



Available online at
ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en



Original article

Comparative assessment of mechanical, chemical and electrochemical procedures for conservation of historical lead

Teresa Palomar^{a,b,*}, Emilio Cano^a

^a Centro nacional de investigaciones metalúrgicas, CENIM-CSIC. Avda. Gregorio del Amo 8, 28040 Madrid, Spain

^b Unidade de Investigação VICARTE-Vidro e Cerâmica para as Artes, Campus de Caparica, FCT-UNL, Quinta da Torre, 2829-516 Caparica, Portugal

ARTICLE INFO

Article history:

Received 14 July 2017

Accepted 20 October 2017

Available online xxx

Keywords:

Lead
Alteration
Cleaning methods
Electrochemical reduction
Conservation

ABSTRACT

Lead has a good resistance to atmospheric corrosion because it forms adherent, uniform and protective layers which prevent the corrosion advancement. Nevertheless, the exposure to the acetic and formic acids – emitted by wood and other materials used in museums' showcases, cabinets and storehouses – induces a corrosion process which can damage the surface of the objects. In order to improve their conservation, restorers apply different conservation treatments which depends on the degree of corrosion, the products formed, the skills of the conservator and the access to specific equipment, if is required. With the aim of evaluating the impact of successive conservation treatments on lead surface and assessing their efficiency, four usual treatments for lead were selected and six cycles of alteration and treatment were carried out. The assessed procedures were mechanical cleaning (suspension of CaCO_3), chemical cleaning (immersion on EDTA solution) and two electrochemical treatments (potentiostatic reduction, and potentiostatic reduction followed by passivation). The samples were characterized before and after each treatment with gravimetry, colorimetry, rugosimetry, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The effects observed on lead coupons depended on each treatment procedure. The mechanical cleaning with CaCO_3 produced a significant mass loss and it left an irregular surface due to the granulometry of the abrasive. Additionally, it experienced a fast re-alteration. Chemical cleaning with EDTA produced moderate mass and gloss losses due to the etching of the metallic surface after successive cycles. However, the color of the samples was the closest to the original one. Finally, the electrochemical reductions produced a scarce mass loss and a slow re-alteration, although they produced crystalline deposits on the surface which modified the color of the coupons towards bluish hues.

© 2017 Elsevier Masson SAS. All rights reserved.

1. Research aims

The low hardness of lead makes it particularly susceptible to the damage during the conservation practices; moreover, it requires additional security procedures due to the high toxicity of its corrosion products. The main alterations in the lead surface due to the conservation treatments are the change of color, luminosity, surface texture and chemical composition. The application of successive treatments along several years can intensify these alterations and, therefore, severe and irreversible damages can be produced on lead.

The aim of this study is to evaluate and compare the impact of different procedures for the conservation of historical lead. To achieve this objective, the most commonly used conservation

procedures were identified, the effects on the lead surface after successive treatments were characterized, and the stability of the treatments was assessed.

2. Introduction

Lead is the most common heavy metal in the Earth crust. It presents a bluish-gray color, is very soft and has high density [1,2]. Historically, lead is one of the earlier used metals, lead rivets were used to mend pottery since 3000 B.C. in the Middle East [3]. Its low melting point and high workability favored the production of several objects such as coffins, funeral urns, epigraphic sheets, seals, medals, plummets, sinkers, military objects, soldier toys, printing types, organ tubes and other decorative and utilitarian items. In addition, lead has been used in objects with urban and structural function such as water pipes, roofing and lead came for stained glass windows [1].

* Corresponding author.

E-mail address: t.palomar@fct.unl.pt (T. Palomar).

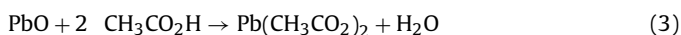
Lead has good resistance to atmospheric corrosion because it reacts with environmental oxygen to form a passive layer of lead oxide (PbO) (reaction 1) [4].



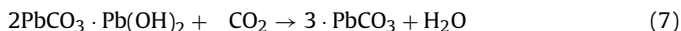
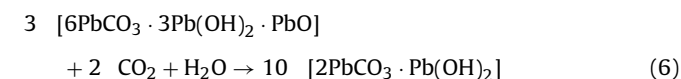
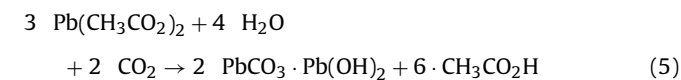
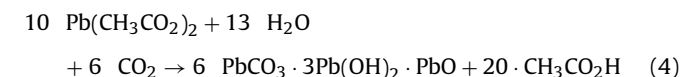
The CO₂ dissolved in the rain and the condensation water can react with the oxides to form carbonates such as the plumbonacrite (6PbCO₃ · 3Pb(OH)₂ · PbO) (reaction 2) which form an adherent, uniform and protective layer [5].



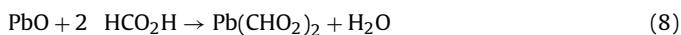
However, some volatile organic compounds (VOCs) can break the protective layer and trigger the degradation process. The main alteration agent is the acetic acid which, dissolved in the condensation water, can react with the protective passive layer to form hydrated lead acetate (reaction 3).



Lead acetate acts as a catalyst because favors the transformation of environmental CO₂ to lead carbonates. The result is the formation of a whitish, powdery and low-adhesion alteration layer on the lead surface. The reactivity of acetate has a direct relationship with the environmental humidity, mainly at relative humidity above 67% [5–7], and the species most common formed are plumbonacrite, hydrocerussite (2PbCO₃ · Pb(OH)₂) and cerussite (PbCO₃) (reactions 4, 5, 6 and 7), although plumbonacrite is the most favored one because it is the most stable compound in the system PbO–CO₂–H₂O [5,8].



Contrary to the plumbonacrite formed from lead oxides upon atmospheric exposure (reaction 2), this layer is poorly adherent and does not protect the metallic surface from further corrosion. Furthermore, formation of carbonates according to reactions 4 and 5 release the acetic acid which further reacts with the unaltered metal. The formic acid also catalyzes the corrosion of lead, although to a lesser extent than acetic acid because the lead formate (Pb[CHO₂]₂) is less soluble than acetate and, therefore, the corrosion layer is more stable (reaction 8) [9,10].



The principal risk to the heritage of lead in museums is the accumulation of the VOCs inside the cabinets, showcases and storehouses, whose concentration could be up to 20 times higher than inside the museum [6]. These VOCs are emitted by the building materials of the museum enclosures, such as natural woods, silicones, paints and varnishes [1,11–14]. This attack has also been registered in historical organ pipes due to the alteration of the wood from the wind system [4,10,15,16] and in the lower side of lead roofs due to the alteration of the wooden roof supports [17].

Those objects with a severe state of corrosion require a conservation treatment to restore its legibility and its conservation

state. Historically, the most commonly used procedures were the mechanical treatments with abrasives, scalpels or fiberglass brushes, although the low hardness of lead makes it particularly susceptible to be damaged during the cleaning [2,18,19]. Lead has a hardness of 1.5 on the Mohs scale, lower than its most common corrosion products such as PbO (2.0), PbCO₃ (3.3) or PbSO₄ (2.8) [20]. Among the most usual abrasives, CaCO₃ has a hardness of 3, similar to the corrosion products of lead. Abrasives with higher hardness such as TiO₂ (5–5.6), SiO₂ (7) or Al₂O₃ (9) could produce several damage on the objects, while abrasive with lower hardness such as kaolinite (2–2.5) or talc (1) could not clean the corrosion products on the surface [21].

The most commonly applied chemical treatments were acids and bases, which can remove thick corrosion crusts [2,19]. The Caley method is the most renowned, consisting in the cleaning with an aqueous solution of HCl (1:10) followed by the treatment with CH₃COONH₄ to remove the PbO₂ and neutralize the acidity [19,22]. The problem of this method is the amphoteric nature of lead. The objects can be severe damaged if the pH was not controlled or the remains of the solutions were not well cleaned. Chelating agents, as ethylenediamine tetraacetic acid (EDTA), have also been applied for the chemical cleaning of complex corrosion crusts because it dissolves most of the species of lead, instead of PbO [19,23,24]. In case of ion exchange resins, they are useful to clean carbonates because the resin absorbs the lead ions and releases water soluble compounds to media [2].

Electrochemical procedures have also been applied for the conservation of historical lead. This treatment allows the electrochemical reduction of the corrosion products to consolidate the lead objects minimizing the mass loss [25]. The galvanic reduction (normally named “electrochemical reduction” in conservation literature) has been widely applied. In this procedure, the object to be treated and a less-noble metal, usually zinc or aluminum, are kept in contact in a conducting solution. The main inconvenient of this procedure is the lack of selectivity and control of the reactions that takes place [2,26]. The reduction treatment can also be applied with an external power source, known in the conservation literature as “electrolytic reduction”, both under current (galvanostatic treatments) or potential (potentiostatic treatments) control. The galvanostatic treatment maintains stable the current which permits to treat different objects simultaneously; although water dissociation can easily occur and objects can be damaged by hydrogen evolution [27]. A refinement of this procedure, known as “consolidative reduction”, involves the use of low currents to hinder hydrogen evolution and effectively reduce the corrosion products back to the metal, but it is a slow process and the formation of hydrogen is not completely avoided [28,29]. The potentiostatic treatment controls the potential applied to the object; it is possible to discriminate between different reactions and to control them, so only the desired ones take place [28,30]. The most common electrolytes to treat lead are aqueous solutions of NaOH, Na₂CO₃, H₂SO₄ and Na₂SO₄, although the Na₂SO₄ seems to be the safest solution both for metal and for its corrosion products [29].

Given the importance of the preservation of cultural heritage in lead, it is essential to know the impact of the conservation procedures on it. Several works have proved that treatments produce chemical and morphological changes in the lead surface, which can be unperceived by conservators. Adams [24] carried out a comparative study on the effect of three chelating agents (ethylenediamine tetraacetic acid [EDTA]; diethylenetriamine pentaacetic acid [DTPA]; and sodium triphosphate [STP]) on lead coupons and demonstrated that the DTPA was the most effective chelating agent for lead carbonate, the EDTA induced the distortion of the surface, and the STP acted too slow and the chelated products precipitated on the metal. Schotte et al. [31] proved that the reduction of the corrosion products of lead could stabilize the corroded metal, although

Download English Version:

<https://daneshyari.com/en/article/7445959>

Download Persian Version:

<https://daneshyari.com/article/7445959>

[Daneshyari.com](https://daneshyari.com)