The protective behavior of organic coatings containing carboxylic functional groups on lead metal substrates

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Until recently, lead artifacts never showed signs of corrosion, because of the formation of a lead oxide passivation layer on the lead metal. From the 19th century on, 15th - 17th century organs in churches all over Europe began to lose their sound due to 'active' corrosion caused by the increase of humidity, temperature, and organic acids (mainly acetic acid) in the ambient atmosphere [1]. The production of these organic acids is a consequence of hydrolysis of acetyl groups of hemicellulose present in wood of the wind chest. Further research, conducted in the European COLLAPSE (Corrosion of Lead and Lead-Tin Alloys of Organ Pipes in Europe) project (FP5), showed that central heating installed in the churches at that time was the primary malefactor. The lead corrosion ensures irreversible damage of the organ pipe.

Lead corrosion also causes problems on lead artifacts in wooden display cases present in museums all over the world. The increase of the temperature and the relative humidity create an acidic microclimate in the wooden cases. Other sources for the formation of organic acids are the presence of plastics, glues, human bodies, varnishes, formaldehyde, etc. [2].

Efforts to protect lead-based artifacts against corrosion involve two approaches: (1) reduce the corrosive substances in the ambient environment and/or (2) apply a surface protection treatment. The use of corrosion inhibitors should produce a stable, reversible, inexpensive and aesthetically suitable coating.

Our approach makes use of organic inhibitors containing carboxylic functional groups, which are composed of a polar hydrophilic group and a non-polar hydrophobic group. These inhibitors have many advantages compared to other organic compounds, such as high inhibition efficiency, low price, low toxicity, easy production and simple deposition [3-4].

In a first study, an interesting candidate in the class of the surfactant inhibitors has been found in the deposition of non-toxic saturated linear monocarboxylates of the type $CH_3(CH_2)_{10}COONa$ (NaC₁₂). An initial study of our group [5] showed that the immersion of lead metal substrates in NaC₁₂ solutions results in their protection due to the growth of a coating consisting of a crystalline lead monocarboxylate complex, $(CH_3(CH_2)_{10}COO)_2Pb$ (Pb(C₁₂)₂). A statistical and microscopical analysis predicts the protection of the coating depends on the inhibitor concentration, the deposition method, the immersion time, the crystal structure of the coating and the temperature [6].

A second study uses a mixture of cheap hydrogenated dicarboxylic acids (or dimer acids trying to enhance the stability of the coating. Using the immersion method, a protective coating is deposited with a solution of the dimer acid in ethanol or an aqueous neutralized dimer acid solution. The dimer acid seems to form a gel-like solid layer which protects the lead substrate, while the neutralized acid reacts with the lead substrate to form a layer consisting of formed clusters. The results of the impedance measurements show clearly that the neutralized and unneutralized dimer acid form a protective coating on a lead oxide covered lead metal substrate. A longer immersion seems to increase the corrosion resistance, which indicates an increase in the corrosion protection.

In a very recent study, a random poly(acrylic acid-co-ethylhexyl acrylate) film was deposited using an ethyl acetate solution. The first experiments show low protective behavior, but during immersion in the corrosive acetic acid solution, the resistance of the coating seems to increase.

References

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