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# The Application of Organic Coatings in Conservation of Archaeological Objects Excavated from the Sea.

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## 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 boatbuilding, 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.

## Introduction:

### 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. When excavated, metals especially iron undergo corrosion in a much faster manner due to higher oxygen concentration [1-2]. 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 are 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].

Fig. 1 and Fig. 2 presents exemplary objects from General Carleton Shipwreck. Fig. 1 (a,b) shows the bronze bell before and after conservation process. This English Bark Coal Carrier was built in 1777 at Whitby and sank on 27<sup>th</sup> May 1785 during a catastrophic storm in the Baltic sea about 400m from Plasnica. The underwater excavations started in 1995 and were completed four years later. The main procedure commenced with mechanical cleaning of 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].



a

b

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



a

b

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

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 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.

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 adhere too strongly, they should be almost transparent and they must be removable by stripping or dissolution. Conservation professionals from the National Maritime Museum use coatings that fulfill the above requirements. Among coatings that have proved to be reliable are PMMA, epoxy, polyurethane and acrylic coatings. In addition in some cases some particular inhibitors together with paraffin wax in benzene i.e. benzotriazole, ethylenediamine are used.

Due to various limitations (costs, human resources) conservators have been evaluating the coating's performance 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. Overall though, when it comes to selecting coatings, it is very much a question of trial and error. At present the applicator cannot be really confident that a homogenous coating at the correct thickness has been applied. Nor can one be sure that the optimum coating for that particular object is being used. Nor is there any measurement method currently available that can monitor the coating's performance other than visual observation. 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. How to approach this is discussed below.

### **Electrochemical Techniques**

Use of electrochemical techniques is one way of assessing the ability of coatings to protect metal substrates. These methods can be used to both rank the effectiveness of different candidate coatings; and to assess different application methods (dipping, brushing, spraying). They also offer the possibility of monitoring the coatings in their "field" situation. The main premise that such work is based on is that ionic resistance is a very important controlling factor in preventing corrosion, hence a measurement of this parameter will indicate the protection ability of the coating. The original work by Bacon Smith and Rugg indicated for full paint systems immersed in sea water that coatings with resistances  $>1 \times 10^8 \Omega \cdot \text{cm}^2$  offered good,  $1 \times 10^6 - 1 \times 10^8 \Omega \cdot \text{cm}^2$  fair and  $<1 \times 10^6 \Omega \cdot \text{cm}^2$  poor protection [9]. These figures may need to be reduced somewhat for the types of coatings used in preservation. A working hypothesis is that, in 3% NaCl, less than  $5 \times 10^4$  is poor, between  $5 \times 10^4$  and  $1 \times 10^6$  is fair and above  $1 \times 10^6$  is good. In terms of a measurement method there are three main candidates: ENM, EIS and DC Resistance. These three were compared in a fairly recent publication [10]. ENM (Electrochemical Noise Method) normally requires two identical samples which can be difficult to find. EIS is popular in laboratory investigations and has been used to assess external structures. However the method is not simple to apply: it takes time to make a measurement and requires fairly complex equipment. The preferred approach (and the only one employed in this paper) is DC resistance (Fig. 3). This has the advantage of being quick to get a reading and providing just one number. The successful use of the DC Resistance method was reported recently in work assessing the effect of surface finish on the performance of alkyd and vinyl based paints [11]. Note that although electrochemical techniques have been used to assess rusty steel on outside structures and coatings on exterior bronze sculptures [12], their use for assessing coatings used for preservation of museum's objects has been limited. In the case of objects that are exposed to high levels of chlorides electrochemical techniques have been used so far either to monitor storage of the objects immersed in solution or to clean and stabilise them [13].

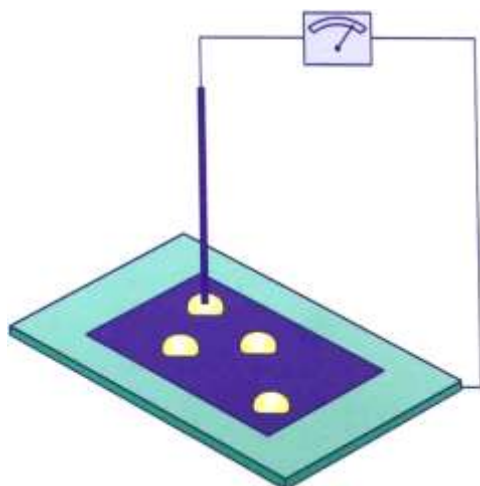


Figure 3 Method of making DC resistance measurement

### Experimental

In the experimental work outlined below, coatings which are typically used in conservation were prepared on steel Q panels (Low carbon steel, from Q panel company) and on pure copper foil (Goodfellow metals). Apart from visual observation the samples were also assessed by DC resistance measurement. This was done using a quick test where drops of solution were applied in up to a dozen places on the sample. The drop test is applicable in these circumstances (rather than the more standard approach of sticking cells on) as the relatively low protective ability of the coatings when exposed to salt solutions means results can be obtained within a relatively short period of time (hours rather than days).

### Materials

#### Coatings

Four solutions of coatings were obtained from the National Maritime Museum of Gdansk. These are shown in Figure 4 (Fig. 4) and were supplied in different solvents (benzene, toluene, or methanol) and given numbers 1-4: (1) Paraffin wax in benzene (2) McKenic (Hellfeier Sp. z o.o., Ruda Śląska (Poland)) in toluene, (3) Paraloid B82 (Blik, Toruń (Poland)) and (4) Paraloid B44 (Blik, Toruń (Poland)). These coatings are all used for conservation of metal objects at the museum. They dry by solvent evaporation to form a thin thermoplastic layer. Three out of the four were commercial products. It is understood that B44 and B82 are based on acrylic copolymers. None of them had deliberate inhibitor additions. Further information is not available.





Figure 4 Coatings used (as solutions)

### **Substrates : Steel Q panel and pure copper foil**

*Application of coating to steel* The panel surface was cleaned with xylene. Then the solution was dropped on the surface and drawn down, using the 120 $\mu$ m Kbar . The wet film thickness should be 60 $\mu$ m But due to the very large amount of solvent in these coatings the dry film thickness was only a fraction of this. One layer of coating was applied from all solutions. Two layers of coating were applied using 3 and 4. Air drying in fume cupboard with a small inlet of air was used to form the coating.

*Application of coating to copper* The McKenic (2) coating was applied to the copper by dipping and then drying in the laboratory air to form the coating.

*Solutions* 3% NaCl and 0.5% NaCl were prepared from AR sodium chloride and distilled water.

### **Techniques**

*Thickness measurement* A Defelsko Positest thickness DFT gauge was used. This has two settings One for non-ferrous metals (presumably using eddy current) and one for ferrous metals (presumably using magnetic effect) It was operating very much at the limit of its sensitivity. It appeared that the thickness achieved with single coat films were all low (less than 5 $\mu$ m). Double coat films were between 5 and 10  $\mu$ m.

*DC resistance measurement* A single Calomel reference electrode was used in conjunction with a DC Keithley electrometer (Fig. 3). This instrument measures DC resistance accurately up to 1E11 ohms. Furthermore it can measure resistance when what is being measured is itself generating a voltage. However in this work, it is being used towards the bottom end of its range ( $1 \times 10^3$ - $1 \times 10^7$ ). To make the measurement the minimum value of current required to get a measureable “kick” was used. Drops of 3% NaCl solution were placed on the surface (Fig. 5).

Measurements were made after 30 minutes and after overnight exposure, typically a time period of 18 or 20 hours (evaporation was prevented by covering the samples and using a water seal).



Figure 5 Picture showing the way of measuring DC resistance using drop method

*Visual assessment* Normally assessment was by eye and photographs were taken; sometimes a Binocular microscope was used.

## Results and discussion

### Single coat on steel (coatings 1,2 3 and 4)

Several attempts were made using different K bars and draw down rates to get a good single coat on steel with all four solutions. But the resultant coatings were all very thin, less than 5  $\mu\text{m}$ . When drops of 3% NaCl were applied, coatings 1,2 and 3 showed some corrosion almost immediately (within half an hour) Fig. 6 and 7).



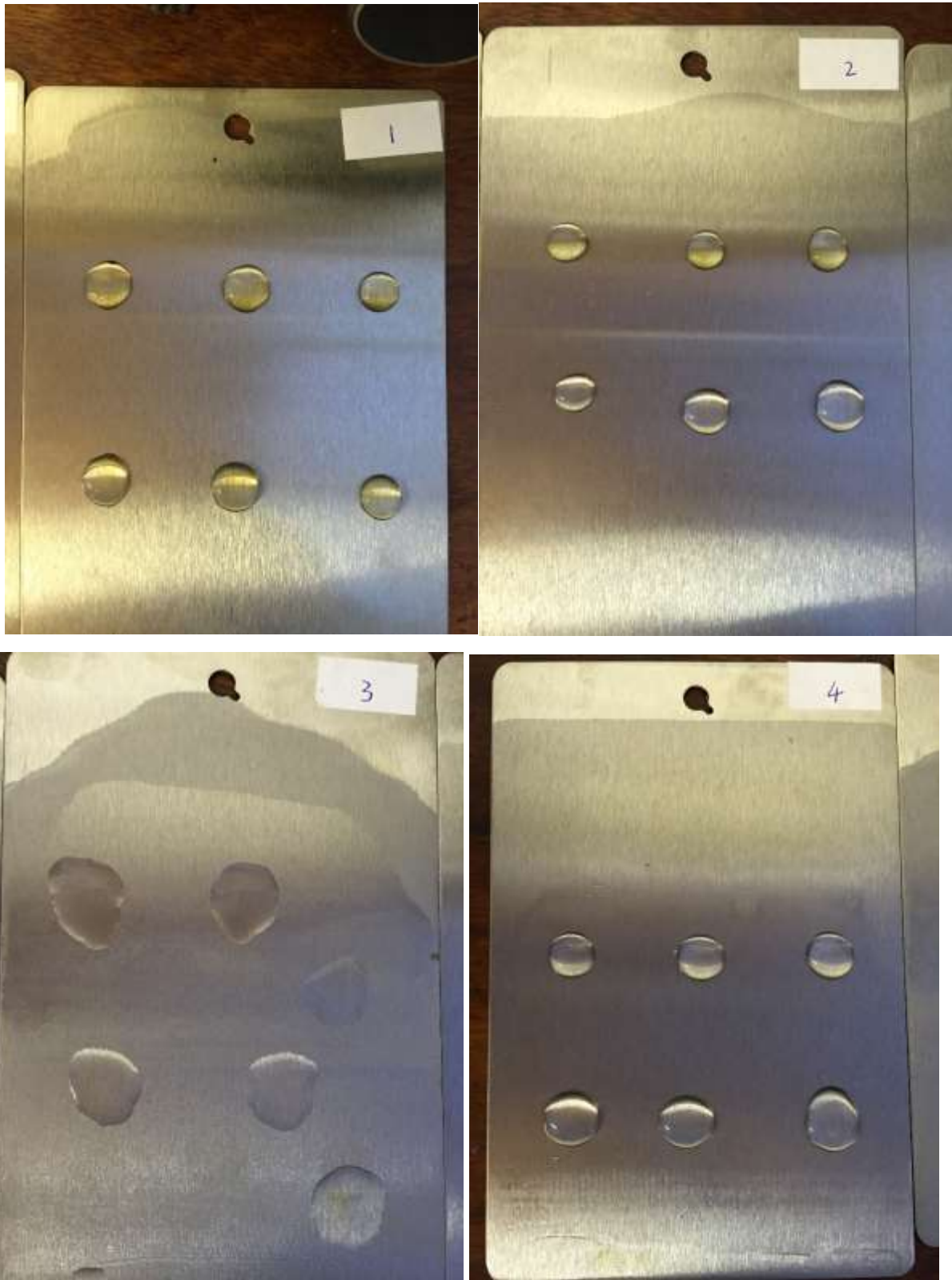


Figure 6 Appearance of single coated steel samples with drops of 3% NaCl applied after 30 minutes: 1) Paraffin Wax in Benzene 2) McKenic in Toluene, 3) Paraloid B82, 4) Paraloid B44



Figure 7 Appearance of single coated steel samples with drops of 3% NaCl applied after 20 hours : 1) Paraffin Wax in Benzene 2) McKenic in Toluene, 3) Paraloid B82, 4) Paraloid B44

**Table 1 DC resistance in Ohms of single coat films (<5µm) on steel in 3% NaCl drops in top row in Figures 6 and 7) (a, b and c are values from, left to right in the pictures,**

Type of wax	area letter	DC resistance (30mins)	DC resistance(20hr)
Paraffin Wax in Benzene	1a	$5 \times 10^3$	$5 \times 10^3$
Paraffin Wax in Benzene	1b	$4 \times 10^3$	$4 \times 10^3$
Paraffin Wax in Benzene	1c	$5 \times 10^3$	$6 \times 10^3$
MacKenic in Toluene	2a	$2 \times 10^4$	$8 \times 10^3$
MacKenic in Toluene	2b	$1 \times 10^4$	$6 \times 10^3$
MacKenic in Toluene	2c	$3.4 \times 10^4$	$7 \times 10^3$
Paraloid B82	3a	$5 \times 10^3$	$5 \times 10^3$
Paraloid B82	3b	$5 \times 10^3$	$5 \times 10^3$
Paraloid B82	3c	$9 \times 10^3$	$4 \times 10^3$
Paraloid B44	4a	$7 \times 10^7$	$4 \times 10^4$
Paraloid B44	4b	$5 \times 10^7$	$5 \times 10^4$
Paraloid B44	4c	$4 \times 10^7$	$6 \times 10^4$

Also, as shown in Table 1, all the DC resistance for coatings 1,2 and 3 values were low ( $5 \times 10^3$  or less). They were somewhat higher for coating 4 and with that wax coating initially no corrosion was visible. By the following morning the values of resistance of all four samples were low and corrosion was now also occurring to a limited extent under coating 4. The experiment was repeated with 0.5% NaCl (results not given). But again the resistances were all low and again corrosion, although it took a little longer to appear, was visible after a relatively short time. It was nonetheless possible to rank the four coatings in order that their ability to prevent corrosion with the Paraloid B44 being the best and the McKenic being the second best. However because thickness is a critical variable and it may be that the more poorly performing systems were thinner, the inability to measure the thicknesses of any of the single coatings accurately means that no very definite conclusions can be drawn.

#### **Double coat on steel (coatings 3 and 4)**

Double coatings were prepared by spreading a second coating using the K Bar on the first coating's surface after the latter has dried. Two types of wax coatings were applied, the Paraloid B82 and Paraloid B44. The thicknesses were now measurable at around 5 to 10 µm. Small (d=1-2cm) discrete drops of 3% NaCl solution were introduced onto the coated panel in six

places on the Paraloid 82 coating and in three places on the Paraloid 44 coating. Figure 8 shows the distribution of the areas measured. 30 minutes later DC resistance measurements were made. The samples were left overnight and again DC measurements were made after 20hrs.

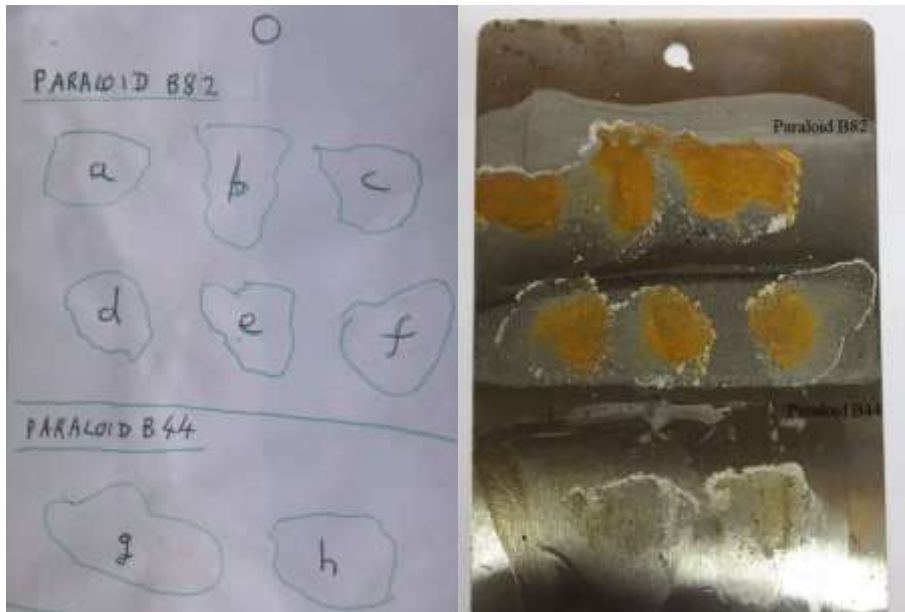


Fig. 8 Distribution of areas measured Fig. 9 Appearance of double coat coatings

for double coat coatings on steel Q panel on steel Q panel after twenty four hours

Fig 9 show the appearance of the samples after 20 hrs respectively. The picture shows (as expected from the single coat results ) that the double coat Paraloid B44 is still somewhat better than the Paraloid B82 although the difference is not as marked as when they were applied single coat. Resistance results are shown in Table 2. They show higher values than the single coat. There is some indication of greater resistance values from the Paraloid B44 than the Paraloid B82 at the same thickness. But neither coating would be expected to provide protection to steel objects for more than a day or so in 3% NaCl.

**Table 2 DC resistance in ohms of areas of two coat Paraloid 44 and Paraloid 82 films (4-10µm) on steel to which drops of 3% NaCl had been applied (position of individual areas shown in Figure 8)**

Type of wax	area letter	DC resistance (30mins)	DC resistance (20hr)
Paraloid B82	a	$5.2 \times 10^5$	$2.6 \times 10^4$
Paraloid B82	b	$5.2 \times 10^5$	$2.6 \times 10^4$
Paraloid B82	c	$5.3 \times 10^5$	$2.7 \times 10^4$
Paraloid B82	d	$5 \times 10^5$	$2.5 \times 10^4$
Paraloid B82	e	$5.1 \times 10^5$	$2.6 \times 10^4$
Paraloid B82,	f	$5.1 \times 10^5$	$5.5 \times 10^4$
Paraloid B44	g	$2.8 \times 10^5$	$8 \times 10^4$
Paraloid B44	h	$6 \times 10^5$ .	$4.3 \times 10^5$

#### **Double Coat on Copper (McKenic (2) only)**

The McKenic system was applied on copper by dipping. The first coat was allowed to dry and then the second coat was applied. Drops of 3% NaCl solution were then introduced similar to what had been done with the coatings on steel. Resistance measurements (not given here) showed the one coat to be ineffective. But as shown in Table 3 the two coat system showed values of about  $1 \times 10^6$  -  $1 \times 10^7$  initially (somewhat more variable among different areas) and these only reduced by a factor of two or three overnight. The uncoated metal showed very low values throughout. Regarding appearance (Fig. 10) it was noted that the two coat was protective after 20 hrs. But when the coating was not present some corrosion of the copper foil had occurred.

**Table 3 DC resistance in Ohms of individual areas of two coat films (10 μm) on copper to which drops of 3% NaCl had been applied ( a,b : top row, c,d bottom row)**

Type of wax	area letter	DC resistance (30mins)	DC resistance(20hr)
McKenic in Toluene	a	$1.2 \times 10^5$	$1 \times 10^5$
McKenic in Toluene	b	$9 \times 10^5$	$4 \times 10^5$
McKenic in Toluene	c	$7 \times 10^6$	$7 \times 10^5$
MacKenic in Toluene	d	$5 \times 10^5$	$3 \times 10^5$
Bare copper	a	$4 \times 10^3$	$4 \times 10^3$
Bare copper	b	$4 \times 10^3$	$5 \times 10^3$
Bare Copper	c	$5 \times 10^3$	$3 \times 10^3$
Bare Copper	d	$9 \times 10^3$	$6 \times 10^3$

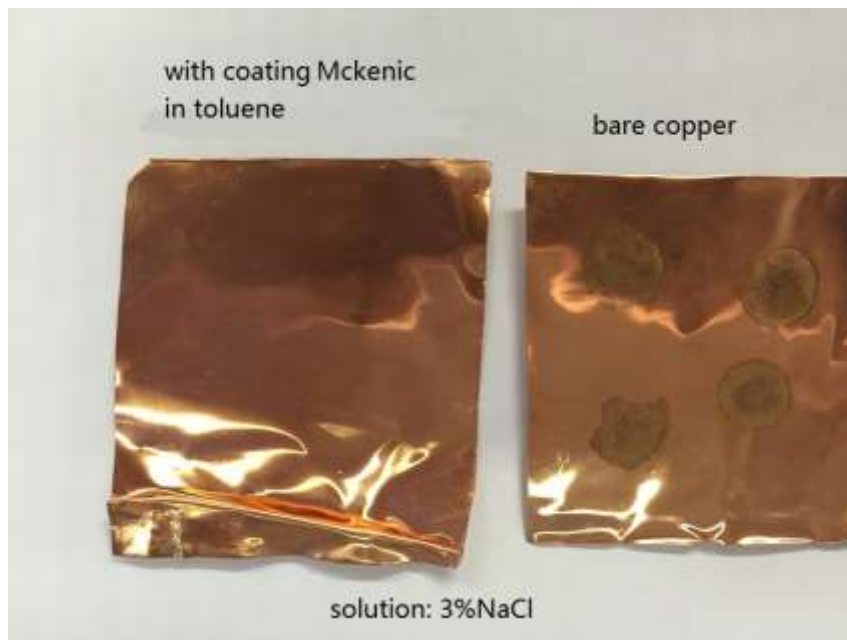


Figure 10 Appearance of 5x5 cm Copper foil sample with 2 coating layers and without coating on which four drops of 3% NaCl solution had been left overnight.

### General Discussion

This preliminary work has shown that the DC resistance method is capable of assessing the ability of these types of coatings to protect against corrosion and enables differentiation between fair and poor coatings to be achieved. The results correlate with visual appearance of corrosion. A method of more accurately measuring the thickness (an important variable) of these thin coatings



needs to be found. Although there is evidence of a fairly homogenous resistance and hence homogenous corrosion protection ability on a 1-5cm<sup>2</sup> scale, visual observation of the samples under the binocular microscope showed some of the coatings not to be uniform on the sub mm scale (particularly the one containing paraffin wax) with particles visible. This needs to be further investigated.

### **Further work**

There are several possible continuing lines to this investigation. It is intended to use the same techniques to look at wax coatings applied to rusty steel and to corroded copper. These latter surfaces will be prepared by exposure of the metals to Baltic sea water in the lab for periods of up to one week, then brushing off most of the corrosion product before applying the coatings. Also McKenic and Paraloid 44 can have inhibitors added to them for instance benzotriazol and ethylenediamine. These inhibitor containing coatings will be investigated both on clean and corroded steel and copper.

In the longer term it is hoped to use the DC resistance technique to assess the coatings on actual Heritage objects being stored (or even exhibited) in the National Maritime Museum in Gdansk. It is likely that a less aggressive solution than 3% NaCl will be used for this eg diluted Harrison's solution (0.35% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.05% NaCl). Although lower in salt than 3% NaCl, this solution is slightly acidic and also may well be more representative of the composition of condensation in the museum environment or outside (also more representative of any contamination due to handling and other reasons). Although Calomel electrodes and mains operated DC resistance measuring equipment may be used initially for this, a portable system of resistance measurement will eventually be needed.

### **Conclusions**

What has been reported here is very much preliminary work. Nonetheless it appears that, despite the differences between "normal" paints and these conservation coatings (the need for transparency and ease to removal means they are thermoplastic and have to be applied thinly), an electrochemical method for monitoring /assessment of such a coating can be developed not only to assist formulation but also for quality control and monitoring. There are various candidates for the electrochemical method. But this work has indicated that the simplest method viz DC resistance measurement shows considerable promise. This project is on-going and it is hoped that further work will be reported in the fairly near future eg at EuroCorr 2016.

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## References

1. F. Kergourlay, C. Remazeilles, D. Neff, E. Foy, E. Conforto, E. Guilminot, S. Reguer, Ph. Dillmann, F. Nicot, F. Mielcarek, J. Rebiere, Ph. Refait, *Mechanisms of the dechlorination of iron archaeological artefacts extracted from seawater.*, Corros. Sci. 53 (2011) 2474-2483.
2. E. Guilminot, D. Neff, C. Remazeilles, S. Reguer, F. Kergourlay, C. Pele, P. Dillmann, P. Refait, F. Nicot, F. Mielcarek, N. Huet, J. Rebiere, *Influence of crucial parameters on the dechlorination treatments of ferrous objects from seawater.*, Stud. in Cons. 57 (2012) 227-236.
3. M. Rimmer, D. Thickett, D. Watkinson, and H. Ganiaris, *Guidelines for the Storage and Display of Archaeological Metalwork.*, (2013) Swindon, English Heritage.
4. N.A. North, C. Pearson., Stud. in Cons. 23 (1978) 174-186.
5. K. Schmidt-Ott, *Plasma-Reduction: Its potential for use in the conservation of metals.*, Proceedings of Metal (2004) National Museum of Australia Canberra ACT.
6. Z. Raskova, F. Krcma, *Plasmachemical reduction for the conservation of archaeological artefacts.*, Astron. Obs. Belgrade No. 82 (2007) 159-170.
7. W. Ossowski (Ed.) *The General Carleton Shipwreck, 1785* (2008) The Polish Maritime Museum Gdańsk.
8. H. S. Campbell and D. J. Mills, *Marine Treasure Trove - A Metallurgical Examination.*, Metall. and Mater. Technologist 551 (1977).
9. R. C. Bacon, J. J. Smith, F. M. Rugg, *Electrolytic Resistance in Evaluating Protective Merit of Coatings on Metals.*, Ind. Eng. Chem. 40 (1948) 161-167.
10. D. J. Mills, *Comparison of ENM, EIS and DC Resistance for Assessing and Monitoring Anti-Corrosive Coatings.*, J. of Corros. Sci. and Eng. 8 (2008).
11. D. J. Mills, K. Schaefer, *Use of Electrochemical Methods to examine different Surface Preparation Methods for Organic Coatings on Steel.*, Prog. in Org. Coat. 69 (2010) 193-198.
12. E. Angelini, S. Grassini, M. Parvis, F. Zucchi, *An in situ investigation of the corrosion behavior of a weathering steel work of art.*, Surf. Interface Anal. 44 (2012) 942-946.
13. C. Degrigny, *Use of Electrochemical techniques for the conservation of metal artefacts: a review.*, J Solid State Electrochem. 14 (2010) 353-361.