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1. INTRODUCTION

The corrosion product most commonly found on lead antiquities is basic lead carbonate, the mineral hydrocerussite [1], which under normal atmospheric conditions forms a thin homogeneous layer on the surface of the lead, protecting it against further corrosion. However, under museum conditions it often forms as a loose powdery mass which does not protect the lead underneath. Lead is normally regarded as a stable metal which withstands corrosion very well, but exposure to the vapour of organic acids in the presence of oxygen, carbon 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 can cause complete destruction of a lead object. In museum storage conditions the commonest contaminant 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 this 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 the vapour of organic acids.

2. SURVEY OF TREATMENTS

This section compares various methods which have been published and advocated for the conservation of lead.

Lead antiquities 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 organic 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 must be 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 problems arise because the reagents will actually attack the metallic lead as well as dissolving the basic lead carbonate, or the 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 are 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 this 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 must penetrate 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 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, the objects treated with EDTA have been particularly bad. On the other hand, objects which have been kept in good conditions have not re-corroded, and in theory EDTA is a very stable compound which should not decompose and leave traces of acetic acid on the object.

Caley's method of treating lead antiquities uses dilute hydrochloric acid and ammonium acetate [5]. This can be 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 electrolytic reduction.

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 must 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 for electrolytic reduction would be just as efficient as a method of stripping corrosion products from lead.

The electrochemical reduction method using a solution of sodium hydroxide and zinc granules to produce nascent hydrogen is quite a successful way of stripping lead and has the advantage of not requiring an external source of energy, although heating does speed up the process [7]. The main disadvantage of the method is that the zinc is often plated on to the surface of the lead antiquity giving it an unnatural blue grey appearance which is difficult to remove.

By far the best method for removing basic lead carbonate from lead antiquities is to use the electrolytic reduction technique in which the object itself is made the cathode in a suitable electrolyte. A current of 2 to 5 amps per square decimetre of surface area is passed at about 12 volts [7]. The electrolytic process needs very little supervision, although it is important to check frequently that the current is passing, as otherwise the antiquity will start to dissolve. The electrolyte should be one which is harmless to the antiquity and the operator and for these reasons solutions of cyanide and of acetic acid are not recommended. Sodium hydroxide is perhaps the most commonly used electrolyte but adequate ventilation is required to remove the fine alkaline spray which is given off during the process, and a 5% solution of sodium carbonate is more satisfactory. The current should be running before the antiquity is lowered into the electrolyte. A 10% solution of sulphuric acid has also been used, but once again the current must be switched on before the antiquity is lowered into the electrolyte to prevent the layer of basic lead carbonate being converted to lead sulphate. Sulphuric acid can have the disadvantage of leaching out certain elements from the lead alloy. A reason for its use is to try and form a chemical layer on the surface of the lead, when the reduction is complete, to act as a protection against further corrosion attack. At the end of reduction the current is switched off to give a layer of lead peroxide [8].

The material for the anode must be compatible with the electrolyte. Iron anodes may result in the deposition of iron on to the lead object when sodium hydroxide is used as the electrolyte, but this is of little importance during the final washing it rusts and is easily brushed away. When sodium carbonate and sulphuric acid are used iron anodes are very quickly attacked and so cannot be used. Stainless steel will tend to become pitted and is a possibility of chromium or nickel being deposited on the lead. However, it is possible to select a stainless steel stabilized with molybdenum which does not suffer from this defect. Platinized titanium is ideal and does not clean and lasts indefinitely, but it is very expensive. Carbon anodes are quite useless in all electrolytic processes.

The lead object should be connected up to the supply of electricity with a suitable wire which will support the weight of the object and which will not dissolve in the electrolyte or under the conditions of reduction. Copper wire is normally used and, if the antiquity is very heavy, padding, such as foam rubber, should be used between it and the wire at the points where the weight is supported, to prevent marking the soft lead.

Those objects that still retain a metal core with some design visible in the basic lead carbonate layer can only be treated by a technique that will prevent the formation of a corrosion layer so as to retain the design, that will at the same time stabilize the lead to prevent further corrosion that will allow the object to be handled without loss of the powdery surface, and that will ensure that the object has the appearance of lead. Such a technique was described by Organ as Consolidative Electrolytic Reduction at the IIC Conference in Rome in 1961 [9]. Reduction is carried out at a very low current density, reducing the basic lead carbonate to a compact mass of lead in situ, the lead ions being reduced exactly in the same place on the surface of the object instead of being removed into the electrolyte and forming a loose sludge, which is removed in the finishing process after washing out the electrolyte [8]. In this process the surface detail is retained and the organic acids are removed, but no further design will be revealed. This is due to the structure of basic lead carbonate which tends to prevent the formation of original surfaces in the lead layers as is sometimes the case with some bronze and silver antiquities.

In the original procedure the fragile lead object was connected to the cathode by stainless steel wire, supported by polyurethane foam pads held together by spring-loaded anodes of platinized titanium, iron or stainless steel. The electrolyte was 5% sodium hydroxide and the current density was 100 mA/dm². The evolution of hydrogen bubbles indicates that reduction has been completed. It is very important that no hydrogen is given off during reduction as these come from the metal surface and would therefore cause reduction in situ, causing the lead to deposit elsewhere on the object, resulting in a mass of reduced lead with little resemblance to the original appearance. This will happen at a current density over 250 mA/dm². The current must be low enough to prevent this, yet high enough to ensure that the metallic lead is cathodically protected.

Lead anodes should not be used as they quickly deposit lead on the object in an alkaline electrolyte. Lead wire should be used for the negative connection; tinned-copper wire is recommended. If foam is needed they can be held against the object by plastic-covered wire instead of spring-loaded anodes.

Since Consolidative Reduction had been successfully carried out on silver objects [10] using different materials and electrolytes, it was decided to carry out further experiments on fragile lead [11]. As 10% sulphuric acid had been used as an electrolyte in normal reduction to give a protective surface layer in the finish it was tried out for consolidative reduction [8]. The same current density was used, but the anode was lead wire. Other materials such as tinned-copper wire, iron and stainless steel soon disintegrated and fell onto the object. If there are some smooth areas of uncorroded lead on the object, lead foil should be used to connect the cathode rather than lead wire, which tends to mark the smooth surface. The foil can be used to support the fragile lead instead of foam pads and it can be reused. The reduction takes longer than in normal electrolyte, and depends on size and amount of corrosion. Hydrogen gas bubbles are only occasionally seen on the completion of reduction; therefore it is necessary to take out the object and examine it during the treatment to determine whether reduction is complete. The reversal procedure at the end of reduction is as follows:

insoluble lead sulphate if the current is dropped below 50 mA/dm^2 . Therefore the acid electrolyte should only be used when dealing with small objects having small areas of heavy corrosion, and the alkaline electrolyte for treating objects with large areas of heavy corrosion.

In the case of larger objects a nominal current of 100 mA/dm^2 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 antiquities 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 it is more difficult to get the current to pass through the object when it has an easier by-pass route. Therefore the quoted current density must be used as a 'not infallible' guide. The lead must be regularly observed and, if any bubbles are 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 pitted lead surface and the basic lead carbonate surface are so porous that the insulating coating will flood through the pores under the wire and insulate it from the object so that no electrical contact to the lead object is established. The powdery formation of the basic lead carbonate is easily completely impregnated with the coating which will insulate the molecules from the corrosion, preventing any treatment taking place.

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

Some lead antiquities have areas of corrosion that can be seen to consist of a mass of cracks across the 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 the surrounding corrosion often masks this fact. If an attempt is made to remove the corrosion or carry out consolidative reduction 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 the 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 the corrosion product to be basic lead carbonate, and emission spectrographic analysis revealed traces of silver, copper, tin and iron, with up to 5% tin in the original metal. From specific gravity measurements using toluene as 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 result of over 99% metallic lead.

It should be noted that after treatment by consolidative reduction the lead is very porous and fragile, and very little final mechanical cleaning can be done, so that the treated lead has a darker appearance than normal. It is also 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 on the part of the conservator.

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