An EIS Method for assessing thin oil films used in museums

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Abstract

Electrochemical impedance spectroscopy (EIS) is a well established technique for evaluating the corrosion preventive properties of protective coatings. National Museum of Australia (NMA) staff have used this technique in the past to evaluate and rank the corrosion performance of a number of commercial waxy coatings in routine conservation use. This testing procedure is relatively simple and gives quantitative *snapshot* data about the performance of protective coatings, allowing them to be ranked objectively. The EIS test cell presently available is suitable for testing relatively hard, thick coatings. It cannot be used in the investigation of thin, delicate and easy-to-break films such as those formed by engine oil. The objective of this investigation was to fabricate an electrode suitable for testing thin oily films using conventional EIS test cells. We desired an EIS method that could be used for rapidly testing commercial engine oils and ranking their performance. Such a test protocol is particularly crucial to the NMA who aim to identify the best engine oils for use in their functional collection of technological objects and for developing a "just noticeable wear" criteria for use in museums.

Keywords: corrosion, corrosion protection, metals, petrochemical oils, functional objects, corrosion inhibitors, engine oils.

1. Introduction

Mechanical wear inside engines is substantially related to the effectiveness of the lubricant during use and the rate of corrosion when in storage. The problems associated with lubrication are understood by most people at an anecdotal level: that is, if a lubricant is poor or absent, then a working part will wear as a result of friction. In museum practice the lubrication properties of high quality oils produced by reputable manufactures can be considered adequate to meet our requirements providing the lubricant and application are appropriately matched. Corrosive wear (Ricardo, 1992) and internal corrosion are probably a greater issue for museums than for most users. This paper is part of a body of work designed to evaluate the importance of corrosion and wear to museum collections of mechanical objects. Where the effect is significant we aim to develop strategies for reducing its impact.

Operational engines in particular have high potential for corrosive wear. Combustion processes produce hot corrosive gasses, which, with the use of uninhibited lubricants, cause a flash rusting of exposed metal cylinder bores. During the next engine stroke these corrosion products are scraped from the surface, and a proportion of these will enter the oil system and be flushed through the engine as a fine abrasive. Iron oxide (e.g. Fe_2O_3) has a Mohs hardness of six compared to a hardness of 4-5 for iron (Weast, 1986). It is commonly used as a polishing compound in the form of jeweler's rouge. Its abrasive hexagonal crystalline structure gives it potential to damage working surfaces under high load. It exists as a powder down to 0.003 microns, and is not necessarily removed by the filtration system. In addition, a proportion of the corrosive combustion gasses will be passed into the bottom of the engine where they form nitric and sulphuric acids in combination with (Hallam F.S.T (1987)) water. To some extent this type of corrosion has been almost eliminated by modern fuel and oil additives.

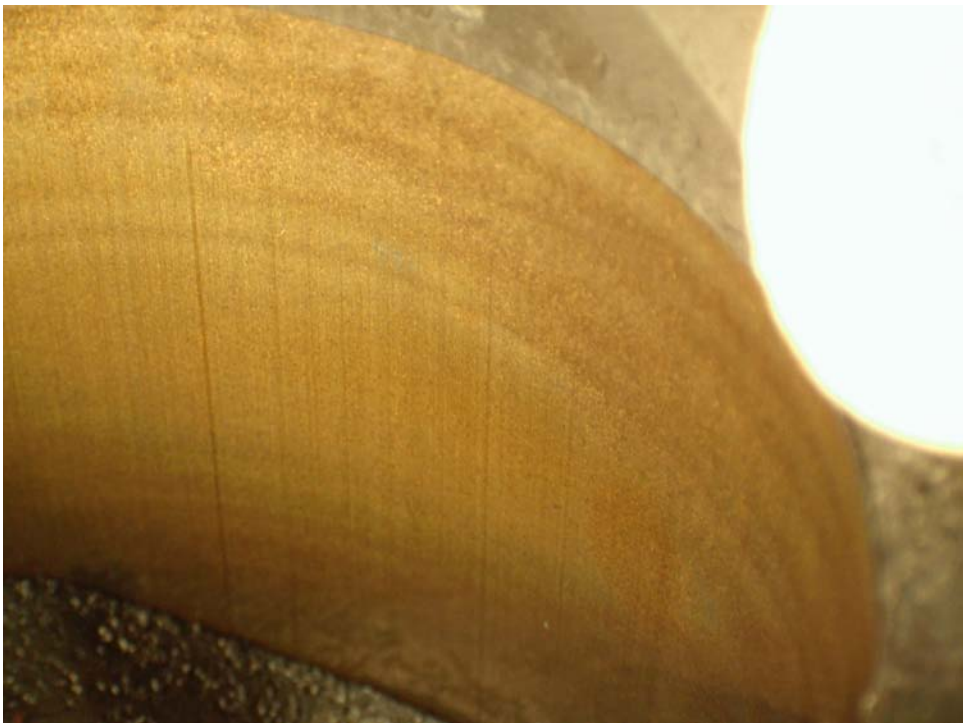

Figure 1 Corroded cylinder bore from an infrequently used Landrover in the NMA's collection. Note the horizontal banding, possibly due to contact with piston rings at rest. The vehicle was operated approximately three years prior to this image being taken.

Of concern to museums is the corrosion that develops during long periods of mechanical inactivity. Most lubrication products are designed for environments of frequent use. Operation has the effect of reforming the protective oil film and distributing inhibitors. In a museum like the NMA use at intervals of 3-6 months is common. An example of the consequence of using standard oils in a museum vehicle can be observed in Figure(1). Over a twenty year period this vehicle was run for a short periods on the basis of irregular display requests, often years apart. During this period condensation and remnant aggressive combustion products combined to result in a thin film of corrosion on the cylinder bore. In particular ring shaped markings are evident where more aggressive corrosion has taken place. These correspond to where the piston ring was in contact with the cylinder bore during a period of inactivity. The processes of differential aeration, which creates a more active localized anodic site at the point of contact, may be the cause of the defined ring markings. The effect can be observed with the unaided eye as pitting in the metal surface. When an engine in this condition is started the immediate effect is that corrosion product is burnished between the bore and the piston rings, having an abrasive effect. Fracture of the crystalline corrosion product from the surface may also tend to leave a more porous metal surface. To combat this, lubricants should

ideally be effective corrosion inhibitors when present as the thin residual films remnant after operation and cool down periods.
There is an increasing awareness in museums about the benefits of additives in chemically engineered oils. Contemporary oils differ dramatically from oils used in the 1920s. These were often only cleaned crude oils that had undergone minimal processing (Thomsen,1926) There does persist in the minds of some enthusiasts a perception that because non-additive oils were used when a machine was new then they should be used now. This is a reasonable approach for a museum if the objective is to replicate the short mechanical life span and high wear rates experienced when the machine was new. There is no advantage of this approach when the objective is to preserve significance. Museums seek longevity from their collections. To accomplish this they need to take advantage of approaches that will allow them to make educated decisions about the care of their collections. A more effective approach exists than that available in manufacturers' handbooks, and searching for bottles of long obsolete products from the back of storerooms. This approach involves the development of a rationally understanding of the problem and the development of a logical approach to resolving the issue based on the best chemical and physical understandings available.

We contend that a majority of the wear experienced by museum collection objects is due to corrosive effects rather than friction effects.

If the corrosive factors can be reduced or removed then it is probable that the safe operational life of the collection object can be increased. The NMA's objective is to develop a set of operational conditions in which we can eliminate most of the corrosive wear. In a method analogous to "just noticeable fade" standards used for (Derbyshire and Ashley-Smith, 1999), we are interested in developing operational standards where the rate of wear is given a similar weighting to the just noticeable fade deterioration level: that is, just as we display paintings under conditions where we predict that their deterioration will be at a particular acceptable level after a particular display exposure, we ought also be able to establish conditions where mechanical wear will be an acceptable consequence of a certain amount of display use. A "just noticeable wear" criteria would facilitate the making of more sophisticated decisions about the care and use of mechanical objects.

It is our hypothesis that if internal corrosion in storage can be substantially reduced, the wear of engines under museum use will be insignificant to the objects long term survival. Just as there is benefit from displaying a painting though it is known to be fading, there are advantages from operating machinery even though it is undergoing a level of wear. By attaching a significance to the level of deterioration, then balance it against any benefits of operation, a museum can make decisions about the justification of a particular level of use. It is possible that with a correct scientific approach to the use of machines in museums that wear will be negligible in long term survival, and it will be factors such as human error, recrystalization of metal alloys, polymer deterioration or loss of knowledge of operation that will be the limiting factor and the greater risk for their survival. We further speculate that the controlled operation of machines can be beneficial to their survival as it facilitates the distribution of inhibitors and lubricants through systems, promotes regular human contact with the object allowing early detection of deterioration, and prevents loss of knowledge surrounding the object. The level and type of appropriate use generally needs to be decided on an individual basis, however the NMA is endeavoring to develop a body of scientific work which will facilitate informed decision making around the preservation of mechanical objects.

A focus of current work is the development of methods to establish if there are differences in the corrosion protection afforded by different types of commercially available engine oils. If particular types of oils can be shown by experiment to provide greater protection from corrosion than others then their performance in the museum environment can be investigated.

Electrochemical impedance spectroscopy (EIS) is a well established technique for evaluating the corrosion preventive properties of protective coatings (Kendig et al 1993, Scully et al 1994). Conservators have used this technique in the past to evaluate and rank the corrosion performance of a number of commercial waxy coatings currently in routine conservation use (Hallam et al 2001, Otieno-Alego et al 2001). This testing procedure is relatively simple and gives quantitative *snapshot* data about the performance of protective coatings, allowing them to be ranked objectively. The EIS test cell presently available in the NMA laboratories is suitable for testing relatively hard, thick coatings. It cannot be used in the investigation of thin, delicate and easy-to-break films such as those formed by engine oil. The objective of this investigation was to fabricate an electrode suitable for testing thin oily films using conventional EIS test cells. We desired an EIS method that could be used for rapidly testing commercial engine oils and ranking their performance. Such a test protocol is particularly crucial to the NMA who aim to identify the best engine oils for use in their functional collection of technological objects.

The fabricated electrode has successfully been used to test and rank six NMA nominated commercial engine oils. In addition, the corrosion performances have been compared to salt spray chamber exposure results.

2. Experimental Procedure

2.1 Test Oils

Six oils were selected to be representative of commercial oils used by old vehicles and numbered 1 to 6. The commercial identity of the products used for experimentation are not revealed here because 1) the objective of this research was to develop a testing method that allowed identification of differences between products and 2) the testing of six products is not considered sufficient for us to begin making product recommendations. If the testing method progressively demonstrates its usefulness, in correlation with other available evaluation techniques, the NMA may begin to identify which product types have been found to be best suited to specific museum applications.

Oil products were selected that were anticipated to display a range of corrosion inhibition effectiveness. Product (1) was a commercially available engine oil marketed for infrequently used older vehicles. Product (2) was an approximately 15 SAE grade mineral oil which contained no additives, i.e. it is the refined mineral oil used by oil manufactures to manufacture their additive package retail product. Product (3) was a commercially available oil designed for daily use in pre-1980 passenger vehicles. Product (4) was an approximately 40 SAE grade mineral oil which contained no additives, i.e. similar composition but higher viscosity than product (2). Product (5) was a low viscosity spray type oil to which tackifiers and corrosion inhibiting agents had been added. The product is designed to both cling to metal surfaces, displace surface moisture and inhibit corrosion reactions. Product (6) was a “new old stock” commercially available 50 weight engine oil from circa 1950. The product was selected for testing because oils of this vintage, with distinctive “inhibitor” odor, are on occasion found in service in museum collections. They are particularly common in differentials and gearbox applications. It is acknowledged that any active ingredients in this product may have deteriorated since manufacture.

2.2. Electrochemical Impedance Spectroscopy

After a comprehensive literature survey, the EIS test procedure published in *Corrosion Science* by Nowosz-Arkuszewka and Krawczyk (1992?) was adopted in this project. After further consultations with Prof. Nowosz-Arkuszewka, we chose to make the working electrode from a commercial mild steel rod of diameter 3.18 mm

and a length 200 mm, coated by dipping in the oil of interest. The simple rod-electrode design fits well with the EIS testing rigs and equipment already available. A special Teflon holder was designed for holding the coated mild steel electrode in the electrochemical cell (see Figure 2). Both ends of the steel rod were rounded (to form a semi circle) using a lathe machine tool. This edge rounding was important to ensure that the thin oily films was not broken by hard corners. Prior to use the electrode was polished using a 1200 grit SiC paper, degreased thoroughly with acetone, then half immersed in the appropriate oil sample contained in a test tube. Care was taken to ensure that no section of the immersed electrode was in direct contact with the sides of the test tube. The electrode was left to equilibrate in the oil for 24 h after which it was removed and clamped vertically to drain off the excess oil (approximately 30 min) before use.
No attempt was made to determine the final thickness of the oil films. The experiment was designed to give information about the efficacy of films formed at museum storage temperatures of approximately 21°C.

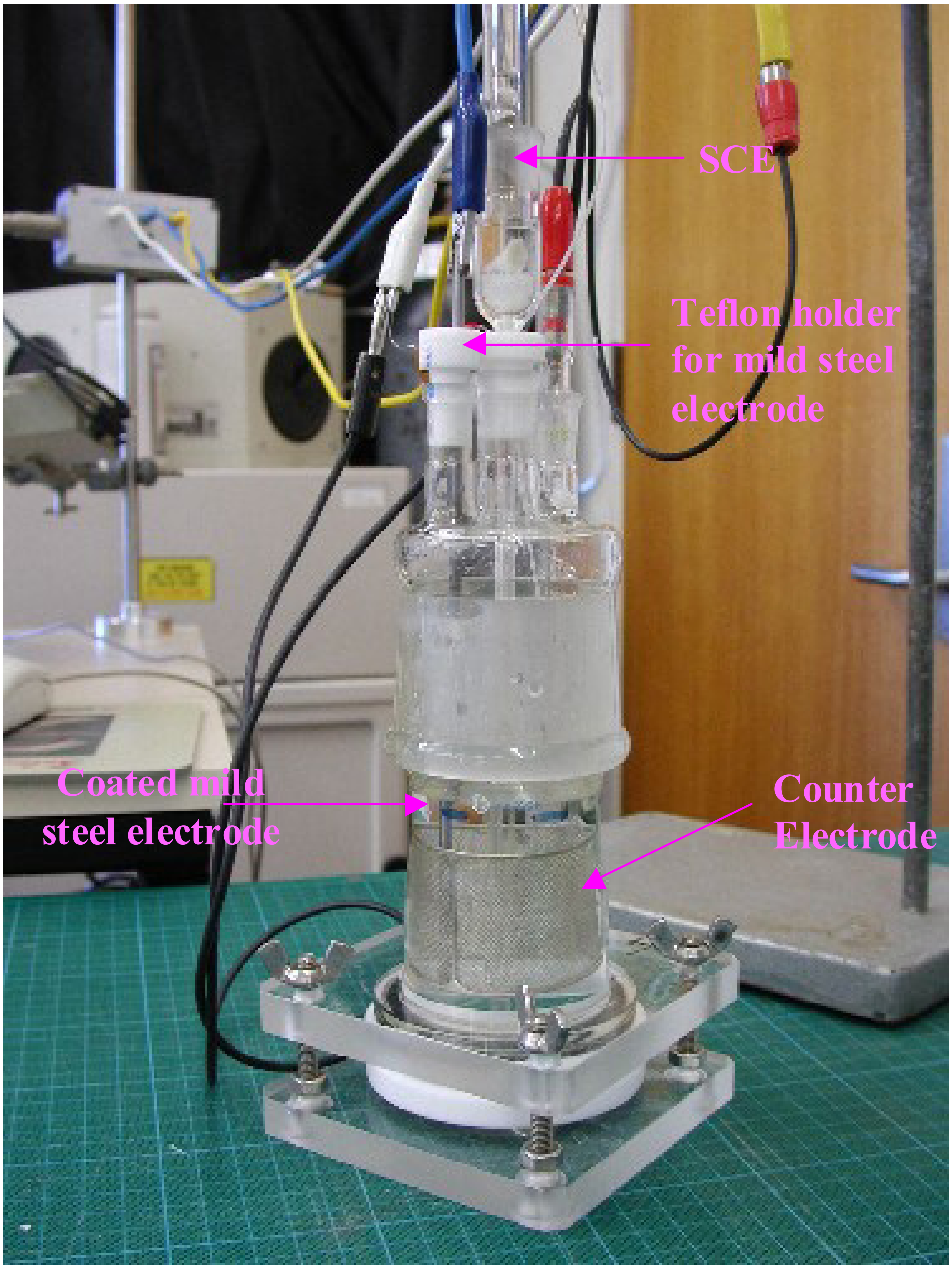

Figure 2.Close-up photograph of the EIS electrochemical cell showing the coated mild steel rod electrode in testing position.

EIS data was collected in quiescent 0.25 M K_2SO_4 with the coated mild steel rod as the working electrode (exposed area = 4.75 cm^2). A large cylindrical platinum mesh and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The 0.25 M sulphate solution was chosen based on the previously published work by Nowosz-Arkuszewka and Krawczyk (1992?). A pseudo-reference electrode made of a gold wire mounted in soda glass except for its tip was coupled to the SCE through a 0.1 μF capacitor. Impedance measurements were performed using a computer controlled EG&G PAR 273A potentiostat coupled to an EG&G M5210 lock-in amplifier. The alternating current amplitude was 10 mV and was applied about the open circuit potential over the frequency range 100 kHz to 10 mHz (5 points per decade). The coated electrode was left to equilibrate in the test solution for 20 min before recording the impedance data. The impedance data were analysed using the circuit analysis program ZSimpWin, Version 2.00 (EChem Software web: http://www.echemsw.com). The capacitors in the circuit were mathematically modelled using a constant phase element (CPE) that takes into account heterogeneity in surface morphology and diffusion related processes (Deflorian et al 1993). Four repeated experiments were conducted for each coating.

Visual observation of the electrode in solution did not suggest that immersion of the electrode caused the oil coating to be washed from the surface. An oil slick on the surface of the electrolyte did indicate some loss of surface protection, however the EIS data collected indicated that all samples had a coherent film present on the electrode when the experiment was commenced. In some instances this film broke down rapidly when current was applied. The immersion of an oily film in an aqueous solution is an extreme test of its corrosion resistance. By exposing the oily films to both this and the salt spray environment we hope to select oils which show some resistance to extreme environments and make trial application under the more benign museum environment.

2.2 Salt Spray Testing

The salt spray test was carried out in a Singleton SCCH Corrosion Test Cabinet. The corrosive nature of the chamber specified by ASTM D117 (ASTM, 1985) is a continuous spraying with a 3.5% (by weight) solution of sodium chloride. In this testing, however, the standard sodium chloride solution was substituted with 0.25 M K_2SO_4 solution (pH ≈ 6.8, temperature 35^{o} C). This modified test environment was adopted to match the EIS test conditions. Rectangular mild steel panels (60 x 45 x 2 mm) were initially sand blasted, polished using 1200 grit SiC paper, washed in deionised water, degreased in acetone and placed in an oven (60^{o}C) for 2 h to dry. The cleaned coupons were then coated by completely immersing them in the different test engine oils for 24 hr before being removed and allowing the excess oil to drain for 30 min. Samples were prepared in duplicates. The coated samples were placed in the salt spray chamber angled at 45 degrees and left to corrode until sufficient corrosion had formed on all the surfaces. Specimen surface was monitored and the degree of rusting was rated by visual examination of the surface corrosion behaviour after every 24 hr. The samples were given a rust grade rating from 0% (no rust on surface) to 100% (surface completely rusted). A total of 6 commercial oils (listed in *Section 2.1*) were tested.

3. Results and Discussions

3.1 Electrochemical Impedance

Representative Bode magnitude plots are shown in Figure 3. The low-frequency impedance (Z_{lf}) estimated at the plateau region of the Bode magnitude plot in the frequency range 0.1 to 0.05 Hz has been proposed as the optimal EIS parameter to evaluate the performance of corrosion inhibiting coatings (Grandle and Taylor 1994). The impedance at this frequency includes the response of the coating as well as part of the response of the oxide and/or corrosion product in the pores at the metal interface. Referral to Figure 3, this *snapshot* method of EIS data treatment shows that all the oily films offered some corrosion protection to the mild steel (i.e. Z_{lf} for all oil coated steel is greater than the impedance of the bare metal). The overall effectiveness of the films could be ranked best to worse for the tested oils as in the product order: 1 > 5 > 3> 2 > 4 ≈ 6. Except for products 1 and 5 which show some capacitive behaviour (ie. The Bode plots in the high frequency regime converge to the same straight line with a slope of approx. –1), all the tested oily films were readily penetrated by the electrolyte after 20 min of immersion.

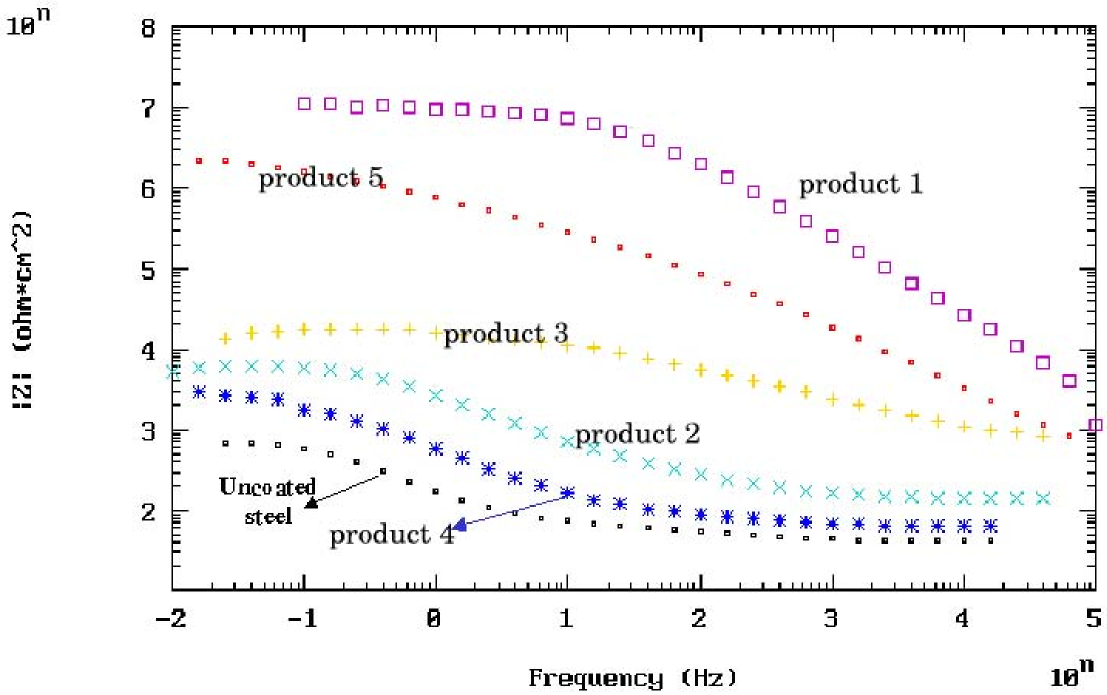

Figure 3. Representative Bode magnitude plots for the uncoated and engine oil-coated mild steel electrodes immersed in quiescent 0.25 M K_2SO_4 solution (equilibration time = 20 mins).

EIS data can also provide kinetic and mechanistic information on the coating's physical-chemical behaviour through the analysis of the equivalent resistance and capacitive elements that contribute to the observed electrical behaviour of the coating. The impedance spectra were analysed by fitting the data to the equivalent electrical circuit shown in Figure 4, where Rs is the resistance of the electrolyte; R1 is the coating or pore resistance; R2 is the charge-transfer resistance of the corrosion reaction; C1 is the capacitance of the coating; and C2 is the double layer capacitance at the metal-electrolyte interface. All the capacitors (C1 and C2 in Figure 4) were mathematically modelled using a constant phase element (CPE). Figure 5 shows examples of overlays of the measured Bode plot and that calculated from the simulated circuit. Good agreement was obtained between the measured and calculated results. The values for coating resistance (R1) and the coating capacitance (C1) can be used as a quantitative measure of the effectiveness of the coating. Table I gives a summary of the calculated R1 and C1 values. Larger R1 values accompanied by smaller C1 values equates to good corrosion protecting coatings. As with the Z_{lf} ranking, the efficacy of the coatings based on the calculated R1 and C1 values (See Table 1) could be arranged in the product order: 1 > 5 > 3 > 2 > 4 > 6, starting from the most resistant.

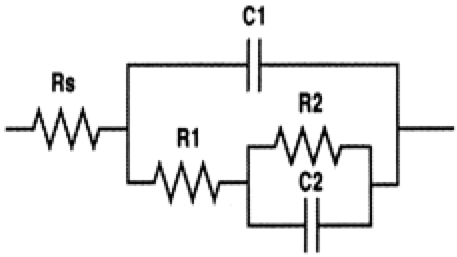

Figure 4: Equivalent circuit model of a coated metal. Rs represents the solution resistance, R1 and C1 correspond to the resistance and capacitance of the coating whilst R2 and C2 correspond to the resistance and capacitance of the metal interface

It is worthwhile noting that the overall impedance of a coating depends on, among other things, the thickness of the coating. In this investigation, the oil film was applied simply by immersion and the excess oil allowed to run off leaving a thin film on the metal surface. The above ranking is based upon this scenario. No attempt was made to determine the actual final thickness of the thin films.

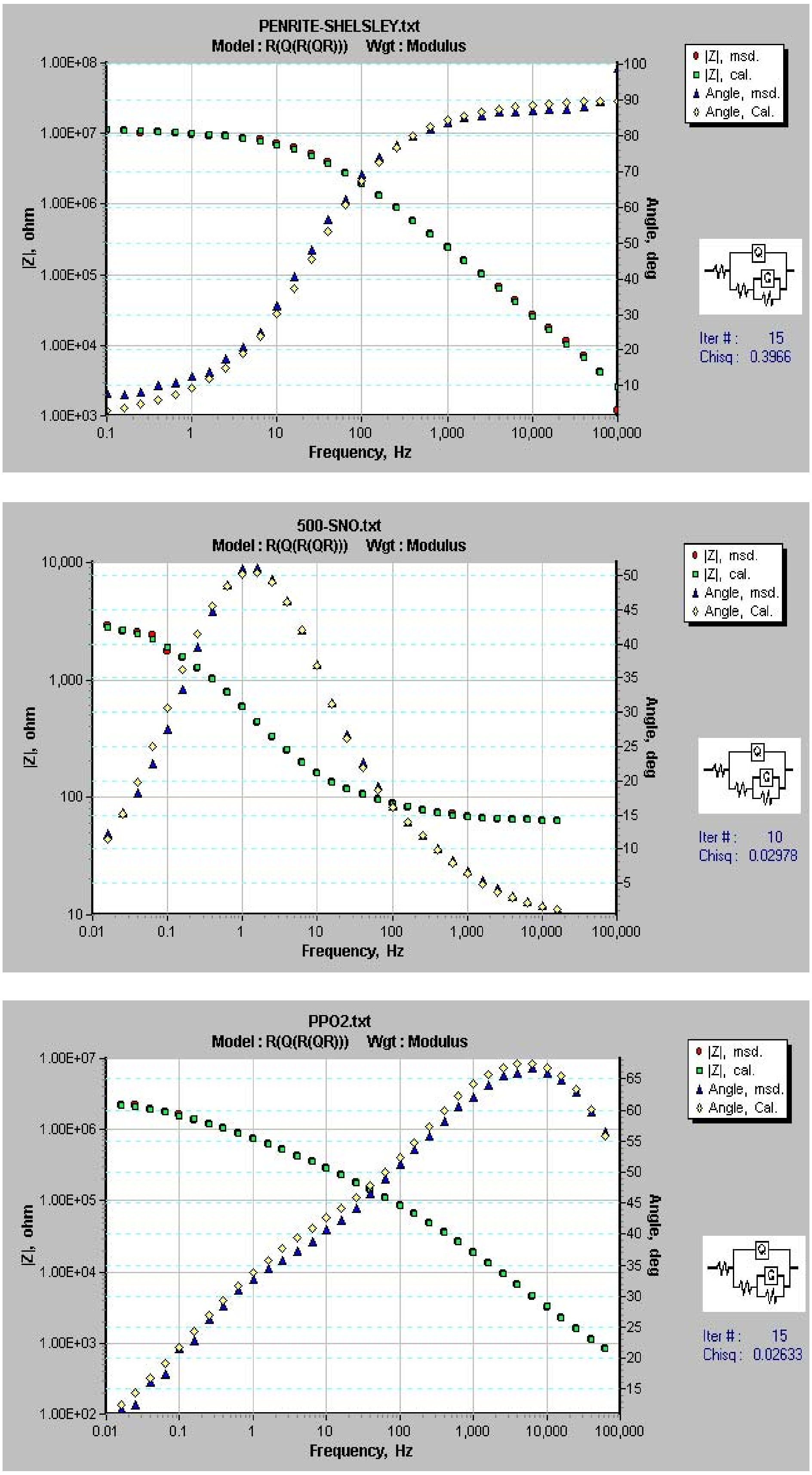

Figure 5. Examples of computer fit for impedance data obtained for oil coated mild steel exposed in quiescent 0.25 M K_2SO_4. Inset shows circuit used for computer simulations

Table I: Electrochemical impedance parameters R1 and C1 calculated for oil coated mild steel immersed in quiescent 0.25 M K_2SO_4 solution.

Product number	Immersion Time (min)	R1 (Ω cm^2)	C1 (μF cm^{-2})
1	20	3.19×10^5	0.0006
2	20	6.57×10^2	46.6
3	20	8.07×10^2	3.88
4	20	9.12×10^1	290.6
5	20	8.75×10^4	0.041
6	20	7.81×10^1	166.5

3.2 Salt Spray

The corrosion performances of the oil coated steel panels exposed to the salt spray chamber are presented in Table II. The samples were given a rust grade rating from 0% (no rust on surface) to 100% (surface completely rusted). It was not possible to effectively rank the performance of the thin oily films under this relatively aggressive salt environment and after a short exposure (24 hr), only the coupons coated with *product 1* experienced some corrosion protection (with ranking of 20%). All the other coatings failed (ranking 100%) and the mild steel coupon's surfaces were heavily corroded. After 48 hr the surface of the steel panels coated with *product 1* showed 60% rust. The observed rapid failure of most of the oily films can be attributed mainly to their poor physical barrier to electrolyte penetration. This observation corroborates well with the EIS data that indicated most of the oil films to be easily penetrated by the electrolyte within the first 20 min of immersion. Corrosion of the underlying mild steel is expected to occur rapidly in this salt laden environment once the electrolyte/metal contact is established. The superior performance of the *product 1* agrees well with the EIS ranking.

Table II. Salt-Spray Test rating of the wax coated steel panels (average of three panels)

Product number	**Ratings$^\theta$ (after 24 hr)**	**Ratings (after 48 hr)**	**Ratings (after 72 hr)**
1	20%	60%	100%
2	100%	F*	F
3	100%	F	F
4	100%	F	F
5	100%	F	F
6	100%	F	F

Ratings$^\theta$ 0% = No rust on surface; 100% = Surface completely rusted
F* Surface of steel panels coated with oil coating showed 100% rust
(ie total failure) from previous recording

4. Conclusions

The thin rod-electrode fabricated in this investigation can be used to establish the corrosion efficacy of thin, delicate and easy-to-break oily films using the technique of electrochemical impedance spectroscopy. The test procedure provided reproducible and quantitative results allowing the performance of the protective coatings to be ranked more objectively and within a short testing time. The system was successfully used to evaluate the efficacy of six commercial oils in a sulfate-containing environment. The thin films exhibited poor barrier properties and were readily penetrated by the electrolyte resulting in heavy corrosion of the base metal within 12 hr of exposure in a salt laden environment. The ease of film penetration may support an argument for regular film replenishment in museum collection vehicles.

Testing by EIS showed product 1 to be orders of magnitude more effective at preventing corrosion under the test conditions than the remaining 5 products. This product was also the only one to exhibit any significant resistance to the salt spray environment. The conventional engine oil, product 3, displayed no meaningful improvement in corrosion resistance over the unimproved base oil samples. The aged oil (product 6) achieved only comparable protection to product 4, an unimproved base oil. The presence of inhibitors in products 1 and 5 has made these oily films more effective at reducing corrosion. A method of accessing the corrosion protection afforded by thin oil films is one of the criteria required in the development of a *just noticeable wear* standard form operational museum objects. By better defining the risk factors to museum collections we have a higher probability of ensuring survival and of effectively applying resources to areas of greatest need.

It must be borne in mind that the engine oils are used in a much milder corrosive environment than the aggressive salt solution used in this investigation. It is envisaged that outstanding oils will be very efficient under natural engine operating conditions

If the lubricant is not effective as an inhibitor in this situation then more proactive measures have to be taken to reduce corrosion during storage, e.g. vapor phase inhibitors, dehumidification, flooding the system with a wax containing oil such as PX115. These “mothballing” techniques render the vehicle not available for display operation without lengthy start up and re-mothballing procedures and are not conducive to the conservation of both the form and function of the object.

The following further research programme is planned:

- ranking commonly available “classic car” oils by the technique described in this paper
- developing a method for the assessment of the relative wear and corrosion rated of engines in storage in museum maintenance and storage programs
- developing engineering conservation procedures and practices to assess the Just Noticeable Wear (JNW) criteria for museum and collector objects.

References

ASTM Standard B 117, *Standard Method of Salt Spray (Fog) Testing*, ASTM Annual Book of Standards, Vol.06.01 (1985)

Deflorian, F., Fedrizzi, L., Locaspi, A. and Bonora, P.L. (1993) *Electrochimica Acta* **38**, pp1945-1950

Derbyshire, A. and Ashley-Smith, J. (1999) *A proposed practical lighting policy for works of art on paper at the V&A* Triennial meeting (12th), Lyon, 29 August-3 September 1999: preprints. Vol. 1 James & James London

Grandle, J.A. and Taylor, S.R. (1994) *Electrochemical Impedance Spectroscopy of Coated Aluminum Beverage Containers: Part1 - Determination of an Optimal Parameter for Large Sample Evaluation* Corrosion **50**, 792-803.

Hallam F.S.T (1987) *Repco engine service manual* Repco Limited Melbourne Australia page 81

Hallam, D., Thurrowgood, D., Otieno-Alego, V., Creagh, D., Viduka, V. and Heath, G. (2002), *Studies of Commercial Protective Petrochemical Coatings on Ferrous Surfaces of Historical and Museum Objects*, In Metal 2001. Proceedings of the ICOM-CC Metals Conference, Santiago, Chile. (Ed. I. McLeod), James and James Scientific Publishers, London. In press.

Kendig MW, Jeanjaquet S and Lumsden, J, (1993), *Impedance: Analysis and Intepretation*, Philadelphia, PA:, ASTM, ASTM STP 1188, eds. J.R. Scully, D.C. Silverman, M.W. Kendig

Nowosz-Arkuszewska and Krawczyk, M. (1992?) Corrosion Science **33**, pp.861-871.

Otieno-Alego, V., Creagh, D., Hallam, D., Viduka, A. and Heath, G. (2001), *In-Situ and Laboratory Studies of the Ageing of Protective Wax Coatings on Metal Surfaces of Museum Objects and Outdoor Statues*, in Les Mallinson (ed.), Ageing Studies and Lifetime Extension of Materials, Kluwer Academic/Plenum Publishers, UK. pp.609-618.

Ricardo, H.R. (1992) *The Ricardo Story : autobiography of Sir Harry Ricardo, pioneer autoimotive engineer* SAE Historical Series SAE Warrendale PA. USA ISBN 1-56091-211-1

Scully, J.R. and Hensley, S.T. (1994) Corrosion **50**, pp705-716

Thomsen, T.C. (1926) *The practice of lubrication* 2nd edition, The McCraw-Hill Book Company, New York, Chapters 1-4.

Weast, R. C. (1986) *CRC Handbook of Chemistry and Physics* Chemical Rubber Publishing Company Boca Ration Florida

