PROTECTION OF LEAD IN ACETIC ACID CONTAINING AIR BY MEANS OF CORROSION INHIBITORS

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Abstract

Lead bulls are often stored in an inappropriate environment with the presence of organic acids to which lead is sensitive. The aim of this work was to test compounds inhibiting the lead corrosion due to acetic acid vapours. Ideally those that will have better application and surface properties than the widely tested carboxylic acid salts. Benztriazole, cyclohexylamine, thiourea and sodium benzoate were used. The effect of individual inhibitors was tested by the resistometric method on the non-treated surface for 2 hours immersed in the inhibitor solution and on the surface coated with the carbonate-based corrosion products with an immersion time in inhibitor for 2 hours. Resistometric sensors with different surface treatment were exposed to atmosphere above acetic acid solution in concentration 0.001 mol·l^{-1}. To evaluate the appearance and characteristics of the lead surface after treatment of the inhibitor, the samples prepared in the same way were used. It has been found that all of the used substances form a protective layer over the lead. The highest efficiency was achieved by cyclohexylamine. The smallest surface changes occurred in benztriazole.

Keywords: Lead corrosion, inhibition, conservation

1. INTRODUCTION

Lead has been highly employed from ancient times to the present day (various artefacts of everyday life, statues, coins, organ pipes, stained glass) [1-4]. Due to its high corrosion resistance,many of these artefacts are stored in museums and archives [1-8]. Lead is susceptible to corrosion by the presence of volatile organic compounds (VOC) in the atmosphere [2, 3, 9-14]. This kind of polluted atmosphere is typical for museum and archive storage cabinets. Preservation of the lead displayed in atmosphere polluted with VOC is based on the use of protective coatings. Today's hot topic is application of coatings with corrosion inhibitors [1, 3, 13-16]. In this paper, benztriazole, cyclohexylamine, thiourea and sodium benzoate, which are discussed in literature, will be examined.

2. EXPERIMENTAL PART

2.1. Chemicals

Benztriazole, cyclohexylamine, thiourea and sodium benzoate were used as corrosion inhibitors. Benztriazole solution in concentration 0.03 mol·l^{-1} was prepared by dissolving the 1,2,3-benztriazole (0.89 g, 99 %, Penta, CZE) in 250 ml of ethanol. Cyclohexylamine solution in concentration 0.03 mol·l^{-1} was prepared by diluting the concentrated cyclohexylamine solution (7.5 ml, Sigma-Aldrich, USA) with distilled water. Thiourea solution in concentration 0.05 mol·l^{-1} was prepared by dissolving the thiourea (0.95 g, 99 %, Penta, CZE) in 250 ml of distilled water. Sodium benzoate solution in concentration 1.4 mol·l^{-1} was prepared by dissolving the sodium benzoate (50 g, 99.8 %, Chemapol, CZE) in 250 ml of distilled water.

Corrosive atmosphere for resistometric measurement was provided by acetic acid solution in 0.001 mol·l^{-1} concentration.

2.2. Lead resistometric sensors and lead samples surface treatment

Lead resistometric sensors with 25 μm thickness lead foil (97 % Pb, 1.5 % Sn and 1.5 % Sb, Goodfellow Company, UK) were used in this work. Different treatment of sensor's surface was applied:

- the non-treated surface was obtained with grinding of the surface with abrasive wadding (3M Scotch-Brite CF-MF), subsequent rinsing with ethanol and then air drying
- the corroded surface was obtained by immersing the non-treated lead samples into 1 mol·l^{-1} Na_2CO_3 solution for 24 hours, subsequent rinsing by distilled water, ethanol and air drying
- the coated surface was obtained by immersing the non-treated or corroded lead samples into the one from different corrosion inhibitor's solutions (benztriazole, cyclohexylamine, thiourea or sodium benzoate) for 2 hours, subsequent rinsing by distilled water, ethanol and then air drying.

Lead samples (Pb 99.9 %) in dimensions 3x3x0.3 cm were used in this work. The lead sample's surface had been grinded with SiC grinding paper up to grain size of P800 before the same surface treatment as for sensor's surface was applied.

2.3. Resistometric experiments

The resistometric method is based on the electric resistance measurement. The corrosion rate (r_{corr}) can be calculated from the decrease of the sensor's lead foil thickness (Δd) caused by corrosion with following equations (1) and (2) [17-18]:

$$\Delta d = d_0 \cdot \left(1 - \frac{R_R}{R_S} \cdot \frac{R_{S0}}{R_{R0}}\right) \qquad (1)$$

$$r_{corr} = \frac{\Delta d}{t} \qquad (2)$$

where:

d_0 - initial thickness of the sensor's lead foil (μm)

R_R - current electric resistance of the reference part of the sensor (MΩ)

R_S - current electric resistance of the sensing part of the sensor (MΩ)

R_{R0} - initial electric resistance of the reference part of the sensor (MΩ)

R_{S0} - initial electric resistance of the sensing part of the sensor (MΩ)

t - time (year)

The resistometric measurements were performed in closed box with the volume of 10 litres in aerated conditions and at laboratory temperature. In the box there were lead resistometric sensors and lead samples with different surface treatment, ventilator and a beaker with 100 millilitres of acetic acid solution in concentration 0.001 mol·l^{-1}. Resistometric sensors were connected to ACD-03 (MetriCorr, DK). The resistometric measurements were started 2 hours before different sensor's surface treatment and finished after 3 days of sensors exposition in atmosphere above acetic acid solution in concentration 0.001 mol·l^{-1}.

2.4. Coating characterization

The lead samples with different surface treatment were used for the inhibitor coating characterization. Samples surface morphology was observed by scanning electron microscope (SEM) TESCAN VEGA 3. The observation of the hydrophobic properties of the samples surface was carried out by the contact angles measurement by goniometer SEESystem (Advex Instruments, s.r.o.).

3. RESULTS AND DISCUSSION

Figure 1 and **Figure 2** report of the long-time resistometric measurement of lead with different surface treatment (**Figure 1** non-treated surface with or without inhibitor coating, **Figure 2** corroded surface with or without inhibitor coating) in atmosphere above acetic acid solution in concentration 0.001 mol·l^{-1}. The sensors without inhibitor coating began to corrode rapidly as soon as they get in contact with acetic acid atmosphere. The sensors with different inhibitor coating were very resistant to the acetic acid atmosphere.

Table 1 and **Table 2** show values of corrosion rate of the lead with different surface treatment during its immersion in corrosion inhibitor solution and 65 hours in atmosphere above acetic acid solution in concentration 0.001 mol·l^{-1}. The increase of lead corrosion rate is observed during the immersion of lead in thiourea or sodium benzoate solution.

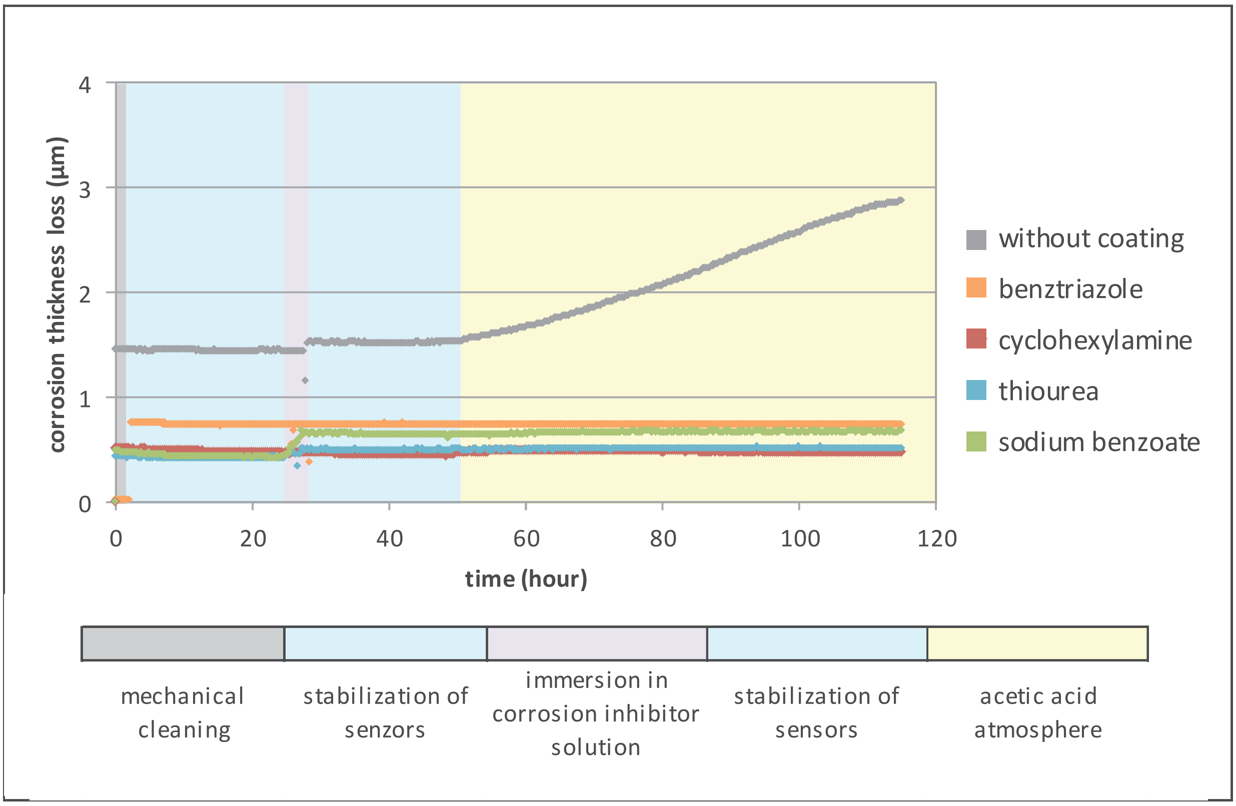

Figure 1 Resistometric measurement of the lead with coated non-treated surface in atmosphere above acetic acid solution in concentration 0.001 mol·l^{-1}, effect of inhibitor coatings is represented as corrosion thickness loss (Δd) in time

Table 1 The values of corrosion rate (r_{corr}) of the lead with non-treated surface during different parts of resistometric measurement expressed in μm per year

r_{corr} (μm·year^{-1})	**without coating**	**benztriazole**	**cyclohexylamine**	**thiourea**	**sodium benzoate**
immersion in corrosion inhibitor solution	-	8	-6	285	590
65 hours in acetic acid atmosphere	194	1	0	3	4

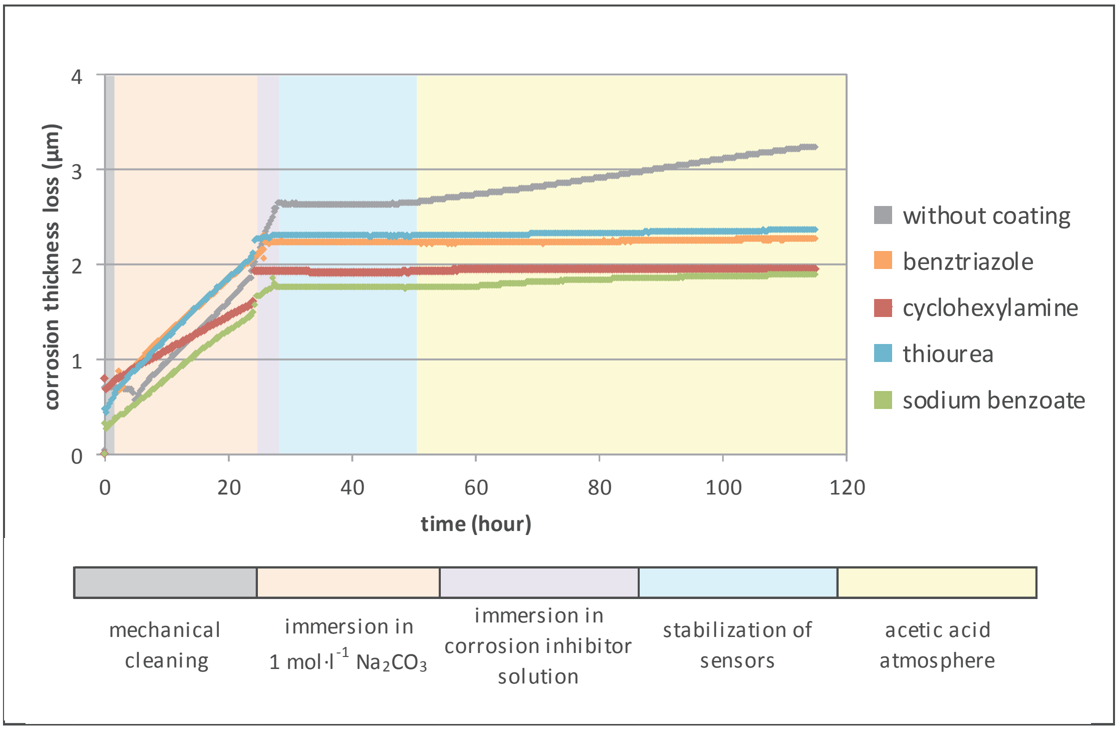

Figure 2 Resistometric measurement of the lead with coated corroded surface in atmosphere above acetic acid solution in concentration 0.001 mol·l^{-1}, effect of inhibitor coatings is represented as corrosion thickness loss (Δd) in time

Table 2 The values of corrosion rate (r_{corr}) of the lead with corroded surface during different parts of resistometric measurement expressed in μm per year

r_{corr} (μm·year^{-1})	without coating	benztriazole	cyclohexylamine	thiourea	sodium benzoate
immersion in corrosion inhibitor solution	-	5	-15	294	725
65 hours in acetic acid atmosphere	82	6	9	3	20

According to **Table 1** and **Table 2** inhibition efficiency for all coated sensors is higher for sensors with non-treated surface than for sensors with corroded surface. For non-treated surface, corrosion rate of lead was very low for all used corrosion inhibitors. For corroded lead surface, thiourea and benztriazole were recognized as the most effective corrosion inhibitors. Because of the high corrosion rate of lead during the immersion in solution of thiourea (**Table 2**), the benztriazole is better for use as a corrosion inhibitor for corroded lead.

The highest hydrophobic character (**Table 3**) was obtained by benztriazole or cyclohexylamine for both the surface states (non-treated or corroded).

Table 3 The values of contact angles (ɣ) of the inhibitor coatings on the lead with non-treated and corroded surface after 2 hours of immersion in corrosion inhibitor solution expressed in °

ɣ (°)	without coating	benztriazole	cyclohexylamine	thiourea	sodium benzoate
non-treated surface	85	131	128	89	117
corroded surface	113	134	129	122	92

Another important aspect is the change of the sample surface colour after the immersion of the sample in corrosion inhibitor solution. All coated samples provided change of the surface colour, however, the smallest colour change occurred on the sample treated in the benztriazole solution.

Detailed observation by SEM (**Figure 3 A-D**) revealed that organic based coatings form on the surface flake-shaped crystals, more or less tangled. The surface of the sample treated in benztriazole or cyclohexylamine was not so well coated with flake-shaped crystals as the surface of the others samples.

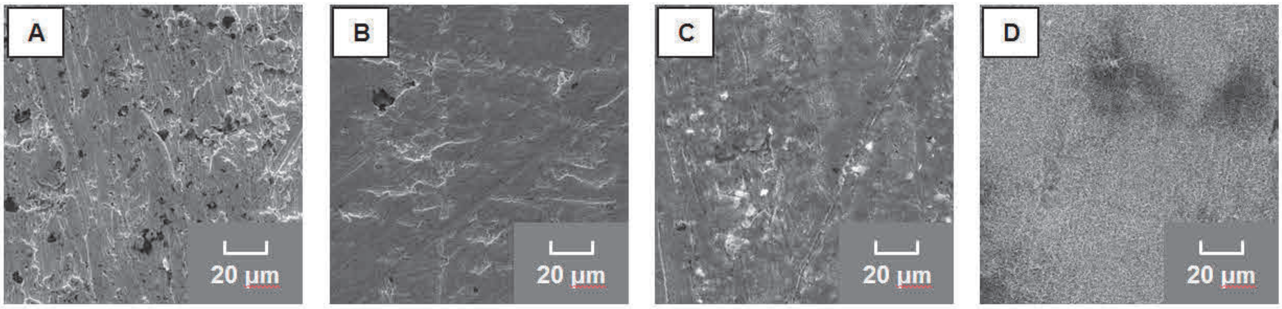

Figure 3 SEM picture of coated lead samples (2 hours of immersion in inhibitor solution) with non-treatedsurface, benztriazole (**A**), cyclohexylamine (**B**), thiourea (**C**) and sodium benzoate (**D**)

4. CONCLUSION

Benztriazole, cyclohexylamine and thiourea provided an efficient protection for lead with clean or corroded surface in atmosphere polluted by volatile organic compounds. The minor surface appearance changes occurred in the case of the treatment with benztriazole. On the other hand, benztriazole and cyclohexylamine are now regarded as a possible health or environmental risk. From corrosion inhibition efficiency and health risk point of view, thiourea is the most promising corrosion inhibitor for lead. However, high corrosion rate during the immersion of lead in thiourea solution is the limitation of its applicability.

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