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Using Novel Electrochemical Test Methods to aid in the Development of low Volatile Organic Compound (VOC) Coatings

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Abstract

Electrochemical Methods have proved useful for assessing coated systems intended for anti-corrosive applications. Three areas of application are to assist new product formulation, quality control and to monitor in service. The Electrochemical Noise Method (ENM) has particular attractions because of its non-intrusive nature, quickness in gathering data and ease of interpretation. It has recently been successfully employed to help the development of new coating systems with reduced level of Volatile Organic Compounds (VOCs). In that work intact organic coatings were monitored using the standard bridge method in the laboratory under immersion conditions on steel substrates. The most common parameter derived was R_n and for the better systems the value started and stayed high throughout the period of the test including after higher temperature excursions in some cases. Comparison with outdoor exposure and salt spray testing confirmed the ability of ENM to predict subsequent behaviour from short term tests. The electrode arrangement for the standard ("Bridge") method of conducting ENM requires two separate working electrodes e.g. two painted Q-panels™ and a reference electrode. Although fine for laboratory use, e.g. the work described above, it is not so satisfactory for monitoring or quality control applications. The technique has been further developed to allow an electrode configuration which requires No Connection to Substrate (NOCS). Such an arrangement would provide a real advantage when attempting to monitor anti-corrosive systems in service. This paper presents the first results obtained using the NOCS method. So far, using the ENM NOCS arrangement with immersion testing has given a good indication of the anti-corrosive properties in comparison with the standard method. Also results have been compared with DC resistance and with the single substrate method.

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Introduction

Making service life predictions for the application of coatings is important for meeting specification requirements. Electrochemical Noise Monitoring has been used previously to rank coatings by their anti-corrosive property [1]. The current ENM methods used to monitor the anti-corrosive properties of organic coatings are well discussed in the literature [2]. The normal ENM arrangement, and most established, is the conventional bridge method. Recently the technique has been used to rank the anti-corrosive protection afforded to a steel substrate by newly developed low VOC coatings. In that work the testing methods used differentiated single coat alkyd and acrylic type coatings [3].

A development some five years ago by Mabbutt [4] was the single substrate technique. The latter is useful because, unlike the arrangement employing a salt bridge, it does not require two nominally identical samples. The need for only one test sample lends itself towards the ability to test coatings in service under less control-demanding conditions. The ability to do this has obvious advantages, in that, ion transfer can be monitored as an instant test or a corrosion monitoring test over any period of time.

Very recent developments in the ENM technique have produced a configuration which requires No Connection to Substrate (NOCS). The technique uses the same method of measuring Noise Resistance (R_n), i.e. there are still two working electrodes generating current and the pair are measured with respect to a reference electrode. However when using the NOCS method, connection to the working electrodes and reference electrode are via saturated calomel electrodes with no connection to the substrate being required.

This paper presents for the first time results obtained using this NOCS method. Also results have been compared with DC resistance and with the single substrate method.

Electrochemical methods

The Electrochemical Noise Method has been described previously [5,6]. ENM has advantages that it is easy to carry out and is non-intrusive, as it is the very small naturally occurring electrical disturbances of the system that are measured. Essentially the very small fluctuations in voltage and current are measured simultaneously. The current is measured using a zero resistance ammeter (ZRA) between the (nominally identical) working electrodes with the potential being measured between the coupled working electrodes and the reference electrode. Typically 512 data points are gathered at 0.5 second intervals and the standard deviation of the current (σI) and voltage (σE) are calculated. Several runs are normally performed with data from the last run used. The Noise Resistance (R_n) is then calculated. Correlation of current and potential noise from uniform corrosion may be used to obtain electrochemical impedance of the corroding interface; weakly stationary or deterministic processes produce these noise signals. Corrosion rates may therefore be evaluated from this low frequency impedance or from the associated but simplified noise resistance, obtained from the standard deviations of the current and potential:

$$R_n = \sigma E/\sigma I$$

The protection afforded by the coatings can be directly related to the value of R_n.

The standard “Salt Bridge” electrode arrangement is shown in Figure 1. In this experiment two separate panels form the individual working electrodes with a salt bridge between them. A calomel electrode is then placed in one or other of the cells and connected to the reference terminal. In the “Single Substrate” method two cells are still present attached to the substrate. Calomel (reference) electrodes are placed, one in each cell, with the substrate connected to the reference electrode terminal. This arrangement can be shown to be electrically equivalent to the Salt Bridge method [4].

The newly developed “No Connection to Substrate” three-electrode configuration is shown in Figure 2. In this case, three cells filled with solution were fixed on to three separate panels all connected together electrically to simulate one large piece of metal. Each cell had a reference calomel electrode inserted into it. Two of these became the working electrodes and the third the reference. As before current is measured between the two working electrodes and voltage is measured between the reference and the two working electrodes.

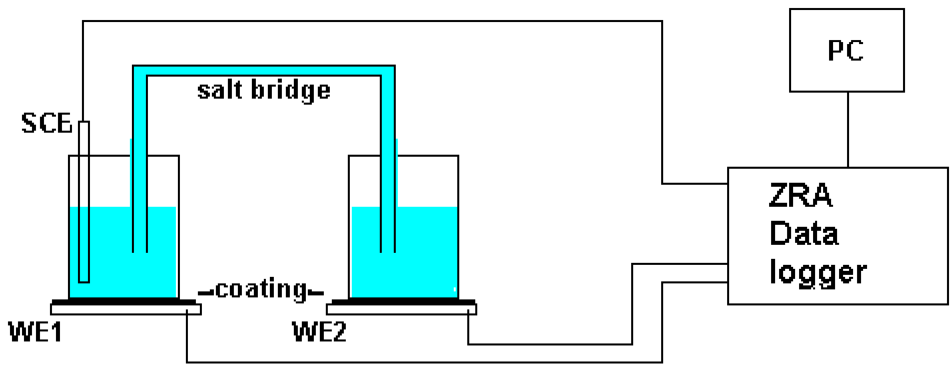

Figure 1. Standard "Salt-Bridge" electrochemical noise configuration – the current is measured by a zero resistance ammeter (ZRA) simultaneously with potential.

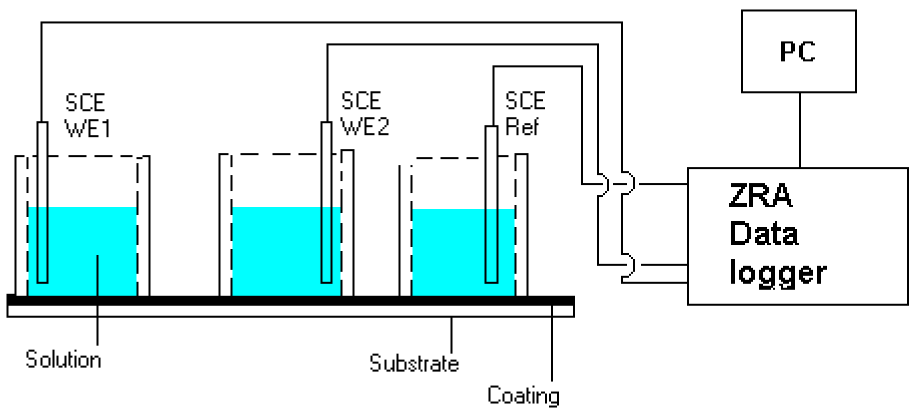

Figure 2. Electrochemical noise – "No Connection to Substrate" configuration – the current and potential are measured as in Figure 1.

Experimental

The paints tested were obtained from one industrial coatings manufacturer and were representative of coatings under development with improved environmental properties.

Coatings were formulated using solvent borne alkyd resins. Results given here are for coatings based on different technologies with varying resistance. All coatings tested had a pigment volume concentration of zinc phosphate of between 10-20%, included for corrosion protection. All coatings were applied to standard low-carbon, cold-rolled steel Q-Panels (complying with ASTM A-336, A-109 and QQS-698) by draw down blade as a single coat (around 70 ± 5μm dry film thickness). The Q-Panels were used as-received from the manufacturer but solvent degreased before application of the coating. Triplicate panels were prepared for each coating for the immersion experiments. Painted samples were kept in a controlled environment for seven days before testing commenced. In the immersion experiments, samples were exposed intact to 0.5% ammonium sulphate solution at room temperature (22°C ± 2°C). For the immersion experiments short lengths of circular PVC pipe were glued to the panels with silicone adhesive, the exposed area in each cell being 11cm^2 and the volume of solution about 100ml. The surfaces of solutions were exposed to air throughout the test.

General Protocol for NOCS test work

Triplicate groups of pre-immersed samples with high (> 1 x 10^7), medium (around 1 x 10^6) and low (< 1 x 10^6) DC resistance were selected from amongst a batch of samples that had been previously tested [3]. Since they already had been immersed for a long period of time the resistances were relatively stable and, thus, unlikely to change between experiments as various connection arrangements were tried (e.g. NOCS, Single Substrate, Salt Bridge). At the end of testing the DC resistance was again measured and was found to be unchanged in all cases.

The NOCS method was compared with sample pairs (in the case of the Single Substrate and Salt Bridge methods) and single samples in the case of direct DC resistance measurement. It was also considered of interest to investigate study the effect of the three panel resistances being different; i.e. to find out which would dominate the NOCS result. Hence High, Medium and Low resistance panels were swapped and results are also presented here.

Thus, the general principles behind this work were:

(a) to use pre-immersed painted panels of known (and stable) resistance;

(b) to measure the resistances of these panels using various electrochemical noise methods;

(c) thus, to determine the validity of electrochemical noise for this application.

Results

Experimental results comparing the No Connection to Substrate method with other methods mentioned above are shown in Figures 3 to 6.

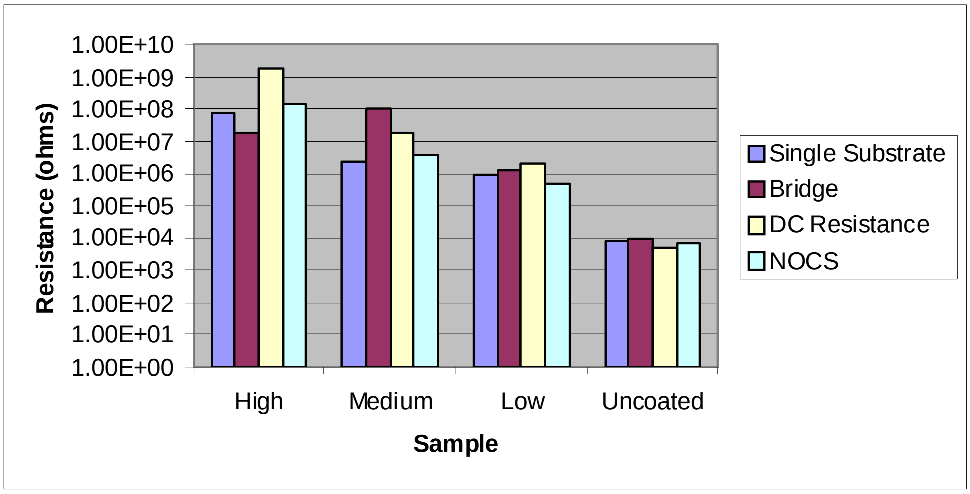

Figure 3: Comparison of resistance values, as a function of exposure time, obtained by the No Connection to Substrate, Salt Bridge and Single Substrate methods and by direct DC measurement.

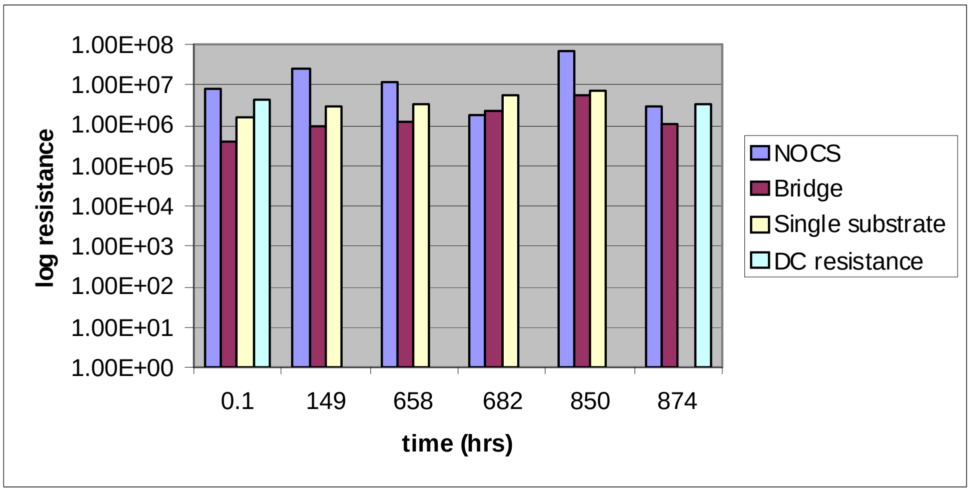

Figure 4: Comparison of resistance values, as a function of varying panel paint resistance, obtained by the No Connection to Substrate, Salt Bridge and Single Substrate methods and by direct DC measurement.

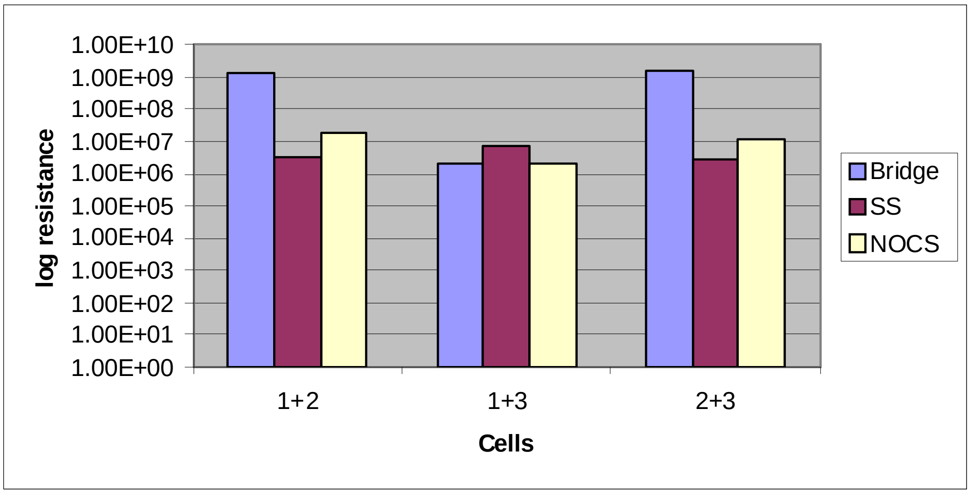

Figure 5: Comparison of the No Connection to Substrate method with the Salt Bridge and the Single Substrate arrangements for different combinations (pairs) of samples.

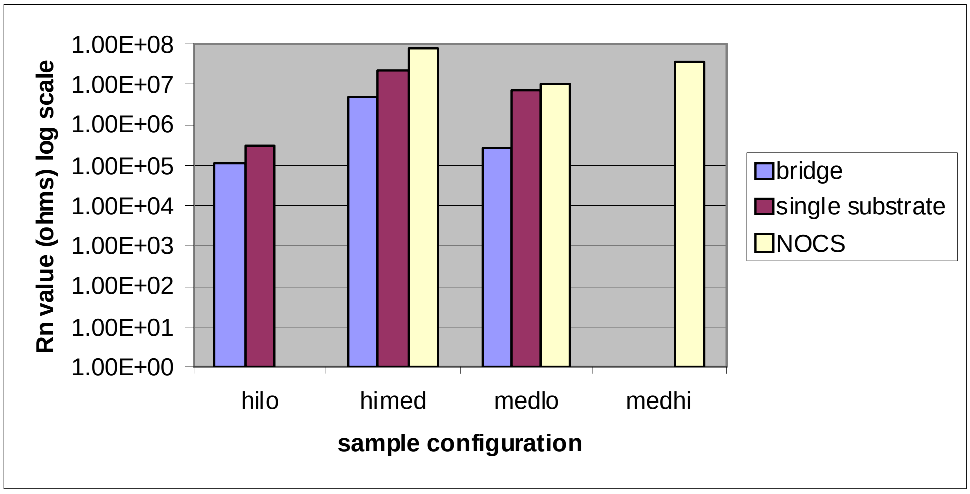

Figure 6: Comparison of the No Connection to Substrate method with the Salt Bridge and the Single Substrate arrangements for different combinations (pairs) of samples with differing resistances.

Figure 3 shows results obtained from one set of medium (DC) resistance samples over a long period of time. At each time period the resistance was measured via the NOCS technique and compared with the Salt Bridge and/or Single Substrate techniques.

To generate the results shown in Figure 4 three similar resistance samples, of either high, medium, low resistance or uncoated, were examined by the three different electrochemical noise measurement methods. Additionally the DC resistance value was used to compare the data after testing. The value shown is the average of the three samples measured.

Figure 5 shows results from measurements made on different combinations of three cells 1, 2 and 3 (Each had a medium DC resistance value). For the Single Substrate and Salt Bridge measurements, pairs of samples were used e.g. 1 and 2, 2 and 3 and 1 and 3. In order to obtain the NOCS values all three cells/electrodes were used for all three measurements. However in each case the reference electrode was varied (i.e. when 1 and 2 were the working electrodes, the ref electrode was 3, when 2 and 3 were the working electrode the ref was 1 etc)

Figure 6 presents the results where the three samples measured had different resistances. The labelling (i.e. "hilo") indicates ("hi") that the two working electrodes are measuring from the high resistance coatings while ("lo") indicates that the reference electrode is connected via the low resistance coating. In the case of Single Substrate and Salt Bridge values, the measurement was taken between the working electrodes.

Discussion

Examining Figure 3 it can be seen that over the time of the test the resistance of the samples remained virtually constant. This is not surprising as the samples used for the testing had been previously exposed to 0.5% ammonium sulphate for a period of ten weeks and were therefore assumed to have stabilised with respect to resistance. The figure also shows that there is a good consistency between the resistance values for all measurement techniques. The NOCS method appears to deliver values slightly higher than the other test methods, which indicates that it may be driven by higher resistance areas of the coating. However, it can also be seen that after 874 hrs on test the resistance measured by the NOCS method and by DC agree completely. This validates the NOCS method and parallels the Bacon, Smith and Rugg [7] criteria for ranking protective coatings.

Figure 4 shows the variation in coating resistance as measured by the different ENM methods confirmed against the values of direct DC resistance measurement. Here, the NOCS method appears to give values of resistance slightly lower than the DC values. However, the resistance values obtained with the Single Substrate and NOCS are clearly separated. They also show a close relationship with the DC values and, as previously, allow ranking of the resistance of the coatings.

Figure 5 shows that variation in the configuration of the tested cells has little effect on the resistance values measured by the Single Substrate and NOCS arrangements. However, the alternative testing configurations can affect the results obtained by the conventional Salt Bridge method. This is probably as a result of the higher integrity areas of the coating dominating the measurement.

Figure 6 shows that despite variation in the configurations of the test cells, the results may still be used to rank the coatings tested and, hence, provide information which is useful in the prediction of the coating's performance in service. It can be seen from Figure 6 that the position of the working electrodes and their substrate, and not the reference electrode, controls the NOCS method giving similar values in two cases out of three to the conventional bridge method.

Concluding Remarks

In conclusion it can be seen from the results that all electrochemical measuring techniques show good correlation in their ranking of the coatings tested. It is also evident that the No Connection to Substrate (NOCS) method successfully ranks the coatings by their resistance, indicating their corrosion protection. This new ENM configuration has many benefits in the form of mobility and site testing and/or monitoring. The NOCS test configuration is essentially simulating connection through one large piece of metal and not through an external solution via reference electrodes. By so doing, it avoids the need for any connection to the test substrate.

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