

How to Preserve Lead Artefacts for Future Generations

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This paper discusses the advantages and disadvantages of different conservation treatments that have been developed over the years to protect the lead cultural heritage. The chemical and aesthetic points of view are looked at.

1. Composition of lead artefacts

Lead is easily alloyed with other metals to form alloys with low melting points which are soft and malleable. These alloys are easily formed into artefacts by casting, hammering, rolling, extrusion, or a combination thereof and it is simple (neglecting environmental concerns) to recover the material for re-use.

The alloy properties of depend on their chemical composition and microstructure. Regarding composition, antiquities are generally made of impure lead. Since the most frequently associated elements have a very limited room temperature solid solubility in the face-centered cubic lead structure (e.g. antimony < 0.01% [1], silver 0.02% and copper 0.005% [2]), a small concentration of these will exceed the solubility limit, and a new crystalline phase will be formed, changing the properties [3]. One of the exceptions is tin, which is soluble in lead up to 19.5% [4].

Knowing this, it is interesting to examine general tendencies in the lead content of old lead artefacts. Figure 1 shows the statistical distribution of lead artefacts according to their lead content; three main groups are discerned. Most of the objects are considered 'pure lead' because they have a lead content higher than 80%. Most of the artefacts contain other elements including copper, antimony and silver precipitating as a second phase (see phase β in Figure 1a). A second group with artefacts containing about 40% lead are characterized by a low melting point. The metal is composed of dendrites of a lead-rich α phase surrounded by

the eutectic $\alpha + \beta$ phase, rich in another element (see Figure 1b). The last group contains alloys with lead quantities lower than 30%. The lead is added in low quantities to improve properties for casting and machining. Once again, the immiscibility between the elements ensures the dispersion of lead rich fine globules in the alloy matrix (see Figure 1c) [5]. When studying lead artefacts, the most frequently used alloys for lead are lead-tin, lead-antimony and copper-lead alloys. Lead is alloyed with tin to boost its corrosion and resonant properties explaining the use in the production of organ pipes. Antimony is added to increase corrosion resistance and hardness as can be seen in a huge amount of printing letters that are kept at the Museum Plantin-Moretus in Antwerp [6]. During the Greco-Roman Age, 6 to 8% lead was added to copper, bronze (lead bronze) and brass, improving the machinability and castability of the metal for the manufacture of coins and statues [7].

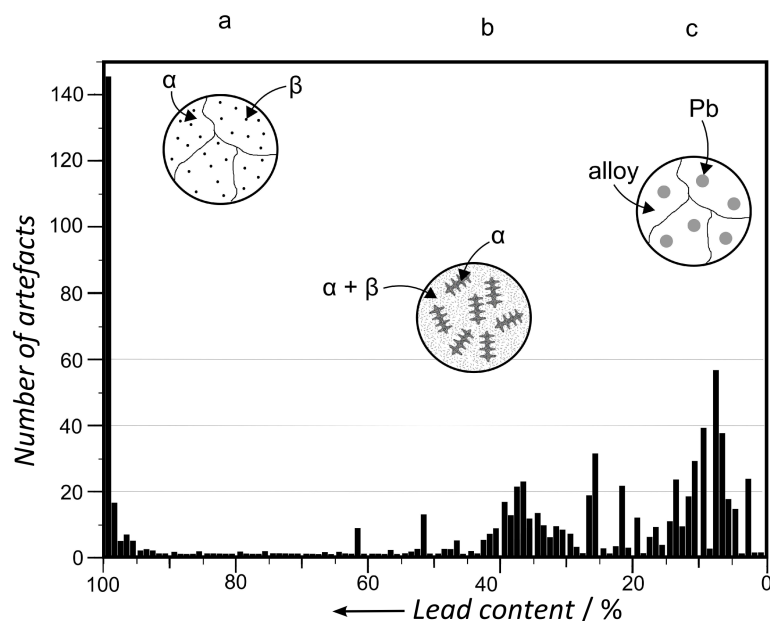


Figure 1. Distribution of lead artefacts according to lead content adapted from [5]. Three compositional groups: (a) high lead content, the structure of which consists of a lead-rich matrix (α) with precipitates of a second phase, minor-element-rich (β); (b) intermediate lead content, corresponding to low melting-point alloys, used in the as-cast condition, revealing lead-rich (α) dendrites in a eutectic matrix ($\alpha+\beta$); (c) low lead content, exemplified by copper-based leaded alloys, where lead is segregated in the form of fine globules.

2. Deterioration of lead artefacts

2.1. Uniform corrosion of lead artefacts

Corrosion is defined by the IUPAC as “An irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment which results in consumption of the material

or in dissolution into the material of a component of the environment. Often, but not necessarily, corrosion results in effects detrimental to the usage of the material considered. Exclusively physical or mechanical processes such as smelting or evaporation, abrasion or mechanical fracture are not included in the term corrosion” [8]. Interaction with compounds in the environment can be devastating for all lead objects. In general, we distinguish two types of volatile compounds uniformly corrosive towards pure lead: inorganic and organic compounds.

2.1.1. Inorganic compounds

Studies on the degradation of pure lead were initiated by Vernon in the 1920s [9]. It was established that moist air forms a native lead oxide following a reaction with atmospheric oxygen. Depending on the temperature and relative humidity of the environment, a water layer starts forming on the metal surface, which then serves as an electrolyte and plays a crucial role in the lead corrosion process. Another problem is air pollution because the aqueous electrolyte provides a medium for the dissolution of a whole range of atmospheric gasses [10]. The formation of a tightly adherent lead oxide layer and, for example, the dissolution of atmospheric carbon dioxide in the aqueous electrolyte opens the path for the formation of lead corrosion products like cerussite (PbCO_3), hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$), plumbonacrite ($\text{Pb}_{10}\text{O}(\text{OH})_6(\text{CO}_3)_6$) [11]. Depending on the composition of the environment, other atmospheric corrosion reactions are possible such as the formation of lead sulfate crystals because of the presence of carbonyl sulfide (OCS), hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) gas [12]. Looking at the atmospheric corrosion of lead in a marine environment, consisting of mainly chlorides, we see the formation of lead chlorides (cotunnite – PbCl_2) together with traces of moderately to poorly soluble lead hydroxychloride (laurionite – $\text{PbCl}(\text{OH})$) corrosion products [13]. An example are lead shots covered with protective layers of various insoluble salts found on the Mary Rose, considered to be complex mixed basic salts, impure and/or compounds [14]. Because these products are not soluble in water, a porous coating gradually protects the underlying bulk lead metal against further corrosion, which means that the corrosion process is anodically controlled [15]. This protective layer is the main reason why, in general, lead artefacts have been preserved so well through the ages [16]. Industrial waste gas emissions containing nitrogen oxides, NO_x , yielding nitric acid through the reaction with water, are very corrosive for most metals, but also for lead. Lead nitrate corrosion is not found as a consequence of its high solubility in water [17].

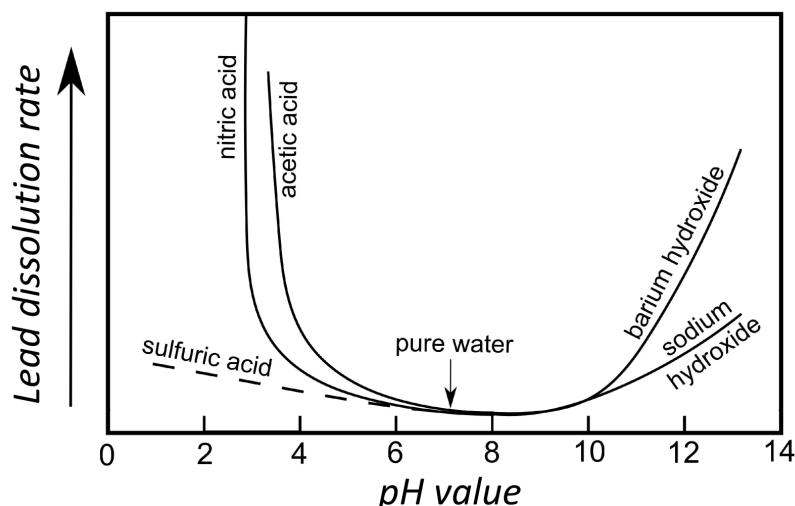


Figure 2. The lead solubility rate as a function of different inorganic acids and hydroxides adapted from [5].

To conclude, we can state that lead is quite actively corroded by corrosive gases and that many different lead salts are formed depending on the characteristics of the environment. The corrosion rate is a very important factor to decide which products will arrest the destruction of lead metal samples. In this respect, we show in Figure 2 the rate of lead solubility as a function of different inorganic acids and hydroxides. It is clear that the solubility and stability of the corrosion product play a crucial role, which means that environments containing nitrates and organic acids are most corrosive towards lead [5]. Next to the environment, corrosion depends on a variety of factors such as inclusions, surface imperfections, differences in the orientation of grains, lack of chemical homogeneity, and localized stresses [18].

2.1.2. Organic compounds

Volatile organic acids have long been known to be corrosive to lead. The most aggressive are acetic acid and formic acid, which form readily soluble lead acetates and lead formates. The lead metal is continuously attacked by organic acids, creating a uniform corrosion pattern [5]. Often, this kind of atmospheric corrosion is noticed when lead is in the presence of wood, but also varnish or paint [19].

A group of hemicelluloses found in the plant cell walls of wood are called xylans, which are polysaccharides made from xylose units. Depending on the type of wood, the xylan content differs from 10-35% in hardwoods and from 10-15% in softwoods. Moreover, on average every second xylose unit is acetylated in hardwoods, which is not the case for softwoods. Deacetylation of these hemicellulose xylan acetyl side chains produces acetic acid [22]. Formic acid, on the other hand, arises from the degradation of furfural derived from the dehy-

dration of xylose [23]. This means that the degradation kinetics depend on the relative humidity and temperature, and that the amount of corrosion depends on the wood type used. Table 1 mentions different wood types according to their harmfulness towards lead metal artefacts. Some wood types are more corrosive towards lead depending on the emission of a variety of acids, aldehydes and other degradation products [24]. Oak often is used to make windchests or wooden organ pipes. Hence, based on Table 1, we can easily explain why organ pipes deteriorate so rapidly [25].

Table 1. Wood types harmful for lead metal artefacts [19–21]

VERY HARMFUL		
unseasoned oak (white and red)	sweet chestnut	plywood and chipboard
fire-proofed woods	teak	rot-proofed woods
MODERATELY HARMFUL		
seasoned oak	birch	larch
beech	ash	red cedar
LESS HARMFUL		
Honduras and African mahony	elm	douglas fire
ramin	pine	obeche

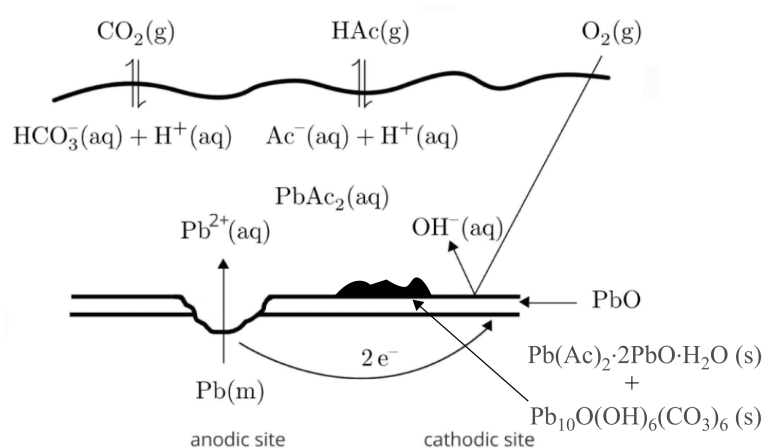
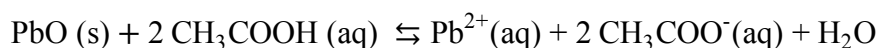


Figure 3. A schematic representation of the atmospheric corrosion processes on lead in moist air containing acetic acid vapour (based on [26]).

Even low concentrations (170-1100 ppb) of acetic acid in moist air are extremely corrosive to lead as found by Niklasson et al. [26], explaining the rapid lead deterioration. The acidity and the high solubility in water of gaseous organic acids are interpreted as their most important properties for lead corrosion. Dissolving into the aqueous electrolyte, acetic acid ensures a decrease of the pH value, which results in the dissolution of the native basic PbO layer [27] explained by



This simple acid-base reaction triggers the electrochemical corrosion process that generates ions producing new solid lead corrosion products as shown in Figure 3. The liberation of acetic acid causes a continuous metal corrosion in an auto-catalytic way explaining the large amount of corrosion by small amounts of acetic acid [5]. Low formic acid concentrations (160 ppb) are also very corrosive towards lead, but less effective than acetic acid. The lower solubility of lead formate in water and the difficulty in forming lead complexes explain why this acid is less aggressive compared to acetic acid [28]. To demonstrate that the combination of lead metal with wood, varnish and/or paint is very common, two examples are briefly discussed below.

2.1.2.1. Organ pipes

In the 1990s, some organs made in the 15th-17th century which originated from different European churches started to lose their specific sounds. Metal conservators established that the air escaped through small holes in the metal organ pipes [29]. Furthermore, they discovered the sudden appearance of white chalky residue all over the pipes' interiors that eventually worked its way through to the outside in small localized spots. Mostly, this type of corrosion takes place on the inside and outside of the foot of the organ pipe where the pipe is in contact with the wooden windchest. When the corrosion moves upwards along the pipe, the mouth of the organ pipe is damaged. First, the sound quality will change, and after a long exposure the pipe will not produce any more sound [30]. At this point, the damage is irreversible and untreatable. To help solve the widespread problem, a team of metallurgists, chemists, organ makers and music historians started the European research program COLLAPSE (Corrosion of Lead and Lead-Tin Alloys of Organ Pipes in Europe) (EC 5th Framework Programme: Energy, environment and sustainable development) to monitor and study the climate conditions close to the pipes [31]. Two causes for the corrosion were [32–34]

- central heating increases the temperature and relative humidity and favors the conditions for corrosion.
- the separation of organic acids by the hydrolysis of wood in the organ's wind chest is a consequence of changes in the churches' atmospheric air.

Both causes are part of the problem, but the second one has a higher impact on the corrosion process, as described by T. Clarke [29]. Conservation scientists believe that close to the wooden parts, an acidic microclimate is created in the windchest. The acetic acid concentrations can range from 0.04 to 2.4 ppm in pipe organ wind chests [35]. It is important to mention that organ pipes alloyed with tin showed less corrosion [31].

2.1.2.2. Museum storage and display cases

Often, wooden construction materials detrimental towards artefacts stored inside are used for building storage and display cases [36–38]. It is also possible that two artefacts stored in one case are corrosive towards one another [39–41]. The fact that the artefacts are stored in a closed environment without ventilation, allowing the organic acid concentration to rise quickly, increases the corrosion rate. High concentrations in the range of 0.05 to 40 ppb can attack and corrode the lead artefacts. In trying to prevent the release of organics or the development of rot, coatings are applied to seal and protect the wood surfaces of case interiors. However, many problems have been reported using this ‘solution’, depending on the choice of sealant or paint [42]. Due to their own volatile content, many coatings are themselves dangerous to the artefacts. In Table 2, we sum up possible destructive coating materials for pure lead and lead-alloyed artefacts. Browsing conservation literature indicates that many myths and contradictions regarding the choice of sealant are still prevalent [24]. Mainly metal artefacts are susceptible to this kind of corrosion. However, paintings filled with metal-containing pigments clearly show the same problems [43]. To be complete, the organic acids produced by the museum visitors also must be considered. Due to the incorrect use of wood and wood coatings together with exposure to anthropogenic gases much of our cultural heritage has disappeared or deteriorated. It is therefore necessary to find protection against the formation of lead corrosion products, which cause the destruction of heritage lead [11].

2.2. Localized corrosion

The microstructure and composition of lead artefacts create active and passive regions on the surface, which has an enormous effect on the corrosion behaviour. For example, an existing passivating layer (due to atmospheric corrosion) can be locally disrupted, making exposed areas more vulnerable to specific types of corrosion. Below, we will briefly discuss three types of localized corrosion on lead artefacts: intergranular, pitting and selective corrosion.

Table 2. Paints, glues and other materials destructive to lead metal artefacts [20,24,44]

PVA glue	some types of wallpaper	contact cement
velvet	plastic wood	burlap
some types of polyesters	rust inhibitors	some types of varnishes
some types of plastics	some types of dyes	jute
low quality paper and card-board	flame-proofed fabrics and wood	products to treat rot and/or insects
oil-based stain	vermiculite	some kinds of wool
unwashed pebbles and sand	some types of silicone adhesives	vinyl
products containing ammonia	vinegar-based products	some types of paints

2.2.1. Intergranular corrosion

In a polycrystalline material, intergranular corrosion starts at preferred sites along the interface between crystallites, called the grain boundaries. These grain boundaries show a higher density of imperfections in the crystal structure, resulting in a more disordered system. Therefore, they have a higher entropy and thus a higher energy, which means that they become more anodically reactive than the core of the grains in certain environments [45]. The resulting localized attack creates electrolyte penetration and further corrosion at boundaries, which can cause weakening of the metal structure. There is almost no perceptible destruction, but the metal's properties such as ductility and strength decrease and production of debris increase very rapidly [46]. The corrosion rate depends on the morphology or shapes and size of the grains, as well as the impurities and their distribution in the matrix of the grains and any segregation to grain boundaries [47].

Observations of lead-tin organ pipes by Chiavari et al. [48] reveal the formation of intergranular corrosion along the grain or dendrite boundaries, forming cracks and very local pustules. When the pipe alloy consists of smaller grains and is more homogeneous due to extensive hammering, the corrosion resistance is improved, yet there is a loss of the strength of the bulk material [49]. Bigger grains, indeed, promote corrosion along cracks in the bulk metal. The same is seen when investigating Roman water pipes [50]. In general, fine-grained alloy structures are more easily deformed than corroded.

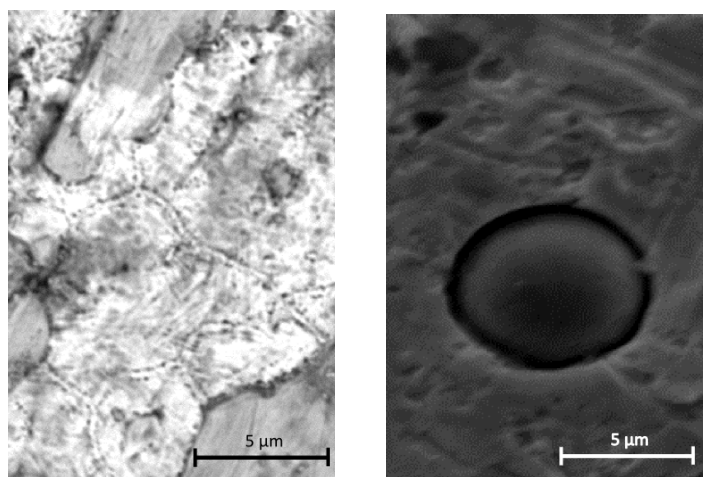


Figure 4. (a) Intergranular corrosion and (b) Copper inclusion in lead matrix. © MDK.

An interesting example of preferential intergranular attack is seen on lead-antimony alloys in the range of 0.5% to about 6% antimony [51]. Furthermore, there exists the interaction in pipe organ metals between low solubility impurities such as copper and the lead matrix as seen in Figure 4. Impurities along the boundaries locally disrupt the native lead oxide film, allowing atmospheric gases easier access to the bulk metal. However, no general tendencies are reported. In trying to predict intergranular corrosion, it is important to look at the nature of the alloy and any impurities together with impurity distributions (e.g. solid solution or segregated) [52]. When in an organic acid environment, for example, tin-alloyed organ pipes have a higher corrosion resistance compared to pure lead pipes, which can be attributed to the protective behaviour of tin in these media [53]. To conclude, we can state that the microstructure and composition of lead and its alloys have an important influence on their corrosion behaviour.

2.2.2. Selective leaching corrosion

Selective leaching corrosion, also called dealloying, is a type of corrosion where one metal component is preferentially leached from an alloyed material. The rate of the process depends on the distance between the alloyed metals in the galvanic series. The less noble or more active metal is selectively removed from the alloy [54]. After the process, the metal is spongy and porous and has lost strength, hardness and ductility. Often this kind of corrosion is seen in copper alloyed artefacts where lead is added to enhance castability and machinability properties. The dezincification of brass is a well-known phenomenon in conservation studies and can be recognized by a change in colour (yellow to orange) [55]. The addition of lead ensures the formation of isolated globules due to its insolubility in the copper-rich matrix, and it is the lead metal which will preferentially corrode. The corrosion products are often referred to as ‘lead worms’ [56]. Other examples are the extensive selective leaching

of lead-antimony alloys, at rates which were not monotonically related to either the acidity of the environment or the antimony content [57].

2.2.3. Pitting corrosion

Pitting is the least usual form of corrosion. The process can be split into three different time frames: pit formation, pit growth and degradation.

2.2.3.1. Pit formation

The lead metal readily forms a relatively impenetrable passive layer as described in section 2.2.1 and shown in Figure 5 (step 1). However, discontinuities in the passive layer expose the bulk lead metal to the environment. On the one hand, weak spots in the film can be a consequence of the lead metal's microstructure and impurities. Examples are galvanic contacts due to heterogeneous distribution of micro-segregations, selective corrosion or crevice corrosion [58]. On the other hand, pits are formed due to local chemical or mechanical damage. In this case, the localized corrosion starts because of coating failure, local condensation of moisture, momentary change in concentration, erosion-corrosion, scratches or thermal expansion [54]. This step is shown in Figure 5 (step 2).

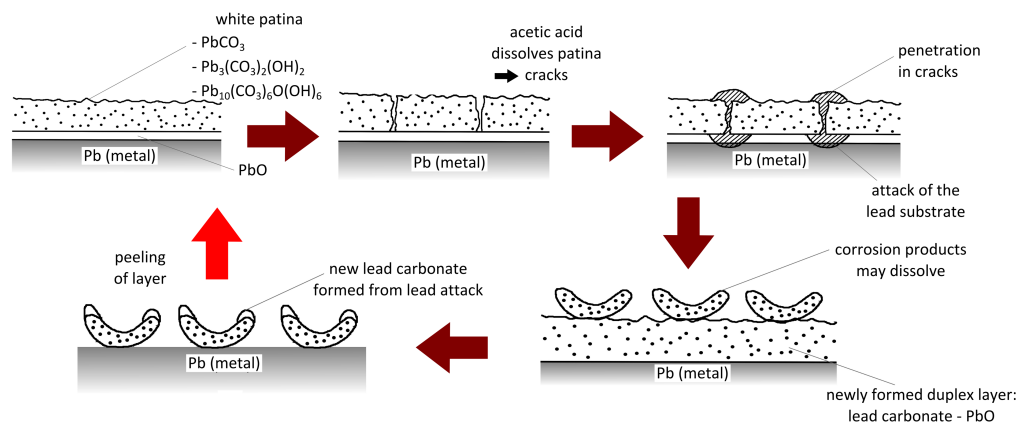


Figure 5. Mechanism of 'active' lead corrosion in the proximity of organic acids (based on [26]).

Depending on the nature of the film, a rapid repair of the film at the breakdown site can stop the corrosion process before it starts [59]. However, in many cases, the damaging conditions persist and a cavity is formed. A reason for this is the formation of soluble and bulky lead corrosion products. At this moment, an active pit exists on a completely passivated lead metal surface, which allows the formation of a potential gradient. Indeed, the initiation of the corrosion process is a result of a change in the local anodic behaviour of the lead material [60].

2.2.3.2. Pit growth

When an opening is formed in the passivated layer (such as a coating or a patina), the pits start to form crevices. Typically, these cracks are filled with the surrounding electrolyte when they are a few micrometres wide, as shown in Figure 5 (step 3) [61]. However, the small dimensions of the fissures prevent circulation of the electrolyte in the surrounding environment, which causes the conditions to become more aggressive inside the crevice. This more severe environment causes local active lead metal dissolution and tends to accelerate the corrosion process [62]. The migration of hydrated acetates (or nitrates) forms an acidic environment in crevices formed on the lead substrate, which permits the continuous production of lead salts due to the formation bulky porous precipitates. The lead acetates (or nitrates) formed dissolve into the aqueous electrolyte and migrate away from the crevice [63]. A reaction with CO₂ forms white powdery precipitates far from the corrosion pit together with new acetic acid molecules ensuring a continuous attack of the lead substrate [11].

2.2.3.3. Degradation

The crevices become deeper and inside them the lead metal is slowly eaten away. After a long time, depending on the thickness of the material, perforations are observed. These holes can have destructive consequences for the object. Some important examples for lead are summed up below.

- Perforations of lead sheets around the base of organ pipes make sure the sound is distorted or vanishes.
- Degradation of lead artefacts makes it difficult to read ancient inscriptions [64]
- Lead roofing corrodes in the presence of wood beams, creating leaks [65]
- Lead sculptures are deformed at places in direct contact with more noble metals and sealing products.
- Localized corrosion produces holes on excavated lead artefacts or lead pipes buried in an acidic environment.
- High nitrate concentrations in drinking water slowly degrade copper-lead solder pipes [66]
- Antique wooden display cases are used to store artefacts and cause pitting and cracking issues on lead objects [67]

3. Treatment of lead artefacts

As established in the previous section, lead metal objects are under constant attack and decay. It is important to note that the treatments used on lead artefacts depend on the aims of the conservator. For example, different treatments are needed to improve the readability of the surface such as inscriptions, repairing mechanical problems and conserving purposes

depending on the environment [5]. In what follows, we focus on the prevention of the deterioration process [68]. To do this, conservators must preserve the artefact's cultural, historical and technological identity in the best possible way [69]. Furthermore, conservators must consider treatments with minimal intervention, which are preferably reversible and repeatable. Recently, only materials with a non-toxic nature towards both the objects, conservator and environment are considered to be used in conservation procedures [70]. Considering all these philosophies, two types of conservation are known: preventive and interventive conservation. Both will be briefly discussed below.

3.1. Preventive conservation

The changing indoor environmental conditions determined by factors such as temperature, light, humidity and air pollution (also from human beings) are crucial in the research towards conservation of lead artefacts [71]. Mainly the seasonal changes and the build-up of pollutants in sealed off showcases have a deteriorating effect on the lead metal collections [24]. Trying to limit these degradation phenomena, it is possible to keep the lead artefacts in a controlled environment in which all variables can be regulated [72]. Preventive corrosion, known as collections care, depends a lot on the museum's policy and resources. When possible, climate control equipment is installed in museums [73]. In the following list, several possible interventions are summed up, which can be combined.

- Dehumidification [74]
- Installation of air conditioning [75]
- Airflow system using filters (activated carbon filter) [76]
- Do not use potentially dangerous woods or wood products such as fibreboard and hardboard [5]

Out of these, controlling the relative humidity (RH) seems to be the most important as discussed in a study by Thomson [77]. Indeed, the RH has an influence on the shape of the exhibits, the rate of the chemical corrosion reactions and the biological deterioration sources [78]. Reducing the RH could already solve a major part of the corrosion problem. Furthermore, some effort is needed to avoid temperature changes and to keep an acceptably low exposure level to pollutants [79]. Museum conservators must also consider the fact that the ideal environmental conditions differ for the preservation of artefacts and the preservation of the building or display case. Also sometimes one artefact is constructed using different materials requiring different preventive conditions [80]. A lot of preparations are necessary before considering a certain controlled environment. Often, for example, lead artefacts are stored in sealed containers or plastic bags [81].

3.2. Interventive conservation

Treatment methods are often developed using an experimental set up with artificially prepared lead samples. In general, in this case, alloys, impurities, the structure and the presence of surface products are not considered [5]. Therefore, applying approved treatments on 'real' objects must be done with care. For this reason, it is important to know the limits and consequences of the approved treatments or to contact specialists [82]. In what follows, we describe different possible treatment methods for lead metal samples with their limitations.

3.2.1. Cleaning of lead artefacts

The first and most frequently used process in the conservation and restoration of lead objects is the cleaning process. Cleaning includes tasks like the removal of the dirt and the dissolution of corrosion crusts [83]. There are, however, different possibilities to clean the lead artefact's surfaces.

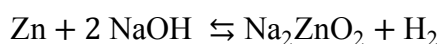
3.2.1.1. Mechanical cleaning

Often the process of mechanical cleaning is used for the removal of the dirt and corrosion products from the surface of the artefact. To remove the top part of the thick crusts, archaeological objects must be cleaned mechanically at least in a first step [84]. In the case of lead, it is difficult to visually identify the original surface, which means a trained eye is required. Furthermore, conservators must be careful using invasive equipment such as scalpels and power-driven tools. These tools may smear or scratch the underlying sample due to the softness of the lead metal [85]. Handling lead artefacts using mechanical cleaning could be hazardous considering that the dust is poisonous. Appropriate safety measures must be used. Overall, the mechanical cleaning of lead is considered difficult.

3.2.1.2. Chemical treatment

After a first rough cleaning, lead artefacts could be cleaned chemically using acids, alkalis, sequestering agents and ion exchange resins to remove the lead corrosion products [86]. In what follows, we evaluate one of each agents for lead cleaning. Different acids, such as nitric and sulfuric acid were abandoned very early in conservation history due to undesirable results. Around the 1940's, an interesting method was developed using dilute hydrochloric acid, which does not attack the lead metal, but forms a thin protective PbCl_2 crust. After that, one needs to immerse the artefact in diluted ammonium acetate, which is the only lead oxide dissolving reagent. The procedure is called Caley's method because he cleaned 56 stable objects from the Athens Agora using this method [87]. Furthermore, superficial layers produced leaves a nice appearance, which does not change for a long period of time. Ideally this treatment is used for lightly corroded specimens. In other cases, electrolytic reduction is more appropriate [88]. The method also requires careful attention to avoid dissolution of the

artefact especially using alloys. Another possible electrochemical method, known as Krefting's method, is the use of dilute nitric acid by Rathgen [89] or an aqueous caustic soda solution by Plenderleith [90] with some metallic zinc powder to dissolve the crust using the following reaction [91]



This powder, in the form of granules, provides a homogeneous current distribution along the artefact. After washing the artefact with tap water, the artefact looks clean, but often residues of metal salts remain on the surface. In the work of Brown [86], an example is mentioned where a seal of Pope Paul III was treated using this method. However, the lack of selectivity and reaction control makes this method problematic for stabilization purposes.

A frequently reported method involves the immersion of the lead and lead alloyed artefacts in a solution of a sequestering agent [92]. Often a 4-10% aqueous ethylenediaminetetraacetic acid (EDTA) disodium salt solution is used, following the procedure developed by Kuhn [93]. In a publication of Van den Abeele et al. [94], EDTA was tested on artificially corroded metal plates (copper, brass and lead). Working on artefacts, Lane [95] warns us that the sequestering agents creep under the crust and start attacking the bare lead. Also, when using EDTA, it is recommended to put the sample in a bath of ammonium acetate to remove the lead oxides [5].

Another example is described by Brown et al. [86] where a lead metal medal was cleaned by using hot-distilled water and an ion-exchange resin in the acid form, which has the advantage of avoiding chemicals and multiple rinsing steps. During the procedure, the resin beads absorb Pb^{2+} ions from the corrosion products while at the same time the CO_2 and organic acids are boiled off [96]. However, for heavily corroded artefacts this method is often less effective. In some cases, conservators have seen damage of the artefacts [97].

Looking at all treatments mentioned, most of the chemicals used are corrosive towards lead. Therefore, treated lead artefacts must be rinsed thoroughly. However, experience has taught us that rinsing is never entirely effective, which means corrosion starts again [98].

3.2.1.3. Laser cleaning

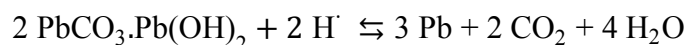
Cleaning lead artefacts using pulsed lasers is a feasible option, despite lead's low melting temperature. Indeed, a short pulse duration and a low repetition frequency, or the use of a water bath, avoid local heat accumulation. Thick crusts can be easily removed, preserving a thin protective patina [99]. Drakaki et al. [100] successfully used this method for the cleaning of Roman coins.

3.2.2. Stabilization of lead artefacts

Whereas cleaning processes dissolve the entire corrosion layer, stabilization processes are characterized by maintaining the details of the corrosion crust. Stabilization methods are often used on artefacts with thick corrosion crusts.

3.2.2.1. Plasma cleaning

A plasma treatment converts corrosion products in the crust to metallic lead by using a hydrogen plasma following the reaction [101]



Depending on the procedure's characteristics, such as the concentration of the gas mixture, the pressure and the type of electrical discharge, the treatment's performance changes. The limiting factor is that the converted lead obstructs further reduction of underlying layers [5]. As a result, the penetration depth of the method is limited to a thickness of 0.1 to 0.2 mm, which means this method can only be used for lightly corroded artefacts. Also, in the case of lead, the temperature must be kept as low as possible [102].

3.2.2.2. Electrolytic treatment

For the conservation of lead artefacts, two processes are considered, based on reduction reactions. (1) The direct reduction of lead corrosion products or (2) the decomposition of water to produce H₂ bubbles which generate a mechanical action at the metal surface to remove crust deposits very effectively. This process can be applied locally or in solution [5].

The use of zinc granules in Krefling's method was inconvenient because of the lack of control over the electrochemical reaction, which inevitably led to the loss of the corrosion crust. A possible solution is the use of a power supply to generate the necessary electron flux. Here, the metal artefact is immersed in a conductive salt solution (such as sodium carbonate) and connected to the cathode (negative pole) of a power supply with the counter-electrode connected to the anode (positive pole). The counter-electrode is often made of stainless steel when used in alkalis, lead when used in acidic electrolytes or also platinum. The latter is usually recommended due to its inertness in all conditions. However, this set-up uses high current densities (around 2-5 A dm⁻²), to initiate a mechanical stripping of the corrosion crust due to H₂ bubbling [103].

A less invasive treatment was proposed in the 1960s by Lane [104]. In this case, the current density is kept low to avoid hydrogen bubbling and to allow the reduction of only the corrosion crust. The poor cohesion and adherence of the newly produced lead metal, make it difficult to consolidate the artefact. Therefore, the use of ion exchange resins in intimate contact with the artefact is often recommended. Three electrolyte solutions have been tested, dilute

sulfuric acid (2 to 10% H₂SO₄ v/v), sodium carbonate (5% Na₂CO₃ w/v) and sodium hydroxide (5% NaOH w/v). Each of these solutions has its advantages and disadvantages, as discussed in recent literature [105].

Later, in the 1990s, a potentiostatic method, based on a three-electrode system, was designed to control the potential applied to the artefact [105]. To start, a polarization plot is recorded to identify all possible electrochemical processes by identifying peaks in the voltammogram. Afterwards, the actual treatment can be executed by applying a constant potential and monitoring the current to check the reaction progress (see Table 3). When using the treatment on composite or fragile objects, it is recommended to perform it locally by using an electrolytic stainless steel pencil wrapped in cotton, known as an electrolytic pencil [5].

Table 3. Summary of the presented electrochemical treatments.

METHOD	MATERIALS	EFFECTS	REF
Krefting's method	Zn granules + dilute HNO ₃	mechanical stripping	[89,96]
	Zn granules + NaOH	mechanical stripping	[90]
cathodic polarization	NaOH	mechanical stripping	[97,103]
	H ₂ SO ₄	mechanical stripping	[103,106]
	Na ₂ CO ₃	mechanical stripping	[107]
consolidative reduction (galvanostatic)	dilute H ₂ SO ₄	reduction of corrosion crust	[108]
	Na ₂ CO ₃	reduction of corrosion crust	[109]
	NaOH	reduction of corrosion crust	[110]
consolidative reduction (potentiostatic)	Na ₂ SO ₄	reduction of corrosion crust	[111]
	H ₂ SO ₄	reduction of corrosion crust	[112]
	NaHCO ₃	reduction of corrosion crust	[113]

Often, authors of publications about metal cleaning forget to mention the stability of the artefacts after treatment. In most cases, however, the treatments are not successful in stopping the corrosion progression. In what follows, we give a short overview of the methods used to decrease the surface reactivity after the treatment of lead artefacts.

3.2.2.3. Fast post-treatments

Early work by Organ [86] talks about rinsing the artefact in a diluted sulfuric acid solution so that a sulphate film is formed. This method does not offer a complete protection but can be helpful in certain conditions. Another, more general, method is anodic polarization. It is used in different media such as sulfuric acid, sodium sulphate and potassium iodide [114]. This technique can also produce lead oxide films. Most of these treatments have been tested on laboratory scale, in specific conditions and often on pure metal samples. Therefore, the complete harmlessness of the treatments cannot be guaranteed in untried cases. For example, treating an artefact, the chances of changing the structure and the surface chemistry are quite high.

3.2.3. Preservation

Lead and its alloys are under constant attack by their surroundings. As proposed, eliminating organic vapours, high humidity environments, mechanical disturbances and galvanic-cell formations makes it more straightforward to preserve lead artefacts. However, in some situations this is impossible and we need to protect the artefact using inhibitors or barrier coatings. In the closing sections, we give an overview of the possibilities.

3.2.3.1. Inhibitors

Corrosion inhibitors are defined by Gräfen et al. [115] as “substances that reduce or eliminate the aggressiveness of a corrosive medium and are either already contained in the corrosive medium or are specifically added to it. A distinction is made between electrochemical, chemical, and physical inhibitors.”

The use of inhibitors for lead is rare due to its resistance to atmospheric corrosion [116]. However, organic corrosion inhibitors, that mainly contain nitrogen, sulphur or oxygen atoms, can adsorb onto the metal surface to protect the underlying bulk material against corrosion [117]. For example, volatile amines can be used in closed museum humidification systems to decrease the corrosion rate of lead metal artefacts, which is probably due to self-assembly [118]. Several amino acids have also been tested to inhibit lead corrosion.

However, surfactant inhibitors with a polar hydrophilic head and a non-polar hydrophobic tail are often used, because of their many advantages such as high inhibition efficiency, low price, low toxicity, and easy production [117]. To illustrate, Sharma et al. [119] used benzotriazole for the protection of ancient and historic leaded bronzes due to the formation of

crystalline polymeric Pb-BTA and PbO-BTA complex film [120]. Brunoro et al. [121] suggested that alloys showed a lower inhibition efficiency because of a weaker metal-triazole bond. Rocca et al. [122] worked extensively on the ability of sodium monocarboxylates to slow down lead corrosion. In this case, the passivation was a consequence of the formation of a crystalline metallic soap layer [123]. Other examples are shown in Table 4. These inhibitors are often used during the treatments to minimize attack from some reactants.

Table 4. Summary of the presented corrosion inhibitors on lead and lead alloys.

INHIBITOR	EXAMPLE COMPOUNDS	REF
volatile amines	diethylaminoethanol (DEAE)	[124]
amino acids	alanine, valine, histidine, glutamic acid and cysteine	[125]
3-amino-5-phenyl-pyrazole derivatives	3-amino-5-phenylpyrazole (PP) and 5-amino-3-(4-methylphenyl)pyrazole (PP-CH ₃)	[126]
benzotriazole (BTA)		[120,127,128]
carboxylates	sodium decanoate and sodium dodecanoate	[127,129,130]
phosphates	poly- or orthophosphates	[131]
sodium dodecyl sulphate (SDS)		[132]
hydrazine derivatives	hydrazine (Hy), phenyl hydrazine (PHy), 2,4-dinitrophenyl hydrazine (2,4-DNPHy), 4-nitrobenzoyl hydrazine (4-NBHy) and tosyl hydrazine (THy)	[133]

3.2.3.2. Barrier protection

As an alternative, a coating is applied to lead artefacts to protect them from corrosive environmental gasses. In literature (see Table 5), lead metal artefacts are often coated by rubbing the sample with a cloth coated with, for example, paraffin wax, microcrystalline waxes or a mixture of both, such as Renaissance[®] Wax (www.renaissancewaxes.com) [134]. Important disadvantages of this method are the susceptibility to the accumulation of dust and reversibility problems. Sometimes, acrylic varnishes or polyvinyl resins are also considered for

treating lead artefacts [135]. However, when these treated artefacts are kept in very humid environments, it is very likely the coating will decompose to form acetic acid [136]. Another example is coating with linseed oil to form a varnish like layer, which allows normal patination on lead roof surfaces or outdoor statues [137].

These examples show it is important to consider the conditions and the corresponding corrosion mechanisms to which the sample will be exposed after treatment. Next to the material choice, however, other important factors are needed to provide definitive conclusions about the coating's degree of protection [5]. These include the application method, number of coats, the aging and decomposition properties, the composition of the artefact and the thickness of the coating. In addition, laboratory experiments conducted using accelerated corrosion or electrochemical tests on clean or coated lead samples do not always agree with results on artefacts, even if they are placed in the same environment. Moreover, coatings which show no corrosion to the naked eye, can allow localized attacks, which indicates that the coating is susceptible to long-term corrosion [82]. Evidently, it is difficult to produce a coating which can prevent lead corrosion in atmospheres with organic acid vapour traces. At this moment, several research groups are still working on a solution for this problem.

Table 5. Summary of coatings on lead and lead alloys.

COATING MATERIAL	SPECIFICATION	REF
natural wax	beeswax, carnauba	[134]
simple waxes	polyethylene wax, paraffin wax	[87]
microcrystalline wax	Cosmolloid 80H	[138]
mixture of paraffin and microcrystalline wax	Renaissance [®] wax	[134,139,140]
acrylic varnish	Paraloid B-72	[135,138]
polyvinyl resin	Butvar B-98	[135]
oil coating	linseed oil	[141]
hydrophobic silicon		[110]
carboxylates	sodium decanoate and sodium undecanoate	[142]
dicarboxylates	hydrogenated dimer acid	[143]

carboxylate polymer hydrophobic acrylate-based polymers [144]
with built-in carboxylic acid groups

3.2.3.3. Restoration

Polyvinyl acetate was once used as a glue for repairing lead artefacts. However, this kind of adhesive was abandoned because of its emission of organic acid vapours [136]. Moreover, sometimes epoxy resins are used as an embedding or restoring material [110].

4. Ethical challenges in conservation

As in other fields of conservation and restoration, the work of the metal conservators is guided by ethical standards. Over the years, a set of universal intervention guidelines has been (inter)nationally established and written down in different codes. All these documents are based on the fact that “the conservation process is governed by absolute respect for the aesthetic, historic, and physical integrity of the work, and requires a high sense of moral responsibility” [145]. Amongst these are the Code of Ethics and Guidelines for Practice of the American Institute for Conservation [146] and the professional guidelines from the European Confederation of Conservator-restorers' Organizations [147].

Specifically, in the case of metal conservation, the main concern is the destruction of valuable scientific data using specific treatments. At first sight, the patina of metallic historical objects simulates the long-lost state of artefacts. However, for technical and architectural reasons it is occasionally necessary to remove the object's patina thereby changing its appearance, allowing misjudgements to occur. Indeed, because of these treatments museum visitors or even professionals have often problems to distinguish between fakes, originals, copies or forgeries [148].

When possible, endangered and damaged historical objects must be preserved. However, a general agreement states that “one must intervene as little as possible and avoid any structural and decorative falsification” [149]. To decide which treatments should be used on valuable artefacts, it is generally accepted that one should seek opinions from a broad range of experts including archaeologists, art historians, historians, scientists and conservators [150].

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6. References

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