Progress in Organic Coatings xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

The application of organic coatings in conservation of archaeological objects excavated from the sea

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ARTICLE INFO

Article history:
Received 22 January 2016
Received in revised form 28 April 2016
Accepted 2 May 2016
Available online xxx

ABSTRACT

Protection of maritime cultural heritage is the mission of the National Maritime Museum (NMM) in Gdansk. This includes preservation of historical, cultural objects related to boat building, shipbuilding, sailing, military science, maritime education etc. Many archaeological objects, made from metal, wood and other organic materials and excavated from a wet environment, are kept at the NMM in Gdansk. In order to prevent the objects from any further degradation after the initial conservation process, different approaches are used including application of coatings, wax, paraffin wax and/or addition of different inhibitors. Due to various limitations (costs, human resources) conservators have been evaluating the performance of the coatings based on visible changes (corrosion signs) to decide when reapplication of the coating is necessary. In most cases the visible changes are indicators of coating damage and are non-reversible in character. Therefore there is a great need to find a method that will allow assessment of the performance of the coating in a relatively short time and efficient way. Electrochemical techniques such as measurement of DC resistance, Electrochemical Impedance Spectroscopy or Electrochemical Noise Measurement offer a way of achieving this. Each produces a number which is a measure of the ability of the particular coatings/inhibitor to protect effectively. In this paper the authors take as examples four coatings used to protect metal objects from particular shipwrecks found in Baltic area. Results are presented of some preliminary work conducted attempting to assess (rank) these four coatings on steel and copper using the DC resistance method. It is anticipated that this work will become one potential strand of a new development plan for better maintenance of archaeological objects.

1. Introduction

1.1. General background

Metallic archaeological objects which have been recovered from the sea are most affected by chloride-induced corrosion. The corrosion mechanism is based on electrochemical processes. Metals undergo corrosion in a much faster manner due to higher oxygen concentration [1,2]. When excavated, metals especially iron are likely to undergo more rapid corrosion. This is because when metal objects are lifted out of the sea, as the sea water dries out, salts concentrate and with oxygen being more readily available this leads to an accelerated corrosion rate. It can cause for instance weeping of iron that is indicative of high chloride content and results in cracking, fragmentation and break-up of objects [3]. Therefore it is crucial to start the conservation process to enable preservation of the object soon after excavation. If this is not possible immediately then the metallic object should be immersed in tap water until it can be treated.

The treatment commences with a preparation process (cleaning) followed by conservation practices. There is a wide scope of activities which include both preventative strategies and remedial treatment. Depending on the state of the object, mechanical or chemical methods or their combination is applied to remove external layers of corrosion products, marine microorganisms or tar etc., as well as chlorides from the inside of the object structure [4]. In comparison to chemical and mechanical treatment hydrogen plasma reduction is a shorter method [5,6].

Figs. 1 and 2 presents typical objects from General Carleton Shipwreck. Fig. 1(a,b) shows the bronze bell before and after a conservation process. This English bark—coal carrier was built in 1777 in Whitby, and sank on 27th May, 1785 during a catastrophic storm in the Baltic Sea about 400 m from Piaśnica. The underwater

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http://dx.doi.org/10.1016/j.porgcoat.2016.05.001
0300-9440/

Fig. 1. The bell from General Carlton: (a) before and (b) after cleaning.

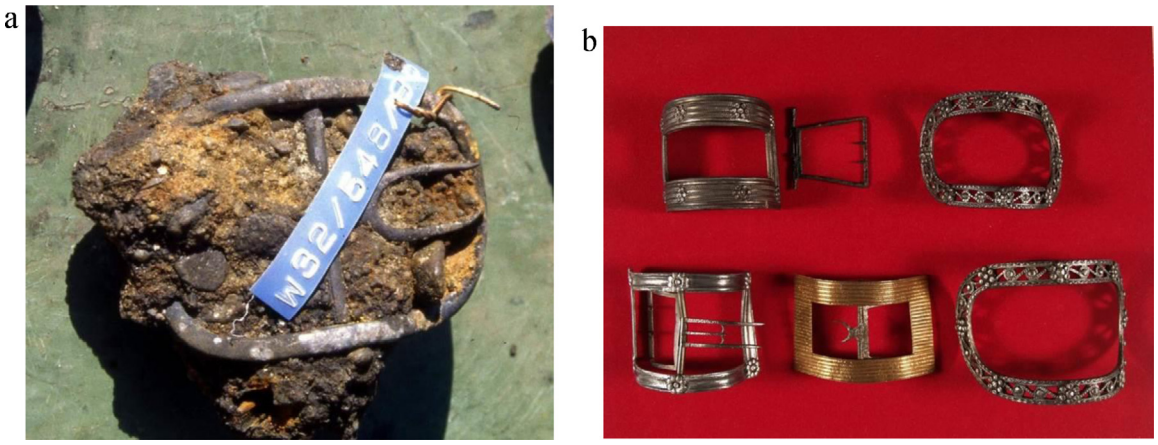

Fig. 2. Buckles from the wreck of the General Carlton: (a) before and (b) after cleaning.

excavations started in 1995 and were completed four years later. The main procedure commenced with mechanical cleaning off the metal surface to remove a thick layer of concretion [7]. Afterwards it was immersed in a 10% solution of EDTA which forms complexes therefore extracting any chloride. It is then mechanically cleaned again and rinsed with water. Later it is dried and degreased with ethanol. The bell has been found in the first period of the excavation, allowing the vessel's identification. This is similar to what happened in the case of the sinking of H M S Association in 1707 off the Scilly Isles where the ship's Bell allowed identification of the wreck. One of the authors worked on the objects from that wreck and from several other ships which sank in that area. A summary of a report on that work is available [8].

Another example from the same shipwreck are buckles used for both clothes and shoes (Fig. 2) made from pewter. The buckles were initially cleaned using mechanical methods and rinsed with distilled water. Then autolysis was performed (this is a galvanic method where the specimen is connected to Al foil in 10% NaOH). Later objects were boiled in distilled water, again mechanically cleaned and one more time boiled in distilled water. In both cases the surface of the objects was degreased and preserved.

For further preservation application of coatings, wax, paraffin wax and/or addition of different inhibitors is one approach. For instance at the end of the initial preservation process the bronze bell was coated (by brush) with paraffin wax dissolved in benzene whereas the buckles were coated with warm paraffin wax (by dipping). The purpose of a protective coating used in the archaeological field is different to that of a (paint) coating applied to a metal surface which will be exposed in service to rural, industrial or marine environments, sometimes quite severe. Conservation coatings have two main purposes. They must protect the object from corrosion during handling and in the (normally relatively benign) environment in the museum (and in its storage area). And they must prevent further deterioration by any corrosion products which have been left on or in the surface. They are more like temporary protectives which should absolutely minimize any change in the appearance of the item. Hence they need different properties: they must not

Please cite this article in press as: K. Schaefer, D.J. Mills, The application of organic coatings in conservation of archaeological objects excavated from the sea, Prog. Org. Coat. (2016), http://dx.doi.org/10.1016/j.porgcoat.2016.05.001