Inhibition efficiency of sodium salts of carboxylic acids on corrosion of lead in archive environment

Inhibiční účinek sodných solí karboxylových kyselin na korozi olova v archivním prostředí

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Lead in archive environment suffers from severe corrosion attack caused by the organic acids' vapours usually presented in such an environment. One of possible ways of corrosion protection of lead is its surface treatment by solutions of sodium salts of monocarboxylic acids (general formula $CH_3(CH_2)_{n-2}COONa$, noted NaC_n, n = 10, 11, 12). The principle of this corrosion protection is a creation of conversion coating on the lead's surface, which decreases corrosion rate of lead in the atmospheric environment polluted by organic acids' vapour. Our research aims at the selection of a suitable protection system that would be applicable to conservation of historical lead in archives and museums. This paper evaluates the corrosion behaviour of treated lead based on the values of polarisation resistance and shape of potentiodynamic curves in simulated corrosive environment (0.01 mol l^{-1} solution of acetic acid). The lead samples with different state of surface (pure, corroded and electrochemically cleaned) were treated with sodium salts of monocarboxylic acids NaC_n (n = 10, 11, 12) having concentration of 0.01 and 0.05 mol l^{-1}. In simulated corrosive atmosphere (above 0.001 mol l^{-1} acetic acid solution vapours), corrosion rate was measured by means of electrical resistance technique. The inhibition efficiency of monocarboxylic acids is dependent on their carbon chain length and their concentration. The greatest inhibiting efficiency in corrosive atmospheres and for all lead samples was observed for the sodium salt of dodecanoic acid having concentration of 0.05 mol l^{-1}. Artificially created corrosion products and salt coatings were analysed by X-ray diffraction analysis and their surface morphology was observed by scanning electron microscopy. A protective salt coatings are mainly composed of metallic soaps in dimer form.

V prostředí archivních depozitářů lze pozorovat významné korozní napadení olova vlivem par organických kyselin, jejichž přítomnost je v tomto prostředí typická. Jedním z možných způsobů ochrany olova proti tomuto typu korozního napadení je jeho povrchová úprava roztoky sodných solí monokarboxylových kyselin (obecný vzorec $CH_3(CH_2)_{n-2}COONa$, zkráceně NaC_n, n = 10, 11, 12). Principem této protikorozní ochrany je vytvoření konverzního povlaku na povrchu olova, jež chrání podkladové olovo v atmosférickém prostředí znečištěném parami organických kyselin. Náš výzkum je zaměřen na nalezení vhodného ochranného prostředku pro historické olovo uložené v archivech a muzeích. Tento článek hodnotí korozní chování olova ošetřeného roztoky solí monokarboxylových kyselin na základě hodnot polarizačního odporu a tvaru potenciodynamických křivek v simulovaném korozním prostředí (v roztoku 0,01 mol l^{-1} kyseliny octové). Vzorky olova s různým stavem povrchu (čisté, zkorodované a elektrochemicky očištěné) byly ošetřeny roztoky sodných solí monokarboxylových kyselin NaC_n (n = 10, 11, 12) o koncentraci 0,01 a 0,05 mol l^{-1}. V simulované korozní atmosféře (nad parami 0,001 mol l^{-1} roztoku kyseliny octové) byla korozní rychlost olova měřena pomocí rezistometrických čidel. Inhibiční účinek monokarboxylových kyselin závisí na délce jejich uhlíkového řetězce a jejich koncentraci. Největší inhibiční účinek v simulované korozní atmosféře byl pozorován u vzorků ošetřených roztokem sodné soli kyseliny dodekanové o koncentraci 0,05 mol l^{-1}, bez ohledu na stav povrchu vzorku. Povrch vzorků před a po ošetření v roztocích NaC_n byl analyzován rentgenovou difrakční analýzou a jejich povrchová morfologie byla pozorována pomocí skenovací elektronové mikroskopie. Olovnaté soli monokarboxylových kyselin se na povrchu olova vyskytují v dimerní formě.

INTRODUCTION

Lead and lead alloyed objects are an important part of European cultural heritage. There are plenty of those artefacts in museums and archives, because lead was used widely in the past, not only for special issues (organ pipes, stained glass), but also in everyday life (dishes, coins) [1-4]. One of the reasons of lead popularity is its relatively good environmental stability and malleability [1-8]. Depending on the environmental conditions, lead objects are covered with corrosion layers constituted of various corrosion products [2, 3, 9-12]. Corrosion layers are usually thin, stable and protective, therefore the corrosion rate of the underlying metal is very small. These layers usually constitute of oxides, carbonates,

chlorides, sulphides or sulphates species [2, 3, 9-13]. Another corrosion layers constitute of carbonate compounds such as cerussite ($PbCO_3$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) or plumbonacrite ($Pb_{10}(CO_3)_6O(OH)_6$) without protective effect and responsible of the "white rust" [1, 8, 10-12, 14, 15].

Major danger for lead in terms of corrosion are volatile organic compounds (especially formic and acetic acids) which are formed during the degradation process of another organic materials stored in the depository (another object made of wood or plastic, glues, colours, packing materials based on paper or plastic, etc.) and emitted into the archive environment [3, 16, 17]. The degradation processes of wood origins in hydrolysis of acetyl groups of hemicellulose in

the wood, fission of hemicellulose molecules causes formation of a range of low molecular weight volatile organic compounds (aldehydes, ketones, carboxylic acids – formic, propanoic, tannic and acetic) [18-21]. The concentrations of emitted organic acids, especially of acetic acid inside museum storage cabinets are at levels less than 500 ppb [22]. The corrosion agents for wood are high relative humidity, temperature, UV rays or alkaline/acidic chemical compounds [18-20]. After a lengthy period of exposure in organic acids environment, the lead surface gets covered with soluble white voluminous corrosion products (white rust) and the corrosion rate of lead rapidly increase [2, 3, 23, 26]. Acetic acid vapours accelerate atmospheric corrosion of lead even at low concentration (0.1-1 ppm), the mass gain is a linear function of time and acid concentration [27]. The mechanism of lead active corrosion process in acetic acid is still unclear. One of the possible theory [3, 25, 26] is graphically summarized on the Figure 1.

According to this theory, in atmospheric conditions, a thin passive underlayer of PbO is formed on the lead surface and a thick corrosion outer layer is constituted of lead carbonates. The process starts when the acetic acid is present in aqueous surface film on the passive doublelayer, preferentially at cracks or defects in the layer (Fig. 1a). The passive doublelayer starts with rapid transformation into soluble lead acetate $Pb(CH_3COO)_2$ or lead acetate oxide hydrate $Pb_3(CH_3COO)_6PbO \cdot H_2O$ (Fig. 1b). Acetic acid and acetate compounds penetrate in cracks and PbO underlayer is dissolved and the lead substrate is then attacked (Fig. 1c). The oxidation of lead substrate causes that new layer of lead carbonate is formed. Because of new voluminous layer forming the oldest corrosion layer is peeling out (Fig. 1d). The acetic
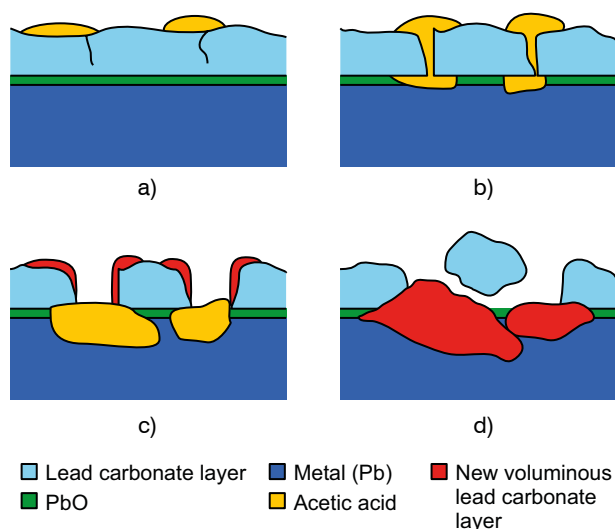
acid is released back to corrosion process during the transformation of lead acetates to lead carbonates and the cyclic corrosion is initiated and leads to a porous and lamellar corrosion layer formation. The carbon dioxide cannot be neglected, this acidic gas dissolves in aqueous surface film, too and then reacts with lead (II) ions to form another lead carbonates [3, 25, 26]. A big problem (especially for coins and lead seals) is that a part of surface details may get lost during the cyclic corrosion process.

There are many possibilities how to protect lead based artefacts against corrosion, e.g. elimination of the corrosive substances in the nearby environment, removal the corrosion products from the lead surface (because the acetic acid released during corrosion products transformation causes a new corrosion process) or today's hot topic – application of corrosion inhibitors [1, 3, 25, 28-31]. Sodium benzoate, cyclohexylamine carbonate and/or cyclohexylamine nitrate are usually used as corrosion inhibitors for lead in atmospheric conditions. Whereas thiourea, phosphates, chromates, amines, benzotriazole or hydrazines are usually used as corrosion inhibitors for lead in organic acids condition [32-37]. In this paper, sodium salts of carboxylic acids, which are in literature discussed periodically, will be examined.

Sodium salts of carboxylic acids are not corrosion inhibitors as the corrosion inhibitors definition says. They form a barrier, conversion hydrophobic coating, on the lead surface. According to another author [34, 37, 43] sodium salts of carboxylic acids can protect lead against atmospheric corrosion, corrosion in aqueous condition and in the atmosphere containing organic compounds. Those compounds are natural, non-toxic and cheap. The effect of monocarboxylic acid salts is that they form stable lead carboxylate lamellar layer on the lead surface (metallic soap) [38, 39].

The lamellar layer has a specific structure, the carboxylate chains are bounded with lead atoms across an oxygen atom. Every lead atom in the structure is surrounded by six oxygen atoms, arranged in the octahedral pattern [38, 40, 41]. Preliminary step of lead carboxylate formation is lead oxidation by an atmospheric oxygen dissolved in aqueous solution ($Pb + \frac{1}{2}O_2 + H_2O \leftrightarrow Pb^{2+} + 2OH^-$ [1, 3, 43]), after this carboxylate anions $CH_3(CH_2)_{n-2}COO^-$ (noted) react with lead(II) ions resulting in soap formation ($Pb^{2+} + 2 \leftrightarrow Pb(C_n)_2$ [44]) [38, 39, 41, 42]. The lead soap formation should be dual [43]:

- the formation of lead soap take place into the electrolyte, lead soap is adsorbed on the lead surface as a continually growing lamellar layer [43].

- carboxylate anions are driven to lead surface where they react with lead(II) ions and form the lead soap, the lamellar layer then grows because of the carboxylate anions diffusion [42, 43].

a)   b)

c)   d)

☐ Lead carbonate layer ☐ Metal (Pb) ☐ New voluminous
☐ PbO ☐ Acetic acid   lead carbonate
                          layer

Fig. 1. Active corrosion process of lead in acetic acid containing atmosphere [3, 25, 26]
Obr. 1. Schéma procesu cyklické koroze olova v prostředí obsahujícím kyselinu octovou [3, 25, 26]

The lead soaps are surfactants, the carbon chain is a hydrophobic part of $Pb(C_n)_2$ molecules [1, 42, 44]. After the process of coating deposition is carbon chain oriented out-side of lead surface, hydrophobic character of lead soap is main parameter [38, 43]. It is obvious that longest carbon chain in molecule induces their highest hydrophobic effect. The lead surface gets wet with aqueous solution (atmospheric corrosion) less, the passive layer dissolution rate decreases [38]. Another presumption is that lead soap on the lead surface can locally neutralize acetic acid and/or carbon dioxide ($Pb(C_{10})_2 + 2CO_2 + 2H_2O \leftrightarrow 2HCO_3^- + Pb^{2+} + 2HC_{10}$) [34]. The inhibition efficiency of carboxylic acids salts grows depending on their carbon chain length and their concentration [38, 42, 43]. Applicability is limited with limited solubility in water of longest sodium carboxylates.

This paper investigates inhibition efficiency of sodium salts of carboxylic acids for lead in non-aggressive (simulated atmospheric corrosion) and aggressive acetic acid containing solutions, by using electrochemical techniques. The investigation has been focused on the effect of carbon chain length and concentration of those salts.

EXPERIMENTAL

Specimens and their surface treatment

The lead samples (99.9 % Pb) with different surface states (non-treated, corroded and electrochemically cleaned surface) were used in this work. The non-treated lead surface was obtained by water grinding of the sample's surface with SiC grinding paper up to grain size of P800, subsequent rinsing with distilled water, ethanol and then drying by a hair dryer. The corroded surface was obtained by immersing of the non-treated lead samples into 1 mol l⁻¹ Na_2CO_3 solution for 24 hours, subsequent rinsing with distilled water, ethanol and drying by a hair dryer. The electrochemically cleaned surface was obtained by electrochemical cleaning of the corroded samples. The electrochemical cleaning of the samples was performed for the total time of 2 hours in three-electrode corrosion cell (working electrode: corroded lead sample, counter electrode: Pt rib, reference electrode: saturated calomel electrode - SCE) connected to computer-controlled potentiostat PC4 (Gamry Instruments, Inc.) maintaining constant potential of -1.2 V/SCE. The 0.5 mol l⁻¹ H_2SO_4 solution was used as an electrolyte. After electrochemical cleaning, the samples were left for 24 hours on free air.

The samples with different states of surface were treated with solutions of monocarboxylic acid salts ($CH_3(CH_2)_{n-2}COOH + CH_3(CH_2)_{n-2}COONa$, $n = 10, 11, 12$) noted as NaC_n ($n = 10, 11, 12$) in order to obtain the salt coating on the samples' surfaces. The procedure of salt coating preparation was obtained from literature [34, 38] and stands as follows: the samples were immersed for 24 hours in 0.01 mol l⁻¹ and 0.05 mol l⁻¹ NaC_n ($n = 10, 11, 12$) solutions. The NaC_n solutions were prepared by neutralisation of the corresponding monocarboxylic acid with NaOH. The proportion of the monocalboxylic acid and NaOH was nearly equimolar (100 parts monocalboxylic acid per 98 parts of NaOH of equimolar amount corresponding to the amount of monocalboxylic acid). The solutions were transparent, without the presence of non-dissolved particles, having pH of 6-9.

In total 21 different types of samples were tested in this work. The bare lead samples with different state of surface (non-treated, corroded and electrochemically cleaned) were used as reference samples.

Environment

All measurements in this work were performed in presence of acetic acid which simulates the aggressive environment of the archives.

The measurement of polarisation resistance and potentiodynamic curves was carried out in the corrosive solution of 0.01 mol l⁻¹ acetic acid neutralised with 0.25 mol l⁻¹ NaOH to pH 7. Thus the resulting composition of the testing corrosive solution is dissociated as well as non-dissociated acetic acid and dissociated sodium acetate ($CH_3COOH + CH_3COONa$). .

The resistometry was performed in a circulated model atmosphere above the 0.001 mol l⁻¹ acetic acid (100 ml of 0.001 mol l⁻¹ acetic acid were placed in 10 litres closed box).

Methods

Electrochemical measurement in the corrosive solution was performed in three-electrode cell (working electrode: lead sample, counter electrode: Pt rib, reference electrode: saturated calomel electrode) connected to the computer-controlled potentiostat PC4 (Gamry Instruments, Inc.). The measurement of the polarisation resistance (R_p) was performed after 2 hours with a scan rate of 0.166 mV s⁻¹ within a range of 40 mV ($E_{corr} \pm 20$ mV). As soon as the polarisation resistance measurement finished the measurement of the potentiodynamic curve with a scan rate of 1 mV s⁻¹ in the range from -50 mV to +800 mV versus E_{corr} began.

The inhibition efficiency (θ) of the salt coatings on the lead surface was determined according to the following formula:

$$\Theta = \left[1 - \frac{R_{p_{\text{surface without salt coating}}}}{R_{p_{\text{surface with salt coating}}}} \right] \cdot 100$$

During the resistometric measurement in the corrosion atmosphere the lead sensors (lead foil Goodfellow Company with thickness (d_0) of 25 μm) were placed in 10 litres closed box with circulated atmosphere. The lead sensors were connected to ACD-03 (MetriCorr). The resistometric method is based on the electric resistance (ER) measurement from which the corrosion rate (r_{corr}) can be calculated from the decrease of sample thickness caused by corrosion (Δd). Following formulas can be employed for the calculation [45-47]:

$$\Delta d = d_0 \cdot \left[1 - \frac{R_{\text{reference part of sensor}}}{R_{\text{sensing part of sensor}}} \cdot \frac{R_{\text{sensing part of sensor (initial)}}}{R_{\text{reference part of sensor (initial)}}} \right],$$

$$r_{\text{corr}} = \frac{\Delta d}{t}$$

The resistometric measurements have following procedures depending on the state of surface of the lead sensors:

- The lead sensor with non-treated surface: 1. Stabilisation for the period of 24 hours, 2. Mechanical cleaning of the sensor's surface with grinding wool 3M Scotch Brite, subsequent rinsing with distilled water, ethanol and drying by a hair dryer, 3. The sensor is placed in a model atmosphere above 0.001 mol l⁻¹ acetic acid solution after period of 48 hours.

- The lead sensor with corroded surface: 1. Stabilisation for the period of 24 hours, 2. Mechanical cleaning of the sensor's surface with grinding wool 3M Scotch Brite, subsequent placing into 1 mol l⁻¹ Na₂CO₃ solution for 24 hours, then rinsing with distilled water, ethanol and drying by a hair dryer, 3. The sensor is placed in a model atmosphere above 0.001 mol l⁻¹ acetic acid solution after period of 24 hours.

- The lead sensor with corroded surface treated by 0.05 mol l⁻¹ NaC₁₀: 1. Stabilisation for the period of 24 hours, 2. Mechanical cleaning of the sensor's surface with grinding wool 3M Scotch Brite, subsequent placing into 1 mol l⁻¹ Na₂CO₃ solution for 24 hours, then placing into 0.05 mol l⁻¹ NaC₁₀ solution for 24 hours, then rinsing with distilled water, ethanol and drying by a hair dryer, 3. The sensor is placed in a model atmosphere above 0.001 mol l⁻¹ acetic acid solution directly.

All the experiments were performed in aerated conditions and at laboratory temperature.

The changes of samples surface morphology after NaCₙ solutions treatment were observed by scanning electron microscope (SEM) TESCAN VEGA 3. The identification of the phase composition of the salt surface coatings was performed by XRD analysis by X'Pert PRO (PANanalytical B.V.). 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.).

RESULTS AND DISCUSSION

Corrosion tests

Polarisation resistance and potentiodynamic curves in simulated archival environment

A polarisation resistance (R_p) of all lead samples was measured in corrosive solution of 0.01 mol l⁻¹ CH₃COOH + CH₃COONa after two hours. The final value of R_p shown in Figure 2 for each type of lead sample is an average of the R_p values measured for two replicate measurements after two hours of exposure. The maximum and minimum values of the error bars in Figure 2 correspond to values of R_p measured for two identical samples. The lead samples with different state of surface without soap coat on their surface was taken as reference samples.

The inhibition efficiency of the soap coat on the samples with different state of surface was evaluated (Fig. 3).

It can be seen in Figure 2 that the lowest values of R_p are shown by the reference lead samples (samples without soap coat and with different surface state – non-treated surface 1 Ω m², corroded surface 1 Ω m² and electrochemically cleaned surface 3 Ω m²). The values of R_p measured for the samples with soap coat considerably increase by 1-4 orders of magnitude compared to the samples without soap coat. Generally, the R_p
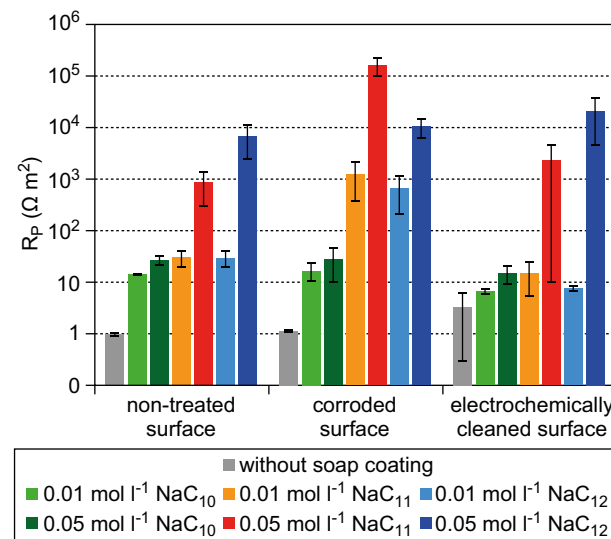

Fig. 2. The average values of polarization resistance (R_p) of the lead samples with different state of surface and with or without soap coat measured in 0.01 mol l⁻¹ corrosion solution. The maximum and minimum values of the error bars correspond to values of R_p measured for two identical samples.

Obr. 2. Průměrné hodnoty polarizačního odporu (R_p) u vzorků olova s různým stavem povrchu a s/bez ošetření v roztocích NaCn naměřené v neutralizovaném roztoku kyseliny octové o koncentraci 0,01 mol l⁻¹. Maximální a minimální hodnoty chybových úseček odpovídají hodnotám R_p naměřeným pro dva identické vzorky

values of coated samples increase with number of carbons in NaC$_n$ molecular chain and with concentration of NaC$_n$ solution used. The 0.05 mol l^{-1} NaC$_{11}$ and NaC$_{12}$ exhibit the R$_p$ values by 1-2 orders of magnitude higher compared to 0.01 mol l^{-1} NaC$_{11}$ and NaC$_{12}$.

The R$_p$ values of the samples with non-treated surface and electrochemically cleaned surface (with/ without soap coat) are very close for the same type of NaC$_n$. When comparing the samples with different states of surface using the same type of NaC$_n$ solution the higher values of R$_p$ are achieved for corroded surface than for the non-treated or electrochemically cleaned surface.

Figures 2 and 3 shows that the soap coat is able to protect the lead with different state of surface very well. The unsatisfactory soap coat is indicated by inhibition efficiency lower than 99 %. According the Figure 3 the inhibition efficiency for all NaC$_n$ corresponds with the values of R$_p$ and the inhibition efficiency increases with the number of atoms in the NaC$_n$ molecular chain and with the concentration of NaC$_n$. The inhibition efficiency of 0.05 mol l^{-1} NaC$_{11}$ and NaC$_{12}$ is 99.9 % for all samples with different surface treatment. It means that the corrosion rate of the samples treated in 0.05 mol l^{-1} NaC$_{11}$ and NaC$_{12}$ solution is by 3 orders of magnitude lower than corrosion rate of the samples without soap coat and by 2-3 orders of magnitude lower than corrosion rate of other soap coated samples with inhibition efficiency less than 99 %. In the case of the samples with corroded surface the inhibition efficiency is higher compared to the samples with non-treated or electrochemically cleaned surface (for the samples with
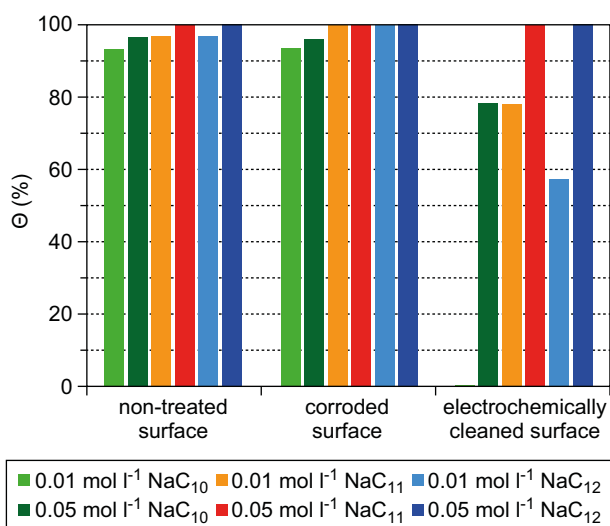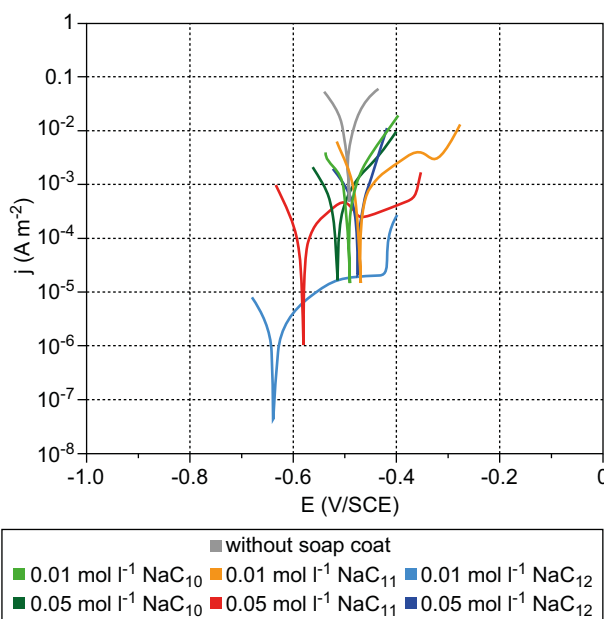

Fig. 4. Potentiodynamic curves of the samples with non-treated surface with and without soap coat measured in 0.01 mol l^{-1} corrosive solution
Obr. 4. Potenciodynamické křivky olověných vzorků s čistým povrchem s/bez ošetření v roztocích NaCn naměřené v neutralizovaném roztoku kyseliny octové o koncentraci 0,01 mol l^{-1}

Fig. 3. Inhibition efficiency (Θ) of NaCn coatings on the samples with different state of surface in 0.01 mol l^{-1} corrosive solution
Obr. 3. Účinnost (Θ) ošetření vzorků olova s různým stavem povrchu pomocí NaCn roztoků v neutralizovaném roztoku kyseliny octové o koncentraci 0,01 mol l^{-1}
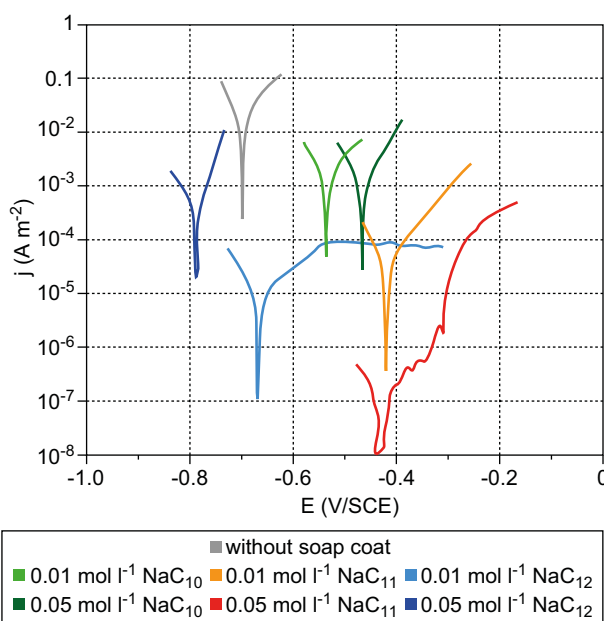

Fig. 5. Potentiodynamic curves of the samples with corroded surface with and without soap coat measured in 0.01 mol l^{-1} corrosive solutionn
Obr. 5. Potenciodynamické křivky olověných vzorků s korodovaným povrchem s/bez ošetření v roztocích NaCn naměřené v neutralizovaném roztoku kyseliny octové o koncentraci 0,01 mol l^{-1}

non-treated and electrochemically cleaned surface is the inhibition efficiency higher than 99.9 % only for 0.05 mol l^{-1} NaC$_{11}$ and 0.05 mol l^{-1} NaC$_{12}$; for the samples with corroded surface is the inhibition efficiency higher than 99.9 % for NaC$_{11}$ and NaC$_{12}$, both in concentration 0.01 mol l^{-1} and 0.05 mol l^{-1}). The higher inhibition efficiency of soap coated samples with corroded surface is due to the synergistic effect of protective layer of corrosion products and soap hydrophobic barrier.

All potentiodynamic curves (Figs. 4-6) were measured in corrosive solution after 2 hours measurement of polarisation resistance. Such measured curves correspond to trends shown in Figure 2; the NaC$_n$ coatings decrease of the corrosion current density for non-treated lead surface (Fig. 4) and corroded lead surface (Fig. 5). For electrochemically cleaned lead surface (Fig. 6) the corrosion current density decreases only in the cases NaC$_{11}$ and NaC$_{12}$ both in higher concentration 0.05 mol l^{-1}. The corrosion potential shifts were in Fig. 4-6 contradictory, we cannot say that the presence of NaC$_n$ coating affected more cathodic or anodic reaction.
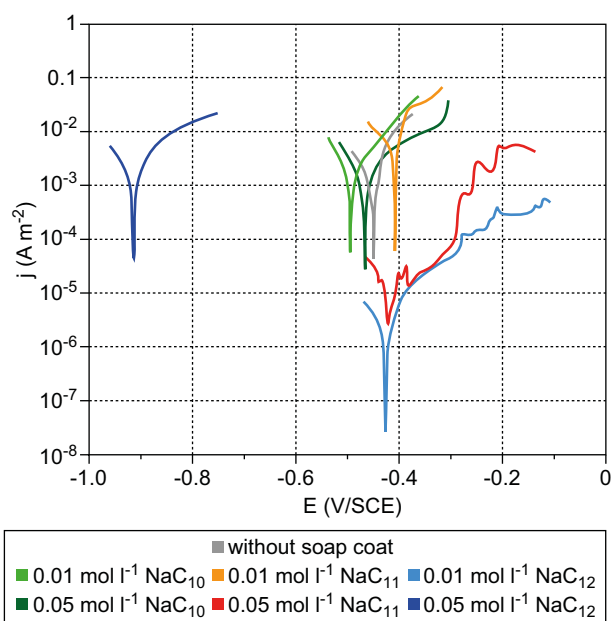
sors used during the experiments had different surface treatment: non-treated lead surface, corroded surface and corroded surface treated in 0.05 mol l^{-1} NaC$_{10}$ solution. The sensor with non-treated surface begins to corrode rapidly as soon as it gets in contact with acetic acid atmosphere (the corrosion thickness loss was 1 μm after 100 hours of exposure). After the 24 hours exposure of the sensor in 1 mol l^{-1} Na$_2$CO$_3$ solution the corrosion thickness loss was 2 μm. After the 24 hours of exposure of the sensor in 0.05 mol l^{-1} NaC$_{10}$ solution the corrosion thickness loss was 0.6 μm. The sensors with corroded surface and NaC$_{10}$ coating were very resistant to the acetic acid (after 100 hours exposure the corrosion thickness loss is negligible).
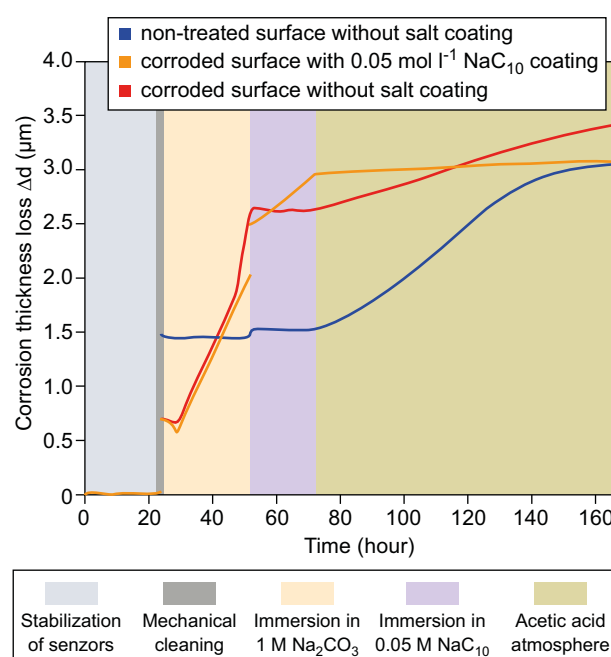

Fig. 7. Effect of NaC10 coating on corroded lead in a model atmosphere above the 0.001 mol l^{-1} acetic acid solution during the time, represented as corrosion thickness loss (Δd) in time

Obr. 7. Účinnost povlaku vytvořeného pomocí roztoku NaC10 o koncentraci 0,05 mol l^{-1} sledovaná pomocí úbytku tloušťky (Δd)olověného čidla s uměle vytvořenými korozními produkty v modelové atmosféře nad hladinou roztoku kyseliny octové o koncentraci 0,001 mol l^{-1} v čase

Fig. 6. Potentiodynamic curves of the samples with electrochemically cleaned surface with and without soap coat measured in 0.01 mol l^{-1} corrosive solution

Obr. 6. Potenciodynamické křivky olověných vzorků s povrchem elektrochemicky očištěným od uměle vytvořených korozních produktů s/bez ošetření v roztocích NaCn naměřené v neutralizovaném roztoku kyseliny octové o koncentraci 0,01 mol l^{-1}

Long-time resistometric measurement in model archival environment

Figure 7 shows the decrease of the lead thickness during the exposure in a model atmosphere above the 0.001 mol l^{-1} acetic acid solution. The resistometric sen-

SEM examination

All bare and coated lead samples with different state of surface were observed by SEM.

Figure 8a shows the surface of corroded lead sample plentifully covered with the needles hexagonal crystals. These crystals are lead carbonates according to XRD analyses. Figure 8b shows the surface of electrochemically cleaned lead sample mainly constituted by the columnar rombic crystals. These crystals are lead sulphates according to XRD analyses.

After 24 hours immersion in NaC_n the surface morphology drastically changed (Fig. 9a-c). The surface was very well covered by flake-shaped crystals, more or less tangled. According to XRD analyses these crystals are lead carboxylates. Highest concentration of the same coating solution induces more generous surface coating. The longest carbon chain length induces more generous surface coating, too. Comparison of Figure

9a and 9c shows that after immersion in 0.01 mol l^{-1} NaC_{10} the electrochemically cleaned lead surface was better coated with flake-shaped crystals than the bare lead surface. After immersion in 0.05 mol l^{-1} NaC_{12} (highest concentration and highest number of carbons in molecular chain) the primary corrosion layer on the corroded lead surface was still visible.
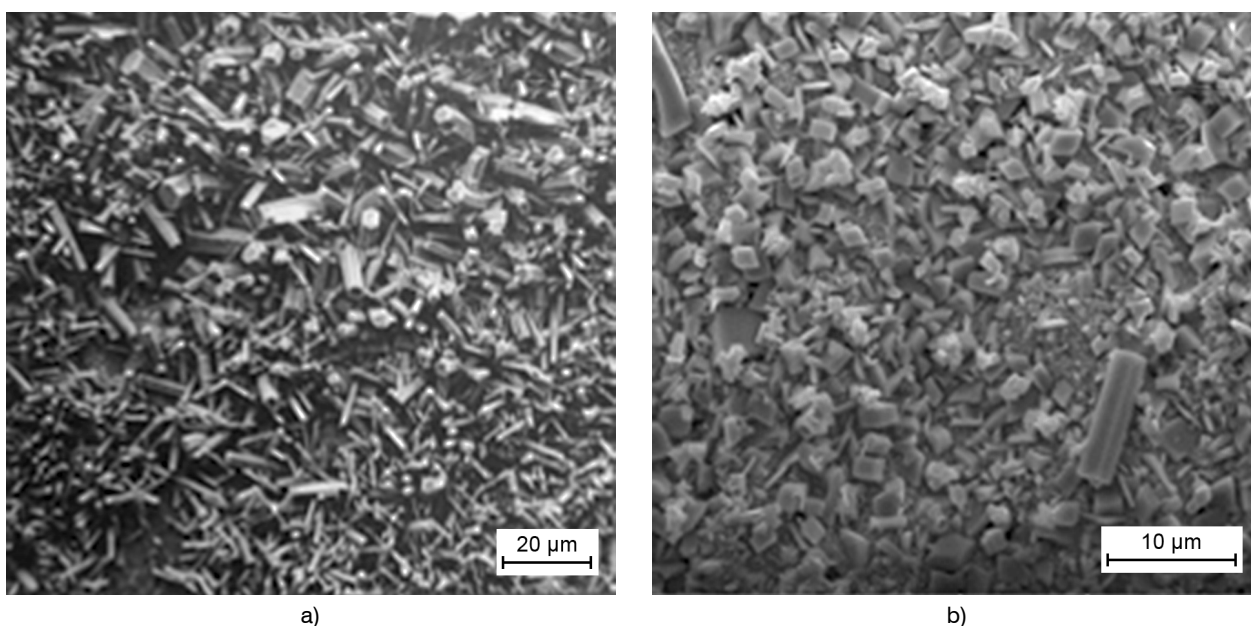

a)

b)

Fig. 8. SEM picture of bare lead samples with different state of surface, corroded lead (a) and electrochemically cleaned lead (b)

Obr. 8. Olověné vzorky s různým stavem povrchu bez ošetření pomocí NaCn roztoků pozorované pomocí SEM, olověný vzorek s korodovaným povrchem (a) a olověný vzorek s povrchem elektrochemicky očištěným od uměle vytvořených korozních produktů (b)
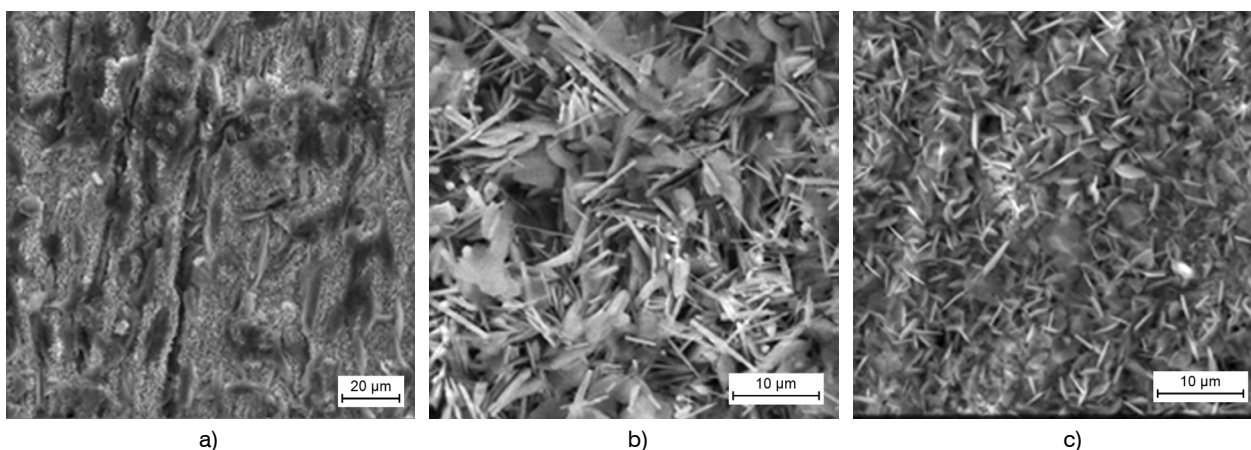

a)

b)

c)

Fig. 9. SEM picture of coated lead samples with different state of surface, pure lead after 24 hours immersion in 0.01 mol l^{-1} NaC_{10} (a), corroded lead after 24 hours immersion in 0.05 mol l^{-1} NaC_{12} (b) and electrochemically cleaned lead after 24 hours immersion in 0.01 mol l^{-1} NaC_{10} (C)

Obr. 9. Olověné vzorky s různým stavem povrchu s ošetřením pomocí NaCn roztoků (ponor do roztoku na 24 h) pozorované pomocí SEM, olověný vzorek s čistým povrchem ošetřený v roztoku NaC_{10} o koncentraci 0,01 mol l^{-1} (a), olověný vzorek s korodovaným povrchem ošetřený v roztoku NaC_{12} o koncentraci 0,05 mol l^{-1} (b) a olověný vzorek s povrchem elektrochemicky očištěným od uměle vytvořených korozních produktů ošetřený v roztoku NaC_{10} o koncentraci 0,01 mol l^{-1} (c)

Tab. 1. Summary of XRD analyses for all samples with non-treated and coated surface, **** the compound occurs on the surface very well (more than 40 %), *** the compound occurs on the surface (20-40 %), ** the compound occurs on the surface weakly (5-20 %) and * the compound occurs on the surface very weakly (less than 5 %) / *Přehled vyhodnocení XRD analýzy pro vzorky s čistým povrchem a po ošetření v NaCn roztocích, zastoupení jednotlivých sloučenin na povrchu vzorku je vyjádřeno stupnicí: **** velmi silné zastoupení (nad 40 %), *** silné zastoupení (20-40 %), ** slabé zastoupení (5-20 %) a * velmi slabé zastoupení (pod 5 %)*

Coating solution	Concentration of coating solution [mol l⁻¹]	Pb	PbO	PbC₂₀H₃₈O₄	PbC₂₄H₄₆O₄
NaC₁₀	0.01	****	*	**	–
NaC₁₀	0.05	***	*	**	–
NaC₁₁	0.01	****	–	***	–
NaC₁₁	0.05	****	–	****	–
NaC₁₂	0.01	****	–	–	***
NaC₁₂	0.05	***	–	–	****

Tab. 2. Summary of XRD analyses for all bare and coated lead samples with corroded surface, **** the compound occurs on the surface very well (more than 40 %), *** the compound occurs on the surface (20-40 %), ** the compound occurs on the surface weakly (5-20 %) and * the compound occurs on the surface very weakly (less than 5 %) / *Přehled vyhodnocení XRD analýzy pro vzorky s korodovaným povrchem s/bez ošetření v NaCn roztocích, zastoupení jednotlivých sloučenin na povrchu vzorku je vyjádřeno stupnicí: **** velmi silné zastoupení (nad 40 %), *** silné zastoupení (20-40 %), ** slabé zastoupení (5-20 %) a * velmi slabé zastoupení (pod 5 %)*

Coating solution	Concentration of coating solution [mol/l]	Pb	PbO	NaPb₂(CO₃)₂OH	PbC₂₀H₃₈O₄	PbC₂₄H₄₆O₄
none (bare sample)	–		**	–	****	–	–
NaC₁₀	0.01	***	***	***	**	–
NaC₁₀	0.05	****	**	****	**	–
NaC₁₁	0.01	***	*	–	***	–
NaC₁₁	0.05	****	**	**	***	–
NaC₁₂	0.01	***	*	****	–	***
NaC₁₂	0.05	**	–	****	–	***

Tab. 3. Summary of XRD analyses for all bare and coated lead samples with electrochemically cleaned surface, **** the compound occurs on the surface very well (more than 40 %), *** the compound occurs on the surface (20-40 %), ** the compound occurs on the surface weakly (5-20 %) and * the compound occurs on the surface very weakly (less than 5 %) / *Přehled vyhodnocení XRD analýzy pro vzorky s povrchem elektrochemicky očištěným od uměle vytvořených korozních produktů s/bez ošetření v NaCn roztocích, zastoupení jednotlivých sloučenin na povrchu vzorku je vyjádřeno stupnicí: **** velmi silné zastoupení (nad 40 %), *** silné zastoupení (20-40 %), ** slabé zastoupení (5-20 %) a * velmi slabé zastoupení (pod 5 %)*

Coating solution	Concentration of coating solution [mol/l]	Pb	PbO	PbSO₄	PbC₂₀H₃₈O₄	PbC₂₄H₄₆O₄
none (bare sample)	–	****	–	**	–	–
NaC₁₀	0.01	****	**	**	****	–
NaC₁₀	0.05	****	**	**	****	–
NaC₁₁	0.01	***	*	**	***	–
NaC₁₁	0.05	**	–	*	****	–
NaC₁₂	0.01	****	–	**	–	***
NaC₁₂	0.05	***	–	**	–	***

XRD analysis

All bare and coated lead samples with different state of surface were analysed by means of XRD.

XRD analyses of coated lead samples confirms the formation of a layer constituted of the metallic soap, $Pb(C_n)_2$, on samples surface (Tab. 1-3). Also, we can see that highest concentration of the same NaC_n solution or longest carbon chain length induces more generous surface coating. The surface layer of bare corroded lead sample was mainly constituted by $NaPb_2(CO_3)_2OH$ and weakly by $Pb_3(CO_3)_2(OH)_2$ and PbO (Tab. 2). The surface of bare electrochemically cleaned lead sample was mainly constituted by $PbSO_4$ (Tab. 3).

Goniometry

The contact angles were measured for all samples with different state of surface. The values shown in Figure 10 are the average values of five determinations. The non-polar molecular carbon chain of NaC_n molecule is oriented outward from the metal substrate and therefore it changes the hydrophobic properties of the metal surface. Longest carbon chain (hydrophobic part) in NaC_n molecule induces their highest hydrophobic effect. The Figure 10 shows what was expected: the samples without soap coat have hydrophilic properties and when treated in NaC_n solution the surficial properties change to hydrophobic. The reference sample with non-treated surface has contact angle of average value of 40°, the sample with electrochemically cleaned surface has contact angle of average values of 62° and the samples with corroded surface has contact angle of average values

of 95°. In this work the NaC_n molecules used differed by 1 carbon atom in molecular atoms chain and their concentrations were very similar as well. Therefore the values of contact angles on the coated samples are very similar – between 120 and 140°.

CONCLUSIONS

Electrochemical observations show that after 24 hours of the exposure of the lead samples in the solutions of sodium salts of monocarboxylic acids, noted as NaC_n (n = 10, 11 or 12 carbons in carboxylic chain), the protecting layer of metal soap is formed on the samples surface. The corrosion of lead samples with different state of surface (non-treated surface, corroded surface, electrochemically cleaned surface) treated by NaC_n solution is significantly decreased. Generally the corrosion rate of the lead samples is decreased with growing number of the carbon atoms in the NaC_n molecular chain and with the increasing concentration of NaC_n solution. The inhibition efficiency of 0.05 mol l^{-1} NaC_{11} and NaC_{12} was 99.9 % for all samples. The XRD analysis of the formed surficial coating showed that this coating is formed by dimer form of lead soap $Pb(C_n)_2$. The SEM anaylsis confirmed the presence of flake-shaped crystals of $Pb(C_n)_2$ on the treated lead surface. Measurement of the contact angles confirmed significant increase of hydrophobic properties of the surface treated by NaC_n. However, significant change in the colour and tarnishing of the surface of the lead sample together with low wear-resistance of formed coating do not determine the monocarboxylic acids salts for treatment and preservation of the cultural objects.
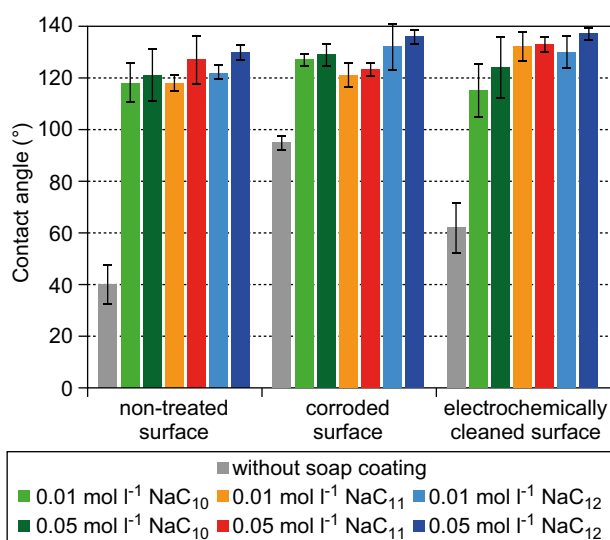
Fig. 10. The hydrophobic character of lead samples with different state of surface with and without soap coat based on the average values of contact angles
Obr. 6. Porovnání průměrných hodnot kontaktního úhlu olověných vzorků s různým stavem povrchu s/bez ošetření v NaCn roztocích

REFERENCES

1. Schotte, B. A study of electrolytic reduction of corroded lead objects and application, characterization and testing of a protective lead carboxylate coating. Disertační práce, Universiteit Gent: Faculty of Science, 2007.

2. Selwyn, L.; et al. Lead (Pb). In Metals and Corrosion: A Handbook for the Conservation Professional. 1st ed.; Canadian Conservation Institute: Canada, 2004; pp 115–123. ISBN 0-662-37984-5.

3. Kolektiv autorů. Konzervování a restaurování olova a jeho slitin. In Konzervování a restaurování kovů. 1st ed.; Technické muzeum v Brně: Brno, 2011; pp 526-544. ISBN 978-80-86413-70-9

4. Costa, V. Electrochemistry as a conservation tool: an overview. Conservation Science, 2003, 88-95.

5. Jareš, V. Metalografie neželezných kovů. 1st ed.; Nakladatelství ČSAV: Praha, 1950.

6. Vojtěch, D. Olovo a jeho slitiny. In Materiály a jejich mezní stavy. 1st ed.; VŠCHT: Praha, 2010; pp 35–36. ISBN 978-80-7080-741-5.

7. Kratochvíl, B.; Švorčík, V.; Vojtěch, D. Slitiny neželezných kovů. In Úvod do studia materiálů. 1st ed.; VŠCHT: Praha, 2005; pp 164–165. ISBN 80-7080-568-4.

8. Costa,V.; Urban, F. Lead and its alloys: metallurgy, deterioration and conservation. *Reviews in Conservation* **2005**, 6, 48–62.

9. Schotte, B.; Adriens, A. The treatment of corroded lead artefacts. *Studies in Conservation* **2006**, 51, 1–8.

10. Lyon, S. B. Corrosion of Lead and its Alloys. Corrosion and Protection Center. University of Manchester: Manchester, 2010.

11. Leygraf, C.; Graedel, T. E. Atmospheric Corrosion of Lead. In Atmospheric Corrosion, 1st ed.; Canada, 2000; pp 295–304. ISBN 0-471-37219-6.

12. Niklasson, A.; Johansson, L.; Svensson, J. The influence of relative humidity and temperature on the acetic acid vapour-induced atmospheric corrosion of lead. *Corrosion Science* **2008**, 50, 3031–3037.

13. Ryhl-Svendsen, M. Corrosivity measurements of indoor museum environments using lead coupons as dosimeters. *Journal of Cultural Heritage* **2008**, 9, 285–293.

14. Angeliny, E.; Grassini, S.: Underwater corrosion of metallic heritage artefacts. In Corrosion and conservation of cultural heritage metallic artefacts, 1st ed.; Woodhead Publishing Limited: Oxford, 2013; pp 236–259.

15. Grayburn, R.; et al. Time-lapse synchrotron X-ray diffraction to monitor conservation coatings for heritage lead in atmospheres polluted with oak-emitted volatile organic compounds. *Corrosion Science* **2014**, 82, 280–289.

16. Sastri, V. S. Vapor phase corrosion inhibitors. In Corrosion Inhibitors Principles and Aplications, 1st ed.; John Wiley and Sons Ltd: Chichester, 1998, pp 787–822.

17. Guidelines for the Storage and Display of Archaeological Metalwork [Online]. Engish heritage, 2013, pp 12-13. http://www.english-heritage.org.uk/content/learn/conservation/2543455/2543024/guidelines-for-the-storage-and-display-of-archaeological-metalwork.pdf (accessed 11 Jan 2019)

18. Ďurovič, M.; et al. Restaurování a konzervování archiválií a knih, 1st ed.; Paseka: Praha, 2002. ISBN 80-7185-383-6.

19. Vávrová, P. Koroze a degradace papíru. Koroze a degradace materiálu. http://www.vscht.cz/met/stranky/vyuka/predmety/koroze_materialu_pro_restauratory/kadm/pdf/1_3.pdf (accessed 11 Jan 2019).

20. Proniewicz, L. M.; Paluszkiewicz, C.; Weselucha-Birczynska, A.; Baranski, A.; Dutka, D. FT-IR and FT-Raman study of hydrothermally degraded groundwood containing paper. *Journal of Molecular Structure* **2002**, 614, 345–353.

21. Ďurovič, M. Vlastnosti papíru a jeho degradace. http://www.vscht.cz/met/stranky/vyuka/labcv/labor/res_vlastnosti_papiru/teorie.htm (accessed 11 Jan 2019).

22. Hatchfield, B. P. Pollutants in the Museum Environment; Archetype Publications: London, 2002. ISBN 1-873132-96-4.

23. Gibson, L. T.; Watt, C. M. Acetic and formic acids emitted from wood samples and their effect on selected materials in museum environments. Corrosion Science 2010, 52, 172–178.

24. Coles, E. L.; Gibson J. G.; Hinde, R. M.: The corrosion of lead by dilute aqueous organic acids, *Journal of Applied Chemistry* **1958**, 341-348.

25. Schotte, B.; Adriens, A. The treatment of corroded lead artefacts. *Studies in Conservation* **2006**, 51, 1–8.

26. Turgoose, S. The corrosion of lead and tin: before and after excavation. In Lead and Tin Studies in Conservation and Technology, United Kingdom Institute for Conservation: London, 1985, pp 15–23.

27. Niklasson, A.; Johansson, L.; Svensson, J. Atmospheric corrosion of historical organ pipes´influence of acetic and formic acid vapour and water leaching on lead. Proceedings of Metal 2004, 179–273.

28. Stambolov, T. The Corrosion and Conservation of Metallic Antiquities and Works of Arts. Central research laboratory of objects of art and science: Amsterdam, 1985, pp 160-173.

29. Nejedlý, V. Restaurování sochy Atlanta z astronomické věže pražského Klementina, Zprávy památkové péče LVII 1997, 2, 46-49.

30. Caley, E. Coatings and incrustations on lead objects from the agora and the method used for their removal. *Studies in Conservation* **1955**, 2, 49–54.

31. Organ, R. Use of ion-exchange resin in the treatment of lead objects. *Museums Journal* **1953**, 53, 49–52.

32. Škeřík, J. Receptář pro elektrotechnika. 3rd ed. Státní nakladatelství technické literatury: Praha, 1982.

33. Fawzy, M. A., et al. Corrosion behaviour of Pb-Sn binary alloys in acid solutions. *Surface and Coatings Technology* **1981**, 14, 257–264.

34. Rocca, E., et al. Inhibition treatment of the corrosion of lead artefacts in atmospheric conditions and by acetic acid vapour: use of sodium decanoate. *Corrosion Science* **2004**, 46, 653-665.

35. Cano, E.; Lafuente, D. Corrosion inhibitors for the preservation of metallic heritage artefacts. In Corrosion and conservation of cultural heritage metallic artefacts, 1st ed.; Woodhead Publishing Limited: Oxford, 2013, pp 570–594.

36. Sankarapapavinasam, S., et al. Hydrazine and substituted hydrazines as corrosion inhibitors for lead in acetic acid. *British Corrosion Journal* **1989**, 24 (1), 39-42.

37. Chiavari, C.; Martiny, C. Conservation of organ pipes: protective treatments of lead exposed to acetic acid vapours. In Metal 04, Proceedings of the International Conference on Metals Conservation, Canberra, October 4-8, 2004, National Museum of Australia: Canberra, 2004, pp 281-293.

38. Rocca, E.; Steinmetz, J. Inhibition of lead corrosion with saturated linear aliphatic chain monocarboxylates of sodium, *Corrosion Science* **2001**, 43, 891-902.

39. Inhibitory koroze kovů. http://ukmki.vscht.cz/files/uzel/0016736/Inhibitory%20koroze%20kov%C5%AF.pdf?redirected (accessed 11 Jan 2019)

40. Lacouture, F.; Francois, M.; Didierjean, C.; Rivera, J. P.; Rocca, E.; Steinmetz, J. Anhydrous lead(II) heptanoate. *Acta Crystallogr.* **2001**, 57, 530–531.

41. Green, L. A re-evaluation of lead conservation techniques at the British museum. International Restorer Seminar, Veszpr´em, Hungary, July 1-10, 1989.

42. De Keersmacker, M.; De Wael, K.; Adriaens, A.: Influence of the deposition method, temperature and deposition time on the corrosion inhibition of lead dodecanoate coatings deposited on lead surfaces. *Journal of Solid State Electrochemistry* **2013**, 17, 1259–1270.

43. Pecenová, Z.; Kouřil, M. Ochrana historického olova proti parám kyseliny octové. *Koroze a ochrana materiálu* **2016**, 60(1), 28-34.

44. Adriens, A.; De Bisshop, F.; et al. Growth and real time corrosion resistance monitoring of lead decanoate coatings. *Applied Surface Scince* **2008**, 254, 7351–7355.

45. Kouril, M.; Prosek, T.; Scheffel, B.; Degres, Y. Corrosion monitoring in archives by the electrical resistance technique. *Journal of Cultural Heritage* **2014**, 15(2), 99-103.

46. Kouril, M.; Prosek, T.; Scheffel, B.; Dubois, F. High sensitivity electrical resistance sensors for indoor corrosion monitoring. *Corrosion Engineering, Science and Technology* **2013**, 48(4), 282-287.

47. Prosek, T.; Kouril, M.; Dubus, M.; Taube, M.; Hubert, V.; Scheffel, B.; Degres, Y.; Jouannic, M.; Thierry, D. Real-time monitoring of indoor air corrosivity in cultural heritage institutions with metallic electrical resistance sensors. *Studies in Conservation* **2013**, 58(2), 117-128.