THE REDUCTION OF LEAD

Hannah Lane, British Museum Research Laboratory, London WC1B 5DA, England

1. INTRODUCTION

The corrosion product most commonly found on lead antiquities is basic lead carbonate, the miner hydrate [1], which under normal atmospheric conditions forms a thin homogenous layer on the surface of the lead, protecting it against further corrosion. However, under certain conditions, it often forms as a loo powdery mass which does not protect the lead underneath. Lead is normally regarded as a stable metal whose withstands corrosion very well, but exposure to the vapours of organic acids in the presence of oxygen, carb dioxide and moisture causes it to corrode quickly. Unfortunately these conditions are often found in museum storage areas. The organic acids catalyse the corrosion of the lead to produce the powdery lead carbonate, and very small amounts of it under laboratory conditions can cause the decomposition of a lead object [2]. In museum storage conditions the commum corrosion cause of lead corrosion is acetic acid given off by many types of wood, especially oak and pine, often used to make showcases and storage cupboards. It can also be present in cardboard boxes in which many lead antiquities have been stored in the past and is one of the causes of re-corrosion of treated lead antiquities in the British Museum. All the cases where lead has re-corroded after treatment have been traced to bad storage conditions. Therefore the essential problem is the protection of the cleaned lead against further attack in the presence of vapour of organic acids.

2. SURVEY OF TREATMENTS

This section compares various methods which have been published and advocated for the conservation of lead. These may be divided into three types:

1. those that are either so badly corroded or so large that only mechanical cleaning is a feasible method of treatment.

2. those objects which are only superficially corroded and have a solid lead core retaining the traces of a design. These may be treated by removal of all the corrosion products together with any traces of organ acids.

3. objects in which there is a core of sound metal but in which the design is only preserved in the corrosion layer. These objects are best conserved by preservation of the corrosion product in a stable form.

Various methods have been advocated for the removal of lead corrosion products but in some of the cases is treat the reagents and chemicals themselves may be difficult to remove completely from the lead after the treatment and may subsequently cause a further outbreak of corrosion [2]. Lead is amphoteric and is readily attacked by both acid and alkaline reagents. This includes distilled water, which has a solvent action on lead, and it should only be used for washing for a very short period, or after it has been boiled to remove any dissolved gases.

Acetic acid has been suggested as a method of removing lead corrosion products but as vapours of this acid in the main cause of lead corrosion in museum environments it cannot be recommended under any circumstances [3]. Although it is volatile it is not always easy to wash the last traces of the acid out of the lead and the small remaining trace will lead to serious re-corrosion problems in the future. Acetic acid has also been used as an electrolyte for the cleaning of lead by electrolytic reduction, but it cannot be recommended for use in any context either.

The disodium salt of EDTA [4] has also been recommended for dissolving basic lead carbonate and, although it is very good for this purpose, it also readily attacks metallic lead. For this reason, particular care must be taken if the antiquity is covered by a compact thick layer of soil and corrosion product. The solution of EDTA penetrates below this compact thick layer and attack the surface of the lead, and it is therefore important to ensure that the solution is regularly agitated and that the surface of the lead is inspected frequently. The lead object should not be left in this solution overnight, but removed and placed in tap water. It is not clear whether traces of EDTA left on the cleaned conserved lead will be harmful in the future, but it is our experience that cases where treated objects have been stored in adverse conditions so that the corrosion has re-started, treated with EDTA have been particularly bad. On the other hand, objects which have been kept in cold conditions have not re-corroded, and in theory EDTA is a very stable compound which should not decompose in the cold environment.

Caley's method of treating lead antiquities uses dilute hydrochloric acid and ammonium acetate [5]. This is very successful on loose corrosion products, but the reaction is very much slower on those objects covered by a compact layer of carbonates and soil. The treatment must be continuously supervised because of the risk that the solution will attack any cleaned areas of lead before all the corrosion products have been removed. Furthermore, the use of hydrochloric acid is not to be advocated in a laboratory where other metal antiquities are treated and on the whole this method of stripping has been superseded by techniques such as electrolysis.

The use of ion exchange resins has also been advocated for cleaning lead [6] but on the whole these methods are not now favoured by conservators. These resins are expensive and have to be regenerated when exhausted. This is time-consuming, and it is difficult to remove all traces of the acid used in the process. The resin itself may be in intimate contact with the surface of the object and the solution needs frequent agitation. It seems likely that there is no particular advantage in using these resins, and the very dilute solution of the acid which was used
The electrochemical reduction method using a solution of sodium hydroxide and zinc granules to remove lead from lead anodes as quickly as possible has been a successful method to do so [7]. The main disadvantage of the method is that the zinc is often plated on to the surface of the lead anode giving it an unsatisfactory appearance. Therefore, the removal of lead from lead anodes is done in a process called leaching. This process is usually done in a leaching tank where the lead anodes are immersed in a solution of sodium hydroxide. The lead ions are then removed from the lead anodes by the leaching process.

The process of leaching involves the following steps:

1. The lead anodes are immersed in a solution of sodium hydroxide.
2. The lead anodes are agitated to ensure that the leaching process is uniform.
3. The lead anodes are removed from the solution and are allowed to dry.

The lead anodes are then ready for use in the electrochemical reduction process. The lead anodes are placed in a leaching tank and are immersed in a solution of sodium hydroxide. The lead anodes are then agitated to ensure that the leaching process is uniform. The lead anodes are then removed from the solution and are allowed to dry. The lead anodes are then ready for use in the electrochemical reduction process.
insoluble lead sulphate if the current is dropped below 50 mA/cm². Therefore the acid electrolyte should only be used when dealing with small objects having small areas of heavy corrosion, and the alkaline electrolyte is treating objects with large areas of heavy corrosion.

In the case of larger objects a nominal current of 100 mA/cm² tends to produce the effect of high current reduction. The heavy lead object will tend to pull down on the wire contact, so that more of the total current output will pass through the object, whereas with small, heavily corroded antiques most of the current passes straight through the wire. The anode/electrolyte/cathode wire provides a complete circuit, which offers the least resistance to the passage of the current. A corroded antiquity has a high resistance, therefore you must be more diligent to get the current to pass through the object when it has an easier bypass route. Therefore the quoted current density must be used as a 'not infallible' guide. The lead must be regularly observed and, if any bubbling is being produced from the object, the current should be reduced, often by as much as four times for large objects particularly in the alkaline electrolyte. If an acid electrolyte is used, care must be taken not to decrease the current too much, to avoid producing lead sulphate. Experiments in insulating the wire with either wax or resin to force the current through the lead were not successful [10] because the painted lead surface and the basic lead carbonate surface so porous that the insulating coating will flow through the pores under the wire as insulating it from the object so that no electrical contact to the lead object is established. The powder format of the basic lead carbonate is easily completely impregnated with the coating which will insulate the molecules of the corrosion, preventing any treatment taking place.

As a result of the treatment of the mineralized silver lyre from Ut [10] the use of partially rectified current was also tried, but no benefits were observed.

Some lead antiques have areas of corrosion that can be seen to consist of a mass of cracks across apparently lightly corroded surface penetrating into the centre of the object. In fact this is a sign of intense corrosion, the whole surface, sometimes the whole object, being formed into separate layers or tiny blocks of corrosion. These cracks are actually filled with soil or dirt, holding all these tiny blocks together, but a surrounding corrosion often masks this fact. If an attempt is made to remove the corrosion or carry out consolidation the soil will fall away and the whole area will disintegrate. Preliminary mechanical brushing will often give an appearance of metallic lead on the surface due to isolated grains of metallic lead in a mass of basic lead carbonate and only mechanical methods of cleaning can be used in these cases.

To test the effectiveness of the consolidative reduction method, specific gravity measurements were carried out both before and after treatment of a series of Indian lead coins. X-ray diffraction analysis showed a corrosion product to be basic lead carbonate, and emission spectrographic analysis revealed traces of tin, copper, tin and iron, with up to 5% tin in the original metal. From specific gravity measurements using two solvents the immersion liquid it could be calculated that from 7 to 20% of the coins consisted of corrosion products. After treatment by consolidative reduction in acid and alkaline electrolytes, specific gravity measurements gave a res of over 99% metallic lead.

It should be noted that after treatment by consolidative reduction the lead is very porous and fragile, and little mechanical cleaning can be done, so that the treated lead has a darker appearance than normal. It may also be necessary to strengthen the object by impregnating it with a suitable consolidant.

Consolidative reduction is not an easy treatment because the physical state of each object has to be carefully evaluated and the process monitored, but the resulting success achieved on objects which would otherwise have been left to corrode away, or reduced to an unrecognizable state by other methods, is worth an extra effort to the conservator.

REFERENCES

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