contributes the most to the overall color change is the parameter L* (lightness) - **Figure 1**. The parameter a* (green - red axis) - **Figure 2** and the parameter b* (blue - yellow axis) - **Figure 3** have a minor share in the overall color change, for which the deviations from the natural aging of lead in air are slightly higher than for the parameter L*. The decrease in the surface gloss of the BTA-treated samples during exposure in air (**Figure 4**) is identical to the natural aging of lead. The increase in the value of the parameter L* (lightening, **Figure 1**) after exposure of samples to an environment with the presence of acetic acid is a consequence of the formation of white corrosion products of lead. The degree of increase in the value of the parameter L* corresponds to the degree of corrosion resistance.

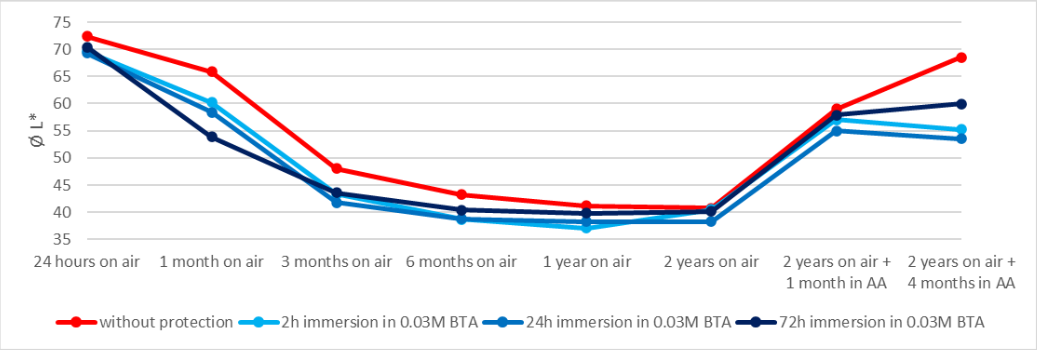

Figure 1 Average value of the parameter L* recorded for BTA-treated and untreated samples during 2 years of exposure to air and subsequent 4 months of exposure in an acetic acid environment

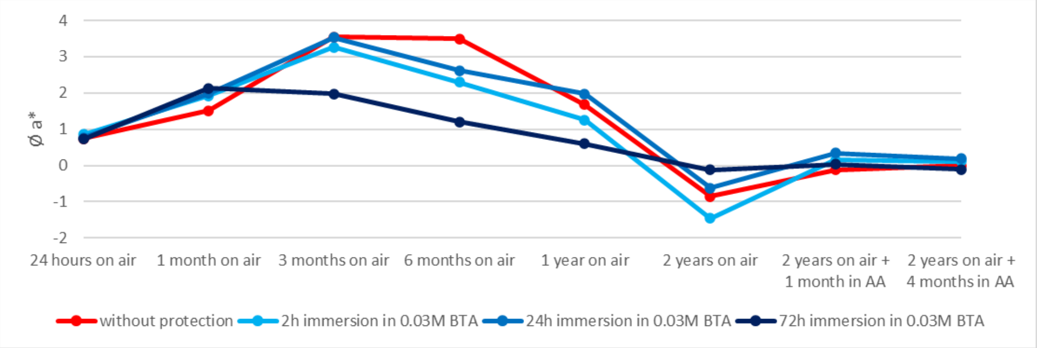

Figure 2 Average value of the parameter a* recorded for BTA-treated and untreated samples during 2 years of exposure to air and subsequent 4 months of exposure in an acetic acid environment

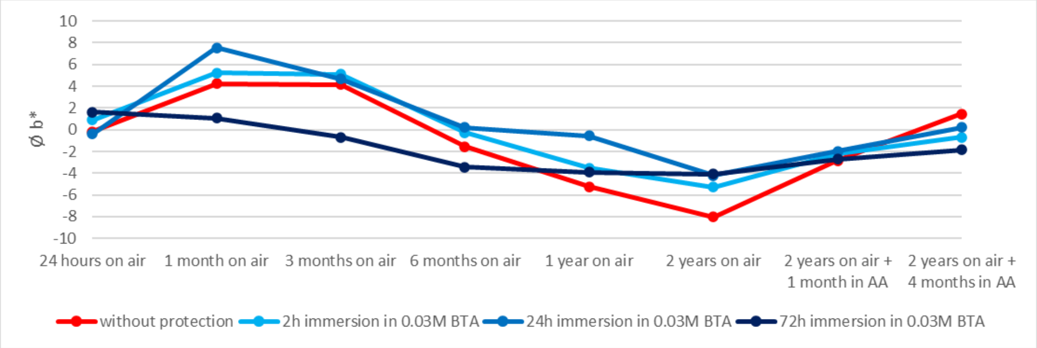

Figure 3 Average value of the parameter b* recorded for BTA-treated and untreated samples during 2 years of exposure to air and subsequent 4 months of exposure in an acetic acid environment

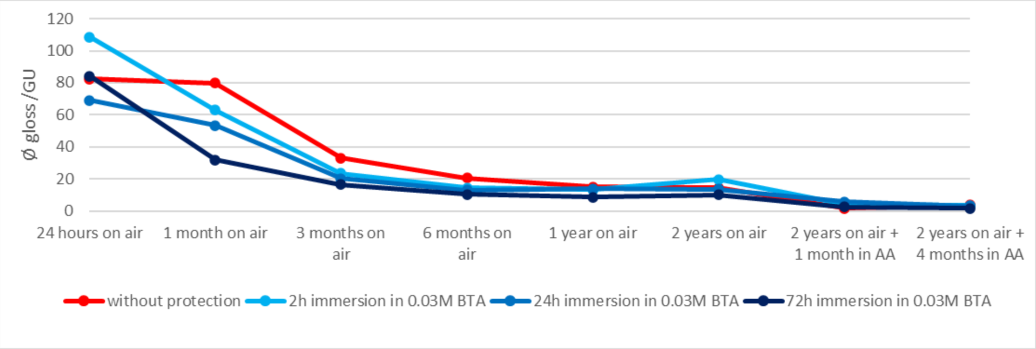

Figure 4 Average value of the gloss (GU = gloss unit) recorded for BTA-treated and untreated samples during 2 years of exposure to air and subsequent 4 months of exposure in an acetic acid environment

From the perspective of lead corrosion resistance, the most suitable application time for the BTA solution is 24 hours (**Figure 5**). When stored in non-aggressive conditions and subsequently exposed to an aggressive atmosphere, the BTA-treated sample initially has a higher corrosion rate than the untreated sample (24 and 72 hours), but subsequently (unlike the untreated sample) the corrosion rate decreases. When lead is immediately exposed to an aggressive atmosphere, the use of BTA shows a significant increase in the corrosion resistance of the underlying lead. The application of BTA for 2 hours is not sufficient to form a long-term effective Pb-BTA layer.

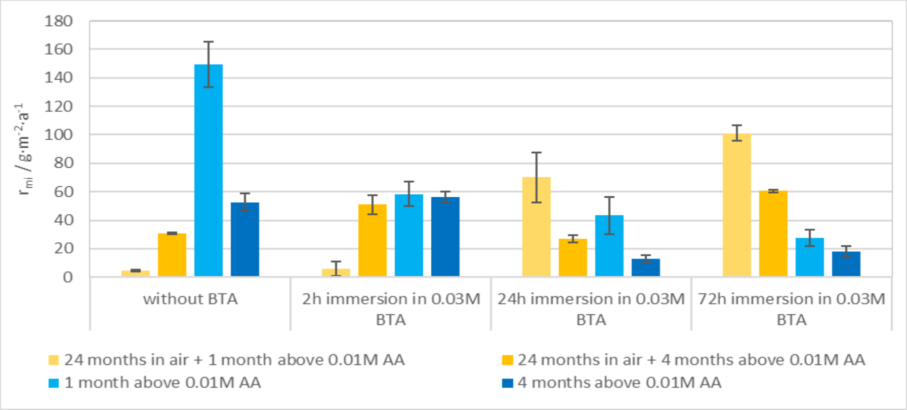

Figure 5 Mass increase values for BTA-treated and untreated samples exposed in an acetic acid environment (4 months) after 2 years of exposure on air or 24 hours after BTA-treatment or cleaning

3.2. Influence of the method of application of BTA in combination with a barrier coating

After the application of barrier coatings (microcrystalline wax, Paraloid B48N), not only is the gloss of the samples significantly affected, but also the color of the surface of the samples changes more significantly compared to the naturally aged sample or the sample treated only with BTA inhibitor (**Figure 6**), in particular the parameters a* and b* are more pronounced, the positive values of which mean a shift in the color of the underlying lead to warmer tones. In the compared samples, the least visually disturbing multi-layer system is the bottom layer of BTA (applied by immersion), then Paraloid B48N and the top layer of microcrystalline wax or the bottom layer of Paraloid B48N with the addition of BTA dissolved in ethanol and the top layer of microcrystalline wax.

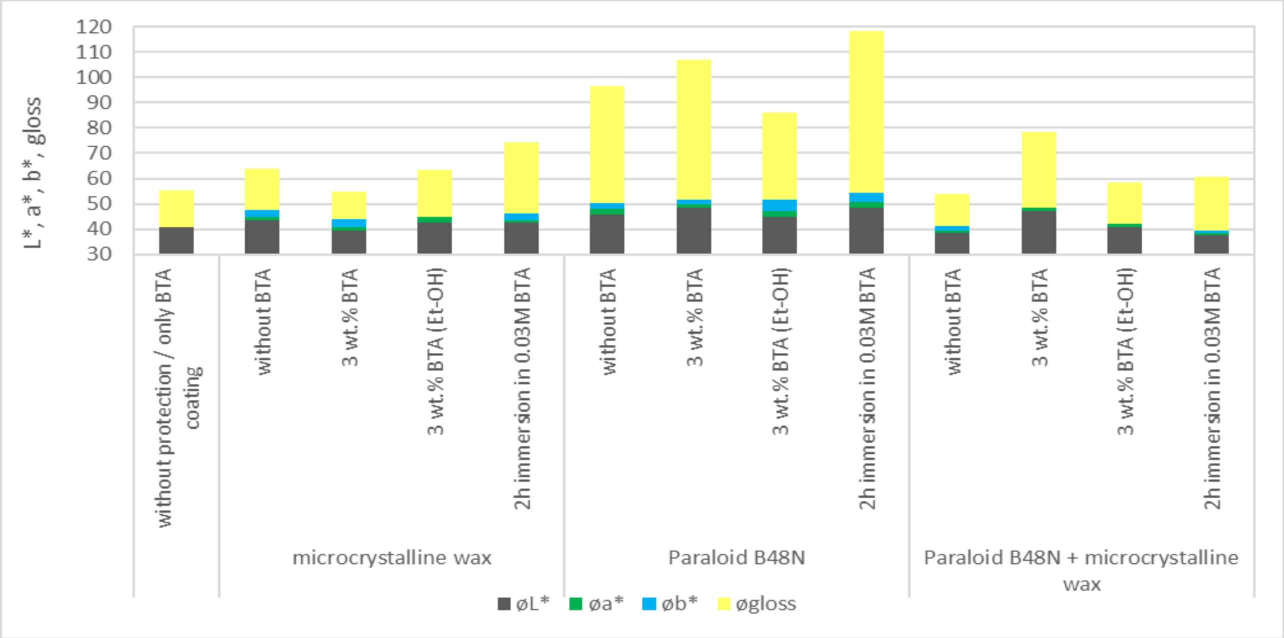

Figure 6 Average value of L*a*b* parameters and the gloss for BTA-treated and untreated samples after 2 years of exposure on air

When comparing the anti-corrosion effectiveness of various methods of application of the BTA inhibitor (**Figure 7**), the addition of BTA in solid form to the barrier coating appears to be dangerous to the underlying lead (in single-layer systems it significantly increases the corrosion rate in an aggressive environment compared to the untreated sample). A multi-layer system of a lower layer of BTA (applied by immersion), then Paraloid B48N and an upper layer of microcrystalline wax appears to be a very effective protective system. A less suitable variant - a lower layer of Paraloid B48N with the addition of BTA dissolved in ethanol and an upper layer of microcrystalline wax.

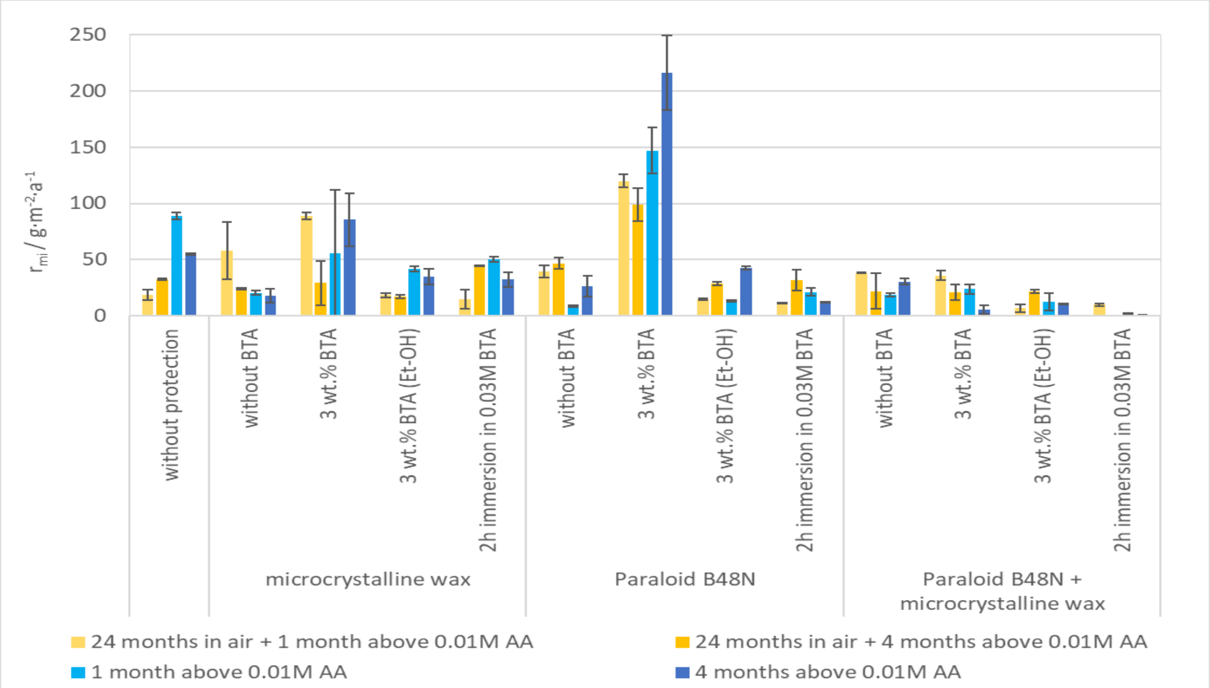

Figure 7 Mass increase values for BTA-treated and untreated samples exposed in an acetic acid environment (4 months) after 2 years of exposure on air or 24 hours after BTA-treatment or cleaning

4. CONCLUSION

Compared to other inhibitors, BTA appears to be the most effective in slowing down lead corrosion and at the same time causes a color change most similar to natural aging of lead (although in both cases it is a very significant darkening of the surface). The length of immersion of the sample in the inhibitor solution mainly affects the useful life of the inhibitor. In combination with a barrier coating, the anti-corrosion effectiveness of the inhibitor is slightly better and longer lasting. A very effective protective system with the least disturbing visual change is a multi-layer system of a bottom layer of BTA (applied by immersion - most conveniently for 24 hours), then Paraloid B48N and a top layer of microcrystalline wax, or a less suitable but still usable variant of a bottom layer of Paraloid B48N with the addition of BTA dissolved in ethanol and a top layer of microcrystalline wax.

REFERENCES

[1] FINŠGAR, M., MILOŠEV, I. Inhibition of copper corrosion by 1,2,3-benzotriazole: A review. Corrosion Science. 2010, vol. 52 (9), pp. 2737-2749. DOI: 10.1016/j.corsci.2010.05.002

[2] MEZZI, A., ANGELINI, E., DE CARO, T.,GRASSINI, S., FARALDI, F., RICCUCCI, C., INGO, G. M. Investigation of the benzotriazole inhibition mechanism of bronze disease. Special Issue:European Applications of Surface and Interface Analysis – ECASIA'11. 2012, vol. 44 (8), pp. 968-971. DOI: 10.1002/sia.4841

[3] WATKINSON, D. Preservation of Metallic Cultural Heritage. Materials Science and Materials Engineering. 2010, vol. 4, pp. 3307-3340. DOI: 10.1016/B978-044452787-5.00172-4

[4] XIANGYU, S., SHENGYU, L., PEI, H., SIYUAN, S., ZHENDA, X., GANG,H., DONGBO, H., MEIGIN, Z. Microscale Corrosion Inhibition Behavior of Four Corrosion Inhibitors (BTA, MBI, MBT, and MBO) on Archeological Silver Artifacts Based on Scanning Electrochemical Cell Microscopy. Analytical Chemistry. 2023, vol. 95 (39), pp. 14686-14694. DOI: 10.1021/acs.analchem.3c02704

[5] DONNICI, M., FERRARI, E., NEFF, D., DANIELE, S. Green protectives on corroded copper artworks: Surface characterization and electrochemical behaviour in simulated acid rain. Journal of Cultural Heritage. 2021, vol. 51, pp. 97-106. DOI: 10.1016/j.culher.2021.08.004

[6] LETARDI, P. Laboratory and field tests on patinas and protective coating systems for outdoor bronze monuments. In: Proceedings of Metal 2004. Canberra: National Museum of Australia, 2004, pp. 379-387.