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for the period 9/1/92 -8/30/94

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Characterization of Corrosion under Marine Coatings by Electrochemical Noise Methods

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ROBERT J. SILVERMAN

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1.0 INTRODUCTION

This research grant focused on electrochemical techniques for the investigation of corrosion protection afforded by organic coatings. The main aim of the work was the study of marine coatings using the electrochemical noise methods (ENM). Skerry et al[1,2,3] had ENM to examine organic coatings (mainly primer) on metal. More specifically the following goals were set:

1) the purchase, installation, calibration of electrochemical noise apparatus and its implementation to study the corrosion in metal/marine coatings systems immersed in salt water;

2) experimental studies on coated metal systems using the ENM apparatus in conjunction with standard coatings test methods such as cyclic salt fog (Prohesion^{TM}), salt water immersion at increased temperature, Electrochemical Impedance Spectroscopy (EIS), DC Resistance, and comparison of results in an ongoing manner;

3) the preparation and study by ENM and other methods of multiple grit blasted steel/marine coating samples in order to develop reproducibility statistics on data;

4) the analysis of the data obtained from the ENM experiments and parallel corrosion studies in order to develop a protocol for interpreting the results *vis a vis* marine coating testing;

5) development of specific data treatment routines to improve accuracy of the resistance noise vs. time data, and analysis of the frequency spectrum of the noise data;

6) development of a mechanistic model for the corrosion protective performance of marine coatings;

7) examination of the use of ENM methods to develop implantable corrosion sensors in coated metal systems.

Many of these goals have been met in the first two years of the project.

The work started by examining primers[4,5] provided by Sherwin Williams but moved on to examine typical marine coating systems prepared here both 2-coat and 3-coat. The protocol established with the primer work[6], i.e. comparison of ENM measurements on panels under continuous solution immersion with visual appearance and with results from cyclic salt spray and hot salt bath testing, was maintained in the marine coatings work. Paralleling the data gathering experiments, some fundamental work was also conducted on the noise method itself and on reproducibility. Various data treatment methods have been tried. Some results have been given in a comprehensive paper[7]. A summary of the current most successful approach will be given in this report. A derivation of R_n (defined as σ_V/σ_I) from first principles [8] and some work investigating the relationship between R_n and R_{dc} has also been done[9]. Because previous work has shown the importance of the coating properties in determining the ability to protect steel some investigation of the properties of detached films has been carried out. These results are also summarized. The main 2-coat and 3-coat work was conducted on specimens sprayed by ourselves with paints provided by International Paint and Southern Coatings Ltd. However as an outgrowth of the main project, several other collaborative investigations involving industrial and/or academic partners such as Miles Inc., PPG, Sherwin Williams, University of Cincinnati have been carried out. All these used the Electrochemical Noise Method as one of the main techniques to examine organically coated metal substrates.

Most of this has either been published or is to be published. The work included investigation of Miles Inc. systems on steel[10], a study comparing the noise equipment used at Sherwin Williams with CML equipment[11], work on electrocoat on steel, and zinc[12], work on Miles primers on both steel and aluminum[13], and an investigation of plasma polymerized silanes as an alternative to phosphating[14] in pretreatment for electrocoat. A short review paper is also in preparation[15].

No attempt is made in this final report to reproduce all the results already given in published[4,5,8-12] or to be published[7,13,14] papers/reports. However a summary of the important conclusions of these pieces of work will be given. Neither will this report include a lot of detail on the actual method of electrochemical noise measurement. This aspect is covered not only in previous reports/papers but also in two internal documents dealing with CML and the Gamry ENM equipment respectively.

The report itself is divided into six main sections (1-6). Following the introduction, the experimental section has details on the coatings, substrate preparation, and application of coating to test panels as well as a summary of the ENM method and accelerated test methods. In the third section, a summary of hitherto unpublished results obtained from the 2-coat and 3-coat systems on steel and a brief discussion are given. This includes the effect of stirring/agitation and the effect of temperature on ENM response. The fourth section gives methods, results and discussion of more fundamental studies. This section is divided into two parts: the first covers detached coating work on the marine coatings including the techniques used and results of their resistance and inhibition behavior; the second relates specifically to Resistance Noise (R_n) including data treatment methods, influencing factors and the meaning and derivation of R_n. Section five contains a brief general discussion and a list of all the conclusions which have been arrived at as a result of the work to date. References/bibliography are in section six. Apart from the classic paper by Bacon et al[16] correlating electrochemical measurement to performance and the original Skerry[1,2,3] work and recent work by Huet[17,18] which is of direct relevance to the meaning/derivation of R_n, the only other references are to papers/reports arising directly from this project. A more comprehensive list of papers which pertain to this investigation can be found in the bibliographies to the papers particularly references 4 and 6. A list of the presentations which did not involve a hard copy is also given.

2.0 EXPERIMENTAL

2.1 Materials and Panel Preparation

Panels: The 200 x 100 mm grit blasted steel panels were supplied by Custom Lab Services (Rochester, New York). They had been prepared to a SSPC (Steel Structures Painting council) 5-10 surface, (equivalent to the Swedish standard Sa 2.5). They were stored in a desiccator until application of the coating.

Paints: Following discussion with NSWC CP Code 691 six paints were obtained. There were four primers: an alkyd (A), a zinc silicate (Z), a green epoxy to MIL-P 24441 type 1 F-150 (G), and a brown epoxy (B), and two top coats: a haze gray epoxy to MIL-P-24441 type 1 F-151 (H), and a silicone alkyd (S). The paints were provided by International Coatings Ltd. (Houston, Texas) except for the brown epoxy primer which was provided by Southern Coatings Ltd. (Sumpter, South Carolina). Very little technical information could be obtained about the paints.

Application of systems: Paints were applied to the grit blasted panels by spray. As far as possible the conditions used were similar to what might be achieved in the actual painting of a ship although on a smaller scale. The aim was to achieve the recommended thickness of approximately 70 μm each coat. Multicoat systems were prepared: four two-coat (AA, BH, GH, and ZH) and eight three-coat. With the exception of ZAS (a non-standard system which might not be expected to perform too well in immersion conditions), the other three coat systems were ones which would be typically applied on ships. Those with a silicone alkyd top coat would find use on the superstructure (AAS, ZAS, and ZHS) or the topside/splash zone (GHS and BHS). The ones with the haze gray topcoat (ZGH, BHH, and GHH) might be used for the hull or boot topping. Each coat was allowed to dry for one week before application of the next coat. The thickness of the paint was measured in 10 places on each specimen using an Elcometer™ 345 gauge. Paint thickness values on all specimens used for the ENM experiments were highly reproducible. There was more scatter for the specimens used for the accelerated exposure tests. Because it is a critical factor in determining the level of protection afforded paint thickness values are given in Table 1. At the same time as the coatings were being applied to grit blasted steel the paints were also sprayed on glass plates. By soaking these in pure water detached films could be produced. For some work involving primers alone (stirring experiments) the coating was applied to polished steel by draw down blade.

Panel Preparation: For static ENM tests at room temperature each of the original panels was cut in half to produce two 100 x 100 mm specimens. Wires were attached and the back and all four edges of each specimen were coated with a Colophony Rosin /Beeswax mixture (3/1). This is applied molten (m.p. 60°C) and is a highly effective, inert, high resistance (> 1×10^{12} ohms-100 mm^2), protective coating. The area of paint left exposed was .005 m^2 (50cm^2).

Solutions were made up in distilled deionized water using reagent grade chemicals. For both the cyclic accelerated test and the ENM immersion tests 3% sodium chloride was generally used. However for some periods of the immersion test the solution was switched to synthetic sea water (3% chloride content). (Sea Salts provided by Sigma Chemicals). We noted no changes in the ENM data with this change in immersion fluid. The hot salt bath accelerated test used either 5% NaCl or more concentrated synthetic sea water (5% chloride content).

2.2 Electrochemical Noise Method for Immersion tests

2.2.1 Room Temperature Static experiments

Set Up: A different experimental cell arrangement was employed to that used previously[2,3]. The two nominally identical painted electrodes and the reference electrode were contained in the same glass vessel. This was filled with solution and 90% covered with plastic film. This set-up is illustrated in Figure 1. In the static tests the area exposed of each painted specimen was $0.005m^2$ ($50cm^2$) (it is an advantage when examining high impedance systems to use as large an area as possible). This arrangement also allows the effect of temperature and agitation to be easily assessed (q.v.). However some of the outgrowth work (mostly single coat) used a different method where short lengths of PVC pipe were affixed to the surface to form individual cells on each specimen. These were joined by a salt bridge. In this case the exposed area was $0.0012\ m^2$. This arrangement is shown in Figure 2. This is the configuration used by Edan and Skerry.

Equipment: The equipment used to make the bulk of the measurements was made by CML (formally Capsis March Limited now Corrosion Management Limited, Manchester England). It is a computer controlled, automated digital electrochemical noise system. A block diagram is illustrated in Figure 3. Two nominally identical electrodes are joined together during measurement via a zero resistance ammeter. When not being measured they are hard wired together. These together with the reference electrode comprise one probe. Up to 12 probes (pairs of electrodes) can be monitored. The machine interrogates each probe for (normally) eight and a half minutes and then moves on to the next returning to the first probe at the end of each cycle. In this mode monitoring is essentially continuous and data can be gathered over days, weeks, months, or even years. Data were acquired at 2 second intervals during the 8.5 minute time period to give a total of 256 data points for each of voltage and current in one set. The computer converts the raw data into a graph of current and voltage against time for each interrogation interval (inspection of these "raw data" plots is strongly advised to see whether extraneous factors have affected the result) (see Appendix 4). Resistance noise (R_n) is calculated by dividing σ_V by σ_I where σ_V is the standard deviation of the voltage V and σ_I is the standard deviation of the current I. Apart from calculating R_n, the computer also produces a value of the mean voltage (V_m) and the mean current (I_m) during each eight and a half minute sampling period. Even when the original data are reduced from 512 points to 3 (V_m, I_m and R_n), this still leads to between 12 (12 probes) and 18 (8 probes) values of R_n being obtained every 24 hours. If the experiment is run for 6 months this can produce 2000-3000 data sets. Data compression programs have been developed to deal with this situation (see Appendix 3). There has been discussion[5] of the limitations of CML noise measuring equipment and suggestions have been made for improvements. When pairs of samples were not being measured they were kept hard wired together.

In some of the later work (agitation experiments and fundamental noise studies), equipment manufactured by Gamry was used. This is similar in general design and set-up to the CML equipment although it differs in some details. It has some advantages (Windows^{TM} based software, greater current sensitivity) and some disadvantages (cannot easily inspect raw data files, reduced voltage sensitivity). Note that although the two pieces of equipment (CML and Gamry) rated coating systems in the same order, the actual values of e.g. R_n particularly from high impedance systems did differ somewhat. Possible reasons for this are discussed later.

Protocol: In 2-coat work, four systems (AA, BH, GH, and ZH) were investigated in quadruplicate. ENM data were gathered for 75% of the time. At times when the specimens were not connected to the ENM equipment they remained fully immersed in 3% NaCl.

In 3-coat work, AAS and BHH systems were investigated in sextuplicate. This was done specifically in order to check reproducibility. The other six 3-Coat systems were investigated in duplicate. All samples were continuously monitored over at least the first twenty days of exposure. However, as with the 2-coat work, equipment and time constraints meant it was not possible to continuously monitor all twenty four samples over the full period of the test. At times when they were not being monitored (indicated as straight line sections on the graphs), specimens were left in 3% NaCl. These ENM immersion experiments were run from June through September 1993 (2-Coat) and from November 1993 to May 1994 (3-coat). The solution was at room temperature (around 22-23 °C). Although 3% NaCl was the bathing fluid for most of the time there were periods when synthetic sea water was used for some of the specimens. If anything the latter proved a less aggressive environment to 2-coat specimens. It caused no apparent difference in the 3-Coat work.

2.2.2 Agitation experiments

The arrangement for the agitation experiments is shown in Figure 4. The solution in all cases was 3% NaCl, the temperature was RT (22-23 °C) and specimens were continuously immersed. Beakers were narrower but taller than those used for the main ENM immersion tests. To get more specimens in one beaker the 100 x 100 mm specimens were cut in half and then these were edge protected to give $0.003m^2$ ($30cm^2$) exposed area. The solution was rotated using a 50mm diameter "paddle" driven by an overhead motor and flowed rapidly past the specimens which are held in position by a dismountable lattice constructed from plastic rod. Each beaker had its own motor which was set at a speed such that the base of the vortex created in the solution was at a level approximately 1/3 of the way down the specimens. Hence the specimens in each beaker were exposed to the same geometrical and solution conditions. Four 3-coat (AAS, BHH, GHH, and ZAS) systems were studied. The experimental set up comprised of eight specimens in a beaker (4 pairs) and three beakers, so each of the four systems was investigated in triplicate. Except on the occasions when ENM measurements were being made, each pair of specimens was electrically joined. Continuous monitoring using ENM was not possible due to equipment demand. When measurements were made, the Gamry equipment described above was utilized. Measurements were made at specific times with specimens either exposed to "whirring solution" (on), "whirring above the solution" (up), or "static" (off). This agitation experiment ran continuously for three months. At the end of that time the usual assessment methods were employed (visual and DC resistance).

Work was also conducted on two primer coats: yellow alkyd (A) and green epoxy (G). The paints had been applied to polished (rather than grit blasted) steel by draw-down blade. In these experiments there were six specimens in each of four beakers. Two beakers were static and two were "whirred" for three months. Again any differences in ENM results between up, on, and off were recorded. For this experiment a particularly accurate visual record was obtained. All specimens were photographed at the beginning and at the end of the test. This is recommended procedure for any future work of this kind perhaps in conjunction with digital image analysis (see below).

2.2.3. High Temperature experiments

One aim of this part of the investigation was to see whether the previously observed reduction in resistance of coatings when the temperature is raised would be reflected in reduced values of R_n. Another was to try to differentiate between the better systems (e.g. GHH, BHH, GHS, and BHS) which had all protected very well in the 6 month (room temperature) immersion test. This work also has relevance as 42°C is a temperature which, although unusual in the sea itself, may well be present in the vicinity of outlets from the ship. Under atmospheric exposure conditions the outer surface of the paint can reach 60°C or higher due to the solar heating and the inner surface can reach similar temperatures particularly if the paint system has been applied to a pipe carrying hot fluid.

The experiments were carried out using similar beakers and similar small type specimens as the agitation experiments described above. Temperatures chosen were 42°C, 55°C and an attempt was made to get some results at 70°C. The normal wax / colophony mix stood up satisfactorily to 42°C. A special type of high melting temperature wax was developed which would withstand 55°C (3 parts hard wax, one part soft wax, supplied by Beeswax Products Ltd., Vancouver, Canada). For the 70°C investigation edge protection was attempted using several coats of paint. A paint with a low temperature coefficient of resistance should preferably be used like the haze gray epoxy.

A similar procedure to that used for the Hot Salt Bath test was employed. Close temperature control was achieved but care was needed to prevent evaporation. Selected systems were immersed at 42°C for three months (BHS, GHS, ZGH, and ZHS) and at 55°C (BHH, GHH, BHS, and GHS). ENM data were gathered continuously using the CML equipment described above for one week towards the conclusion of each of the tests. At the end the specimens were observed visually and DC resistance measurements were made. In the 70°C experiments (BHH and GHS) the specimens were connected to the Noise measuring equipment from the start. These experiments are incomplete at the time of writing and the main results are not included here. The ENM measurements detected lower resistance values than expected and this was attributed to the low temperature coefficient of resistance of the paint used for edge protection (silicone alkyd).

2.3 Accelerated Tests

2.3.1 Cyclic Salt Spray/QUV

Specimens for these cabinet tests were prepared at the same time and in the same manner as those for the ENM immersion tests, the only difference being that they were all subsequently scribed (0.7 mm) by the "Giordano" scribing machine (available at Sherwin-Williams Co, Coffeyville, Kansas). Sets of 2-coat and 3-coat paint systems were investigated in triplicate. The salt spray test was conducted in a Q-Fog cabinet with temperature cycling every two hours between 25°C (fog-salt spray on) and 40°C (dry-salt spray off). The solution was 3% NaCl and the air pressure was 24.5 psi. The 2-coat systems were exposed for 1000 hours.

The 3-coat systems had an extra exposure to a QUV/Humidity cycle. After 500 hours in a Q-fog salt spray cabinet, the panels were then transferred to a QUV cabinet where they were subjected to a UV (2h, 55°C)/100% humidity (2h, 60°C) cycle for a total of 250 h. They were then returned to the salt spray cabinet for a further 300 h. The total test time was 1050 h.

This test protocol is similar although not identical to the modern preferred accelerated test for paint systems for protecting structural steel under industrial atmospheric exposure conditions[7]. The latter is proceeding towards ASTM standardization. In the "standard" test the switch between the cyclic salt spray and the QUV/Humidity is made every week. This was not possible in our test. The other differences were in our salt spray exposure which had a slightly higher temperature (40°C rather than 35°C), a slower cycle (change every 2 hours rather than every hour) and use of 3% NaCl rather than diluted Harrison's solution (0.35% ammonium sulphate/0.05% NaCl). These differences were made to bring the test more in line with service experience and to make it somewhat more aggressive.

2.3.2 Hot Salt Bath Test

This is a relatively straightforward test[19]. Scribed duplicate or triplicate specimens were totally immersed in a 2 liter beaker containing either 5% NaCl or 5% sea water. Plastic film was used to minimize evaporation. Beakers were contained in a water bath closely controlled at 55°C. Each test was run for 170 hours. Either the standard wax (55°C is close to it's upper temperature limit) or the special high temperature wax was used.

2.4 Panel Assessment Methods

2.4.1 DC Resistance

The method of making DC resistance measurements involved using a high impedance multimeter in our case a Keithley Electrometer (either 610C or 617). Details of the method can be found in Appendix 1. In the ENM experiments the DC resistance of the individual specimens was measured near the start to check the "blanking off" and again at the end (occasionally it was used during the run if a "leak" was suspected and if the blanking off was found wanting a simple repair could be effected). Normally the measurement was made by flooding the whole exposed (i.e. unwaxed) area with solution.

DC measurements were also made to assess the panels at the termination of the accelerated tests. In that case several small areas on the face (typically 200-300 mm^2) were measured on each specimen and the scratch was measured separately.

2.4.2 AC Impedance

This equipment used was made by Gamry. The controlling software is incorporated into the same unit as the noise equipment. A Solartron 1250 Frequency Response Analyzer is also used. Multiplexing was not possible for this method. AC Impedance is a perturbing technique and thus its use in this work was restricted to measurements on a few samples at the end of the test.

2.4.3 Visual

All the specimens which had been put through accelerated tests were visually assessed at the end. For blistering and corrosion observed on the face, visual observation was converted to a number on a special scale from 1 (several blisters) to 10 (no blisters). This scale is routinely used in our laboratory and was felt to be more applicable to this particular set of results than ASTM D610 or D714. Scribe behavior was assessed separately on a scale from 1 (lot of spread, lot of rusting) to 10 (minimal spread, no rusting). The scales are shown in table 2. The 2-coat and 3-coat ENM specimens exposed in the immersion test were also assessed using the same scale (face only) at the end of the three or six months exposure.

Note that this method of assessing panels is qualitative, operator dependent, and effective comparison is often only possible by the creation of special scales. Because of these drawbacks some preliminary work was conducted during the project to assess panels by Digital Image Analysis (DIA)[20]. This can produce a series of numbers e.g. % rusting, % blistering, average size of rust spot, average size of blisters, even % delamination (in conjunction with thermal imaging) for any individual panel. The preliminary work using DIA was quite successful but further work is needed to enable it to become a routine method of assessment. Certainly such an approach would greatly facilitate the obtaining of quantitative information on the corrosion/blistering of each panel as a function of time. This would enable time-line electrical measurements to be related to time-line "state of panel" observations, which would be very useful.

3.0 RESULTS ON COATED STEEL

3.1 2-Coat Studies

3.1.1 ENM Immersion Tests

Results were obtained for four 2-Coat Marine systems. These are Alkyd/Alkyd (AA), Zinc silicate/Haze gray epoxy (ZH), Brown epoxy/Haze gray epoxy (BH), and Green epoxy/Haze gray epoxy (GH). The aim was to investigate differences between systems which would not be as protective as the three coat systems discussed in section 3.2. Results have not so far been published elsewhere but were presented at Annapolis (Nov. 93).

Data were gathered over fairly long exposure times (70-90 days). Each specimen was .005 m^2 ($50cm^2$) area and was immersed in 3% NaCl (or sea water) at 22-24°C. The raw data were treated to produce values of I_m, V_m, and R_n.

From graphs showing V_m, I_m, and R_n varying over time the following conclusions were drawn. All four nominally identical pairs from one system were reasonably consistent. With the alkyd-alkyd (AA) pairs there was a dramatic reduction in R_n and a rise in I_m which preceded the onset of visible corrosion. The zinc-haze (ZH) pairs had low value of potential (-0.8V SCE), a moderate current, a moderate R_n, and slight rusting by the end of the test period. The brown haze (BH) and green haze (GH) specimens showed some changes in R_n over time. These corresponded to changes in I_m (R_n appeared to change earlier). A spot of rust was seen on one of the two specimens in several cases. The specimens which spent 3 weeks in sea water were less corroded and the R_n apparantly rose. Upon reimmersion in 3% NaCl the R_n value dropped again.

The DC resistance values measured at the end of the test were similar to the R_n values. The R_n value was closer to the specimen of the pair with the lower DC resistance. This is discussed further in section 4.2.

All the 2-Coat ENM results are given in the tables 3-6 for AA, ZH, BH, and GH respectively. A summary is given in table 7 where all four specimen pairs are displayed for comparison. Visible rust was seen on most specimens. From the table it can be seen that at the end of the test the alkyd-alkyd had significantly worse corrosion rating (5.75). This sample also exhibited a higher current and lower R_n than green-haze or brown-haze. None of zinc-haze, brown-haze or green-haze were fully protective, although they had a similar reasonably high corrosion rating (average 8.5). With zinc-haze the relatively low potential may indicate protection, R_n is lower and I_m higher reflecting a porous film which is "corroding" itself. It is likely that the ENM R_n measurement is a measure of the resistance of the paint film.

3.1.2 Accelerated Test Results

Generally all specimens exposed for 1000 h to cyclic salt (3% NaCl) spray stood up well on the face. The alkyd-alkyd (AA) had a rating between 7 and 8, the other three were all 9 or 10 (see table 2 for definition of scales). However all specimens in all four systems were attacked at the scratch, although somewhat variably, the zinc haze (ZH) being the best (rating of 6 to 7) , then the alkyd (rating of 5), then the brown-haze (BH) and green-haze (GH) (rating of 3 to 4).

In the 10 day hot salt bath test there was more attack on the face of the specimens. Average assessment value in 5% NaCl was 5.75 (AA), 7.5 (BH), 6.8 (GH), and 7.8 (ZH) (These results corresponded quite closely to their performance in the long term (ENM) immersion test described above where a corrosion rating (average) of 5.6, 8.5, 8.7, and 8.8 at the end was found). Reproducibility was fairly good. Compared with the cyclic salt spray test, all systems performed better at the scratch. The zinc-silicate rated 10, the alkyd-alkyd rated 8 and the others between 6 and 7. It was noticeable that when sea water salts solution (5%) was used as the bathing fluid (rather than 5% NaCl), the amount of attack both on the face and at the scratch was somewhat less.

3.2 3-Coat studies

3.2.1 ENM Immersion tests

From November 93 until June 1994 experiments on 3-Coat systems were performed. The systems investigated were AAS, BHH, BHS, GHH, GHS, ZAS, ZHS and ZGH. Most of these (6 of the 8) comprised an addition of either haze-gray epoxy or silicone alkyd top coat to the two coat systems discussed above.

Two (AAS and BHH) were investigated in sextuplicate. This was done specifically to check reproducibility among specimens. Detailed results have been published previously[6]. However a summary of the discussion and main conclusions are given below. The other six systems were investigated in duplicate and have not been reported before. Graphs of I_m, V_m, and R_n against time were generated for all the probes. A few illustrative ones are given for good(GHS), middling(ZHS), and poor systems(ZAS) respectively (Figures 19-27). A summary of the electrical response of all eight systems follows:

AAS Poor: R_n decreased, I_m increased through test;

BHH Good: generally high R_n, low current high potential, two probes showed lower R_n;

BHS Good: Low currents throughout, high R_n, periods of positive voltage (around 0.0V) coinciding with higher R_n values;

GHH Good: very low current, medium value of R_n coupled with a quite negative value of potential suggests may be a tiny hole (like BHH) on one of the specimens;

GHS Very good: low current, high R_n, excursions to positive voltages coincides with even higher R_n values ($>1\times10^9$ at times);

ZAS Poor: had a low current for the first thirty days but then current increased rapidly, voltage drifted up toward iron value (-0.6V), corrosion was visible after about 50 days;

ZHS Fairly good: middling R_n value and significant current, voltage drifts upward from near zinc value to approaching iron value, no visible corrosion;

ZGH Fairly good : measurable current, middling R_n value, voltage stayed low, no visible corrosion.

More detailed discussion of *AAS* and *BHH*

The R_n results for *AAS* were reproducible. After an initial high value of around 1×10^9 ohms-cm^2 the R_n fell and then steadied out at around 5×10^6-2×10^7 ohms-cm^2. This is borderline (Bacon, Smith and Rugg's criteria)[16] between a good and poor paint. After 100 days there was not much actual corrosion (in contrast to the 2-Coat work) but there was significant blistering (6 to 20 blisters) which varied somewhat between panels. AAS is not really intended for continuous immersion. Under such conditions, it appears to take up enough water in just a few days such that within a .005 m^2 (50 cm^2)area some of the ions present in the solution find relatively easy conduction paths through the film. Separate tests (see section 4.1.3) show that this alkyd paint contains an inhibitor. So although visible corrosion may not occur for some time, conditions at the paint-metal interface favor a degree of blistering and eventually corrosion.

The R_n results for BHH were more variable. Two of the probes showed an initial fall to a low value of R_n (2 to $5x10^6$ - borderline on Bacon *et al*'s criteria[16]) which remained fairly steady until they were taken off test after 94 days. At the end of the exposure these specimens were scanned across the face using the DC resistance method (Appendix 1). A small low resistance area was found in the corner of one of the specimens of each pair. Close examination revealed a tiny amount of rust. With two probes, R_n stayed high for around 45 days, but was down to about $1x10^6$ by the end. Two others maintained a value $>1x10^7$ throughout the test (fully protective using Bacon *et al*'s criteria[16]). There was no apparent corrosion on any of the specimens constituting these four probes.

These results were consistent with the behavior of AAS and BHH in the accelerated test. A range of causes for variability have been discussed[7]. The two most important are structural variation from point to point and thickness variation. Regarding the former, in paints which dry to form a three dimensional network structure, there will always be regions of reduced cross-linking. These are small compared with say 100 mm^2 but much larger than a monomer unit and for most coatings at normal (e.g. 35-70 μm) thickness there are always a few per 100 mm^2. They allow easy ion penetration and have a reduced DC resistance. Application of multiple coats reduces dramatically the chance of one of these regions extending through the film[21]. With knowledge of the area to be protected and the %D type of a single coat (see Section 4.1.1), the number of coats required to ensure a uniform high resistance could in theory be calculated. However this assumes uniformity of coating and a coating resistance that is not degraded with time (e.g. by contact with alkali). It appears that even three nominal 70 μm coats were not sufficient to protect .06 m^2 (12 x 50cm^2) area of either BHH or AAS.

Regarding thickness variability, application in a factory by spray, although undoubtedly closer to practice, was inferior to, say, the draw down blade method in achieving uniformity. Examination of the thickness values of the AAS and BHH individual specimens showed no significant difference in the average thickness of those which blistered more (AAS) or had a small area of lower R_n (BHH) compared with the rest. However, variability among the ten individual readings of thickness for each coat was greater in the case of those which showed more blisters (AAS) or lower R_n (BHH). Examination of any of the time line graphs shows considerable variability in R_n value from one time period to the next. Reasons for this are discussed in Section 4.2.2 and 4.2.4.

Summary of 3 Coat ENM results

A broad electrical assessment based on low current, high R_n, non-zinc systems, and high voltage (close to calomel voltage being good) in the case of the non zinc systems and low voltage (close to zinc) being good for the non zinc systems puts them in the following order:

GHS>BHS>BHH>GHH>ZGH>ZHS>AAS>ZAS.

Comparing electrical data with corrosion, the first four systems all performed well both electrically and visually. GHS, BHS, and GHH were only tested in duplicate but it was interesting to observe a significant difference between each GHS and each BHH probe. Only one probe (GHS) exhibited a "very good" electrical profile throughout the test. BHH was also of course quite variable. Ranking of the best four systems is therefore not really possible from these results alone.

The latter four were fairly clearly differentiated in their electrical response but only the last two showed any corrosion (ZAS) or blistering (AAS). The best way of electrically assessing zinc rich systems is still open to question. A moderate R_n and a moderate current may be advantageous to assist in maintaining a low (cathodically protecting) potential.

3.2.2 Accelerated Test Results

The results for all eight systems are given in tables (8,9,10). Table 8 gives the results for cyclic salt spray. This includes both visual assessment (see Table 2) and the DC resistance measured at the end of the test. Generally these results rank the paints in the same order as the ENM immersion test. However there was slightly more attack after the salt spray exposure. The GHS sample system did not do particularly well. This may be because these particular salt spray specimens were somewhat under standard thickness. The scribes were all severely attacked: ZGH and ZHS were the best. It was observed that after the 250 h UV humidity exposure, the rate of attack at the scribe slowed. Also the DC resistance of the specimens was higher. It was concluded that the exposure to the hot pure water in the humidity test had caused consolidation of corrosion product and leaching out of sodium and chloride ions. The DC resistance of the scribe was not significantly variable. The hot salt bath test results (tables 9 and 10) were generally similar to the cyclic salt spray but attack at the scribe was less severe. The simulated sea water (5% solution) led to less attack on the face than 5% NaCl. A summarized table of averages of visual assessment for the specimens is given below:

Test	Average Face value	Average Scribe value
Cyclic Salt spray/Humidity Total 1000h	7.5	4.6
Hot Salt Bath 5%NaCl 240 h	7.7	7.2
Hot Salt Bath 5% Sea Water 240 h	9.3	7.1

3.3 Effect of Agitation/stirring

3.3.1 3 Coat systems

The following systems were examined: AAS, BHH, GHH, and ZAS. Two pairs of specimens of each type immersed in 3% NaCl solution with rotating mechanical stirrers were tested for three months at room temperature. Results are shown in Figure 28. ENM measurements were made three different ways: with mechanical stirrers on, off, and freely spinning above the solution. The agitation of the solution did not influence the average current and voltage values. However both σ_V and σ_I were affected. The voltage noise was highest when the stirrers were on but not immersed in the solution. The lowest values of σ_V were found when the stirrers were completely off, and rotating stirrers immersed in the solution resulted in intermediate values of σ_V. A possible explanation is that the stirrers without load rotate at higher rpm and therefore introduce more noise in the measurements. The σ_I was definitely lower when the stirrers were turned off than with stirrers on or above the solution. As far as R_n was concerned it was difficult to see a specific trend. However the values for R_n measured with rotating stirrers were never the same as measured with the stirrers turned off, being as much as two orders of magnitude different for poor coatings with $R_n = 1x10^5$ ohms.

Regarding corrosion, compared with the static ENM tests, agitation distinctly increased the rate of attack with the less protective systems (ZAS and AAS). However stirring did not appear to lead to earlier failure of the better systems (BHH and GHH).

3.3.2 Primer systems

To clarify the effect of stirring, primers were examined. These were a yellow alkyd (A) primer and a green epoxy (G) primer. Three pairs of each type were placed in a beaker with rotating mechanical stirrers and three were placed in a beaker under static conditions. As noted earlier experiments had a duration of three months in 3% NaCl at room temperature (RT). The R_n of the panels was measured with the stirrers both on and off. On average the R_n of G primers was higher. The R_n values measured with rotating stirrers were always lower than when measured with stirrers off. This can be attributed to the greater affect of agitation on the I_m than on the V_m. When the R_n values of static beakers and those with stirrers (but with the stirrers turned off) were compared, it turned out that the R_n values of the panels exposed to agitation were higher (but not by much) than without agitation.

The agitated specimens exhibited more attack than the static panels. All agitated panels both G and A had some rust spots. A primers showed almost no blistering (just a couple of small blisters on two panels) but had more rust than G primers. The latter had severe blistering but less rust than A panels.

3.4 High temperature experiments

The experiments run at 42°C for 3 months showed lower values of R_n than equivalent room temperature experiments. However in experiments at 55°C, the value of R_n was not significantly lower. A difficulty with these experiments was that the heater cutting in and out caused an error and this was frequent at 55°C. However DC resistance values measured at the end were distinctly lower. Despite this, differentiatiation of the better systems (GHH, GHS, BHH and BHS) was not possible due to the scatter between individual specimens being as great as the differences observed.

Regarding protection it was observed that with the poorer systems (e.g. ZAS) there was accelerated attack compared with three months at RT. There was also extra attack on the better systems compared with RT tests but again it was not consistent enough to enable any confident conclusion regarding which was the best system to be reached.

4.0 FUNDAMENTAL STUDIES

This section includes description of some additional experimental methods.

4.1 Detached films

4.1.1 DC Resistance

Method: Further details on the method and some background can be found in Appendix 2. A diagram of the cell is shown in part of Figure 27. Detached coatings had been prepared as described in 2.1. Measurement on approximately ten small pieces ($100mm^2$) of most of the marine coatings other than zinc silicate were made in 0.5M, 5M, and occasionally 0.005M NaCl. Values given for Log R_I and Log R_D are in 0.5M NaCl. Most of the films were investigated over the temperature range 20-60°C. Because of time and manpower limitations the amount of work done on these marine coatings has been limited. A fuller investigation is recommended.

Results and discussion: Following the procedure above for coatings approximately 70μm the results below were obtained for % D type, Log R_I and Log R_D.

Film	% D Type	Log R (I types) (ohms)	Log R (D types) (ohms)	Q value* (KJ/mole)
alkyd primer	35	10.3 (+/- 0.3)	6.4 (+/- 0.6)	160
silicone alkyd	15	10.0 (+/- 0.2)	7.0	130
green epoxy	80	10.4 (+/- 0.2)	6.8 (+/- 0.6)	60
brown epoxy	20	9.4 (+/- 0.5)	6.2	45
haze grey epoxy	50	9.2 (+/- 0.4)	6.2 (+/-0.6)	20
* Q is apparent activation energy of I types from Slope of log R v 1/T plot over range 20-60 C				

These results are fairly typical particularly the observed difference between alkyd and epoxy values of Log R_D, Log R_I, and activation energies. None of these coatings approached the optimum resistance characteristics (see Appendix 2).

With several of the 70-90μm thick marine coatings examined here, the values of %D type are more typical of coatings half or two thirds that thickness suggesting that application by spray results in less satisfactory resistance behavior than would be obtained with coatings prepared by draw down blade under controlled laboratory conditions. The alkyd coatings have fewer D types than the epoxies. It is however known from other work that the resistance of I type alkyd coatings is quite rapidly degraded by contact with alkali. Certainly the number of D types observed in single coats of all of these paints suggests that at least a three coat system would be needed to ensure a reasonable barrier to ions. This is in agreement with the observed failure of the 2-coat systems to prevent corrosion over a .005 m^2 (50 cm^2) area.

No detached resistance behavior work was conducted on the zinc in ethyl silicate paint. The system proved impossible to detach from the glass. It is not cross linked and is inherently porous. There is evidence from other work that the coating has a uniform low resistance (probably around 3 to $7x10^4$ ohms-100 mm^2). The mechanism by which it protects steel (cathodic protection) is generally considered to be quite different than the other systems.

4.1.2 Electrochemical Noise Measurements (ENM)

Method: ENM measurement using detached coatings are quite similar to normal ENM measurements. Two cells similar to those described above are connected via a salt bridge. The set up is shown in Figure *28*. The reference electrode is placed between the two pieces of coating and the working electrodes (thin strips of steel) are in the other arm of each of the cells. There is considerable scope in these experiments to investigate the effect of different substrates, different solutions etc. However only preliminary work has been done here using steel, similar resistance coatings, and 3% NaCl on both sides. In one experiment copper working electrodes were used.

Results and discussions: Pairs of similar resistance pieces of coating were used and the DC resistances of individual pieces was compared with the R_n value obtained in the usual way (see Section 2.2) using both the Gamry and CML equipment.

DC Resistance Range of Individual Pieces		Rn Gamry	Rn Denis
Low	High		
2E+11	4E+11	1E+10	2E+08
3E+10	6E+10	1E+09	7E+07
8E+08	2E+09	5E+08	5E+07
8E+06	3E+07	-	4E+07
4E+05	6E+05	-	6E+05

Note: 2E+11 = $2x10^{11}$ etc

When two strips of copper were used, the R_n values were within a factor of two or three of those obtained using steel electrodes. By the normal standards of accuracy of noise work, this is good agreement. The differences could be attributed to a greater tendency to drifting with the copper electrodes (see section 4.2). These are very much preliminary results and further work is needed.

The work shows that there is reasonably close agreement between the DC resistance and the R_n value for coatings with resistance below about $5x10^7$ ohms. The Gamry equipment and software appears to give results closer to the DC resistance. The reason for this is discussed below.

4.1.3 Inhibition Tests

Method: The tests were simply conducted. The aim is to find out whether the primer coatings contain any effective inhibitive materials. The haze gray epoxy paint was also included. Four coated glass plates, sprayed at the same time as the grit blasted panels, were immersed for several hours in a 2L beaker containing hot pure demineralised water. The leachate was then concentrated by a factor of 4. When cool, the leachate was put into 100 mL beakers into which two weighed 20x50 mm clean steel specimens were introduced. The steel samples had been prepared by immersing in concentrated HCl for 15 seconds, followed by rinsing in water then acetone before storing in a grease free desiccator for at least 24 h before use. Specimens were left in the solution for between seven and ten days and were then removed and reweighed. The extent of corrosion compared with controls (demineralized water) was observed. Based on weight loss an extract from a paint was either classified as inhibitive (zero weight loss), restrainer (decrease compared with the control), or accelerator (increase compared with controls).

Results and discussions: The weight loss of the small steel specimens in the various extracts (leachates) are shown in the table below.

Leachate from	loss in weight (mg)						average % loss (wt.%/day/cm2)
Red alkyd	0	1	0	7	1	1	0.0003
Yellow alkyd	1	22	21	1	2	1	0.0017
Brown epoxy	28	31	29	31	30	31	0.0061
Green epoxy	27	35	24	29	29	32	0.0062
Haze gray epoxy	48	59	48	79	40	68	0.0065
Zinc rich	8	13	15	11	14	12	0.0025
Control	42	60	47	63	41	46	0.0048

It can be seen from this table that the red alkyd extract was effectively inhibitive and the yellow alkyd was partly inhibitive. The leachates from the three epoxies all increased corrosion by about 50% compared with the control. The zinc in silicate reduced the corrosion to about half. No chemical analysis of the leachate was conducted. However some conductivity measurements using a simple conductivity meter were made. The alkyd extracts had a conductivity of 100μS, the epoxy value was 30μS. Also specimens which had been immersed in the extracts from the alkyd paint (inhibitive) and from the zinc rich paint (restrainer) were examined using ESCA (Electron Spectroscopy for Chemical Analysis). This work showed the probable presence of small quantities of molybdenum on the surface of the alkyd specimen and zinc on the surface of the specimens which had been zinc silicate extract. Interestingly no phosphorus was detected. This suggests that the effective inorganic inhibitor in the alkyd paint is molybdate. The molybdate acts like chromate to repair the passive oxide film. The restraining action of the zinc extract is probably due to precipitation of zinc salts particularly zinc hydroxide.

The tolerance of the inhibitive alkyd extracts to chloride was not very high although it did depend on whether the chloride was added before or after the steel specimens were introduced. If chloride was added before then it was very difficult to achieve inhibition. If a level of about 1×10^{-3} M sodium chloride was introduced after several days, most specimens remained inhibited for a further few weeks. These observations have important practical ramifications.

4.2 Fundamental studies on Resistance Noise (R_n)

4.2.1 Derivation and meaning

From the regular DC measurements made at the end of the test it appeared that R_n relates strongly to the DC resistance of the individual panels. Table 11 reproduced from one of the publications[9] showed values of DC resistance, Z_{max}, from AC impedance and R_n for a number of panels all taken at approximately the same time. These data are summarized as Figure 29. However a question arises as to how the resistances of the two individual specimens should best be combined. In early work it was observed that where the DC resistances of individual panels differed then the R_n value was closer to the lower DC resistance value. However in later work an improved relation was found by taking the geometric mean (log of the two resistances added and divided by two). This weights both specimens equally and seems intuitively proper because the current measurement is made with the two specimens in series, the voltage measurement is made with the two specimens in parallel. A recent publication discusses the effect of area[20]. It is thus assumed that noise originates mainly in the coating system itself perhaps as thermal noise or shot noise (see below).

If R_n relates to DC resistance then it should be possible to derive it from first principles. Such a derivation has been published[7]. Although some criticism of the specifics of this derivation has been made[21], the agreed general conclusions are as follows:

1. To calculate R_n as σ_V/σ_I the system should be locally stationary. This means that drift over the measurement period will introduce an error. Steps can hence be taken to correct the data set for drift.

2. The time over which data are gathered should be long compared with the time-scale of the processes giving rise to the noise. By chance or otherwise, the procedure recommended by CML of gathering 256 data points at 2 second intervals appears satisfactory in this respect.

3. The individual current and voltage data should behave in a Gaussian or Normal fashion. Processes which could give rise to noise are probably either thermal or shot. Both of these approximate to Gaussian behavior.

The equations are:

$$\text{Thermal Noise} \quad V_{nt} = \sqrt{4\mathrm{kTR_sB_w}}$$

$$\text{Shot Noise} \quad V_{ns} = \sqrt{2\mathrm{eI_{DC}B_w}}\,\mathrm{R}$$

k	Boltzmann constant
T	temperature

R_s	source resistance
B_w	band width of measureing system
I_{DC}	constant current running through system
e	electron charge
R	resistance

This implies that "spikes" in the 256 point data set, although quite possibly of interest for other reasons, can be safely removed when the main purpose is to obtain an accurate value of R_n.

4. R_n is closely related to a zero frequency impedance. Normally the Bode plot for all except fairly capacitive coatings (which tend to be high impedance and therefore difficult to measure using ENM) is horizontal between 0.5Hz and say 0.05 Hz. Hence this implies the R_n value should be close to the DC resistance value.

4.2.2 Factors affecting

Environmental disturbance: Some experiments were done to investigate the effect of walking past the apparatus. The systems examined were:
GHH/GHS, BHH/BHS, and ZGH/ZHS

The experimental setup was as for a normal noise experiment. Three R_n measurements were made: one with a person constantly walking back and forth by the ENM cell, one before that, and one after. No major effect on voltage or current measurements was observed; however both I_m and V_m values were affected. The current noise(σ_I) and voltage noise (σ_V) values were always higher with imposed extraneous disturbance. The values for σ_I and σ_V before and after walking were almost the same. It should be noted that the σ_I value turned out to be affected more than σ_V by imposed disturbance, showing differences as big as two orders of magnitude. As a result the R_n values taken without any disturbance were higher than when the cell was perturbed by a movement of a person walking by the apparatus.

Equipment: As mentioned earlier (4.1.2) the R_n results are equipment dependent particularly at the high impedance end. A study was conducted[10] comparing the results obtained at Sherwin Williams with those obtained using the CML equipment at NDSU. Subsequently comparison between Gamry and CML equipment was made. The conclusion from this work was that the instruments differ in the degree to which they are influenced by external sources (see walk past experiment described in section above). Perhaps more importantly their ability to accurately measure high impedance coatings also differs. Generally the R_n reading is between one and three orders of magnitude too low compared with the DC value. The observed lower values may in part be because, as pointed out above, R_n is an impedance and the 0.5 Hz impedance could be an order of magnitude less than the 0.05 Hz (typical DC) impedance. However the main reason is the innate limit in the measurement accuracy of the equipment. This is not surprising considering the very small currents and voltages which one is trying to measure in noise work. The following limitations have been suggested:

	Gamry	CML	Sherwin Williams (old "box")
Current noise (amps)	5E-12	3E-11	1E-12
Voltage Noise (volts)	5E-05	2 to 3E-4	1E-7?

Note: 5E-12 = 5×10^{-12}

This means that there is no way of measuring the correct values of resistances above about 1×10^8 with the CML equipment or above about 1×10^9 - 1×10^{10} with the Gamry equipment. This might not appear to be too important as a coating with a value $>1\times10^8$ ohms is generally protective anyway. However if small decreases in high resistances could be accurately measured this makes lifetime prediction possible.

An observation is noted that although the R_n values observed for high impedance coatings are all lower than those for DC resistance, with both pieces of equipment the correct ranking order is retained.

4.2.3 Data Treatment and ways of improving accuracy

Data Reduction

A computer program has been written to handle and analyze the large amounts of ECN Data generated. This Data Reduction program will compress large amounts of data, e.g. 1000 data points (the number of values of R_n obtained with regular gathering over three months), to something manageable (100 data points) without losing information. Full details on how to use this program are available[17].

C Plot

A more flexible program (C-Plot) allowing more sophisticated treatment of the raw data gathered using either GAMRY or CML equipment has been written[18]. It allows spectral or data analysis to be performed in ways other than those provided by the equipment manufacturers. Particularly useful is this program's ability to remove low frequency drift. The latter can cause error in the estimation of R_n by up to one (occasionally two) orders of magnitude. More details on this program are available[18]. It also has the potential to eliminate spikes caused by people walking past the apparatus or by electrical equipment cutting in and out. Apart from plotting graphs of voltage and current against time over the ten minute measurement period, it gives the number of data points falling within 1,2,3,4,5, and 5+ standard deviations from the mean. This enables the operator to see at a glance whether the raw data set obeys the criteria laid down for accurate derivation of R_n (see section 4.2.1). A further sophistication of this program is its capability to alert when the value of either the σ_I or the σ_v approaches the limit of measurement accuracy of the equipment.

Faraday Cage

Some experiments were done where the measuring cell was surrounded by a Faraday cage. This led to some improvement in reproducibility from one measurement period to the next particularly with the Gamry equipment when high impedance films were being examined. However overall the major limitation on accuracy seems to come from the equipment itself. At low impedance there is little effect.

5.0 Conclusions and Future Work

5.1 Conclusions

Other work

Before summarizing the work here, we will briefly look at some other work which either was preliminary to or grew out from this project. The preliminary work reported at the Houston conference in September 93[4,5] studied primers provided by Sherwin Williams. A vary good correlation between performance in accelerated tests, the ENM test performance, and the ENM values was shown. Subsequently work was done with single and two coat systems on steel provided by Miles Inc.[10], and again good correlation was obtained. Later work looked at several Miles coatings on steel and aluminum[13]. Both in this work and in part of the electrocoat investigation[12] the effect of the substrate was clarified. R_n values are initially higher on aluminum and on phosphated steel or on phosphated zinc. With time R_n remains high on aluminum but on phosphated steel or zinc the value drops so the onset of attack at least in 3% NaCl is only delayed. R_n values are no higher on zinc itself than on steel. The excellent behavior of electrocoat was explained[11] at least in part by the very good DC resistance behavior of the detached film. This leads to good resistance characteristics when it is on the substrate. A paper[13] looking at the application of both the noise technique and AC impedance (joint work with University of Cincinnati) to investigate very thin dimethyl silane (DMS) films as an alternative to phosphating is being submitted. This pre-treatment shows promise and AC Impedance correlated with Noise.

2 and 3 Coat Work

Regarding the work in chapter 3 for results on the 2 and 3-coat systems the following specific conclusions can thus be arrived at.

1) Noise measurements have been successfully used to monitor the protection afforded. R_n, I_m, and V_m are all useful but R_n appears to be the most useful and in general terms. The Bacon, Smith, and Rugg criteria ($>1\text{x}10^8$ good, $1\text{x}10^6$-$1\text{x}10^8$ fair/borderline and $<1\text{x}10^6$ poor) seem to be applicable (all values in ohms-100 mm^2).

2) Regarding I_m and V_m with the important exception of zinc rich primer systems, very low currents(I_m) and high (close to calomel) potentials (V_m) are preferable.
3) A lot of data can be gathered and data handling techniques have been developed to deal with this.
4) In the ENM room temperature static immersion test correlation between electrical measurements (DC resistance at end of test and Noise throughout test) and visual appearance has been high. It was possible to divide the eight systems into four groups. Very good (BHH, GHH, BHS, GHS), Good (ZHS, ZGH), Fair (AAS) and Poor (ZAS).
5) It was difficult to separate out the better systems partly because of lack of reproducibility. This was discussed in one publication[6]. It is recommended that these kind of investigations are conducted with multiple samples, at least three and preferably six samples.
6) Correlation between behavior of scribed specimens in cabinet tests and hot bath tests with the behavior in the ENM test has been high. In immersion test, sea water proved somewhat less aggressive than sodium chloride.
7) Agitation of the solution accelerates the breakdown of the poorer systems and also the noise response is altered. However results were not consistent and whether this change in response is artifact, a genuine effect, or a mixture of the two needs to be investigated in further work.
8) Increased temperature reduced the value of R_n. However again variability between specimens prevented separation between the better systems.

Fundamental work

1) R_n appears to relate strongly to the DC resistance of the individual specimens. When the two specimens have differing DC resistances then the best estimate is to take the geometric mean $\text{Log } R_n = (\text{Log } R_{DC1} + \text{Log } R_{DC2})/2$. This indicates a relation to an activation energy
2) Theory suggests that to get accurate values of R_n, the data set must be locally stationary. Thus one is justified in removing drift. Programs have been developed to do this.
3) The sources of noise in coatings work appear to approximate to Gaussian distributions whether they arise from thermal or shot processes.
4) There are limits to the accuracy with which Noise can be measured and this depends on the equipment. At present R_n values above about $5\text{x}10^9$ ohms-cm^2(100mm^2) cannot be measured accurately.

Mechanism Investigation

The other part of the investigation was to obtain information on mechanism. It was hoped to get this from noise data. However in the time scale of the project this did not prove possible because the analytical tools were not available and an understanding of other factors was deemed necessary first. However some information on mechanism can be inferred from the electrical results obtained in the ENM immersion tests particularly when these are taken in conjunction with the fundamental work on detached films. This has shown the following:

1) The observed correlation between protection and ENM measurements suggest that with all these coatings, other than zinc rich, the ionic resistance of the coating is the major contolling factor.

2) Regarding chemical inhibition only the alkyd primer film (and to an extent the zinc rich) provides significant chemical inhibition. This assists in preventing corrosion in the first thirty days or so when the alkyd (AAS) system protected with a borderline R_n value.

3) With all the epoxy-based systems the main mode of protection is barrier, and attack at a break in the coating will not be easily prevented.

4) The detached resistance characteristics suggest that at 70 μm both alkyd and epoxy coatings have a number of easy conduction paths in .005 m^2(50 cm^3). In all systems at least three well prepared coats at 70 μm would be needed to get adequate barrier protection to ions.

5) The alkyd system appears to develop more high conductivity paths within a month (formulation of the alkyd could be improved to reduce this propensity) such that blistering commences. Eventually chemical inhibition may be overwhelmed and corrosion starts.

6) From their R_n values the zinc rich systems appear quite porous. The zinc silicate coating acts like zinc metal and may itself be responsible for the noise response. Low values of R_n may not be deleterious and care must be taken in interpreting DC resistance and ENM R_n results when a zinc rich paint is being investigated.

The above preliminary mechanism conclusions could form the basis for a spectral analysis investigation e.g. by selecting ENM results from the alkyd system early on, the alkyd system later on, zinc rich early and later and the epoxy barrier either (good and bad or early and later) and seeing whether there are understandable differences in the noise spectra.

5.2 Future Work

1. There is scope for extension of the spectral analysis techniques to routine ENM data analysis. Currently the spectral analysis techniques inherent in the DENIS Software from CML require off-line analysis of results, and the considerable data that has been acquired needs to be reviewed for spectral properties besides the currently analyzed R_n, σ_V, and σ_I values. Re-examination by spectral analysis of already acquired ENM data seems appropriate based on other noise studies.

2. Segmented electrodes, imbedded micro-band electrodes and other differentiated electrode configurations in ENM measurement require development. There is a need to gather ENM data when substrate segments are separated to form electrode pairs beneath a common organic.

3. Detached coating films in immersion could be examined by ENM and EIS methods as well as DC resistance. Also the aqueous extract of free films could be investigated. The transport properties of these films needs to be considered experimentally as well as theoretically because of the importance of ion, chemical, and electron transport on the corrosion control properties.

4. The global and local homogeneity of supposedly identical coating/substrate samples need to be characterized. A key issue is to identify the length scale over which a transition from locally heterogeneous films to globally homogeneous films occurs. STM/AFM

instruments could be used to examine interfacial effects, and local mapping of film properties by other methods such as SEM-EDAX, small area FTIR, local film resistance, small area EIS measurements could be done. These measurements may help identify the source of scatter in film property measurements as seen in the present program. Also examination of the local variation in film resistance as a probe for heterogeneity in film properties could be considered, and data treated based on the local vs. global interpretation developed by Fishman, Kurtze & Bierwagen.

5. Examination of the feasibility of EIS data acquisition by imposed I(t) signal and measurement of resulting V(t) signal, i.e., galvanostatic rather than potentiostatic data acquisition could be done. This may help generate comparative EIS data for comparison to ECN data for high resistance coatings.

6. ENM data acquisition in the presence of an imposed potential is required. This would be an emulation of film exposure in the presence of cathodic protection, a method used commonly for Navy ship protection.

APPENDIX 1 In-situ DC Resistance Measurements

Measurement of DC resistance is simply made using two electrodes and an Electrometer. In the case of in-situ measurements, the coated panel acts as one electrode and a reference (e.g. calomel or silver/silver chloride) as the other (the external current is so small that a separate counter electrode is not required). DC measurement on paints requires an electrometer input because resistances are high, (Mohms, Gohms, and Tohms). The instrument normally imposes a small known current, measures the voltage drop across the cell and hence allows R to be calculated. For measurements on detached coatings two identical reference electrodes are used, one in each arm of a small glass cell. The need to impose a small current means DC in-situ resistance measurements cannot be made continuously . They can however be made intermittently with minimal intrusion and at the end of the test.

Usually there is a voltage between the two coated panels in the test cell and between the coated panels and the reference electrode (V_{ext}). When using an analog Keithley Electrometer (610A or 610C) this can easily be compensated for. The voltage range is set (e.g. FSD = 1V) then starting at the highest resistance range, move down until the needle "kicks" to a new value (at this stage if the value, and hence, kick, is small it may be possible to move to a more sensitive voltage range (e.g. FSD = 0.1V)). To calculate R : if the kick occurs on the 10^8 range and it moves, (i.e. $V_{1E8} \sim V_{1E12}$) say 0.15V, then R= $0.15 \times 10^8 = 1.5 \times 10^7$ohms. In this mode the electrometer acts as a galvanostat delivering a current which is the reciprocal of the ohms range, in the case above $1/10^8$A = 10 nA. The charge passed if left 10 seconds (typical time) is 0.1μC. If required the current direction can be reversed , the value measured again and the average calculated. In practice the two values are normally the same.

If the digital Keithley Electrometer 617 is used, measurement for in-situ DC resistance is still possible but is a little more difficult. It is best to use the V/I mode where the operator sets the voltage (V_{app}) rather than the ohm mode. However, in both modes the resistance value the Keithley displays assumes the voltage used is the one the instrument applies. A significant error will be introduced unless the $V_{ext} = 0$.

To get around this in the V/I mode, the circuit voltage ($V_{a\rightarrow b}$) is recorded and the resistance ($R_{a\rightarrow b}$) is measured. Then the direction of the imposed current flow is reversed (this normally reverses the direction of current through the specimen unless $V_{ext} > V_{app}$). The voltage ($V_{b\rightarrow a}$) and resistance ($R_{b\rightarrow a}$) are measured again. If operating voltage V = V_{app} then

$$R_{true} = \frac{R_{(a\rightarrow b)} * (Vapp + V_{a\rightarrow b}) + R_{(b\rightarrow a)} * (Vapp - V_{b\rightarrow a})}{2V}$$

In comparing DC resistance with ENM measurements each panel is measured separately using the reference electrode. Observations so far indicate that the ENM R_n strongly correlates with the geometric mean value of the DC resistance of the separate panels.

Appendix 2 DC Resistance Measurements On Detached Coatings

Knowledge of the resistance behavior of free films can help explain the protection afforded by a coating system when on the substrate[23]. The DC resistance measurement method is a fairly standard procedure. Details have been given in at least one publication arising from this work[11]. Pieces of film are mounted in small glass cells (shown in part of Figure 27). The area exposed depends on the size of the cell. In most of this work it was 1.0 cm^2 ($100mm^2$). The side arms of the cell are filled with solution. Reference electrodes (either saturated calomel or silver/silver chloride) are inserted in the two arms and connected to a Keithley electometer or similar high impedance measuring equipment. Different solutions can be used in the two halves; however in this work the same solution was used on both sides. This was either 0.5 M (3%) or 5M NaCl or 0.005 M NaCl . Cross-linked polymer films at thicknesses between 30 and 100 μm are normally highly heterogeneous in their resistance behavior. The resistance value in concentrated chloride solution compared with dilute solution characterizes an area of film as either D type (resistance of film higher in more dilute chloride), or I type (resistance of film lower in more dilute chloride.) In solutions with ionic concentation equivalent to 3% NaCl or greater, there is a very large difference in resistance between D and I type pieces of film. A typical value for I types is around $1x10^{11}$ ohms (reasonably closely grouped); D types are more scattered and a typical range is from $1x10^6$ to $1x10^8$ ohms in 3% NaCl. To characterize a coating at least ten and preferably twenty pieces of film are needed. It is essential that all pieces have the same thickness preferably within a few %. The number of D types divided by the total number examined (i.e. both D and I types) gives a Figure for the %D type of that coating at that thickness. Note that early work by Bacon, Smith and Rugg who measured the in-situ DC resistance of some 300 paint systems over a period of 3 years in sea water concluded that coatings with resistance > $1x10^8$ ohm-cm^2 were good at protecting the substrate, coatings with resistance <$1x10^6$ ohms-cm^2 were poor and coatings with resistance $1x10^6$-$1x10^8$ were borderline. D types fall into the poor/borderline range and I types are good. The %D type of a coating has been found to be the most useful value to characterize the resistance properties and, in many cases, also the protection afforded. Better coatings have low values (e.g 20% D type or lower), fair coatings are between 20% and 90% and poor coatings are > 90% D type.

When reporting detached resistance characteristics one should also include the number of pieces of film examined and values for the average resistance of the D types and of the I types along with their standard deviations. Because of the wide range it is strongly recommended that the Log Normal distibution is employed (i.e. Log R_I, Log R_D) and %D type. Generally a D area in cross-linked coatings is considered a relatively poor barrier, so that in concentrated (0.5M or greater) chloride solutions ions will penetrate the paint sooner or later.

Easily examined and very important is the effect of temperature. Both the effect of long exposure (days or weeks or months) at high temperature and the effect of temperature over relatively short times can be investigated. Apart from indicating the likely level of protection which the coating will afford at any particular temperature these experimenst give the activation energy for the conduction process which is important to an understanding of mechanism. They also can show whether the coating is above or below the glass transition temperature, and under favorable circumstances an actual value of T_g can be obtained.

An optimum coating would have a 0 (zero) %D type and a Log R_I of 10.5 or higher with a low (less than +/-0.3) standard deviation. It would also have a relatively low activation energy (<80 kJ/mole) to ensure that the resistance remains above $1x10^8$ ohm-cm^2 even at high (60-70 °C) temperature. Additionally the coating resistance should not decrease with time either at room temperature or when held at high temperature both in chloride solution or in alkali (the latter property was not investigated in this work). This sounds a "tall order" but detached electrocoat at only 32µm had resistance characteristics that approach the optimum[11].

Appendix 3 : Data Compression In Fortran

INTRODUCTION

Experiments which determine properties as a function of time often generate large quantities of data. Electrochemical Noise, for example, may sample one data point every 2 seconds for several weeks. This translates into thousands of data points! A graph of this type of data, showing the individual data points, will appear as a smear of points (Figure I) unless plotted on a very large paper.

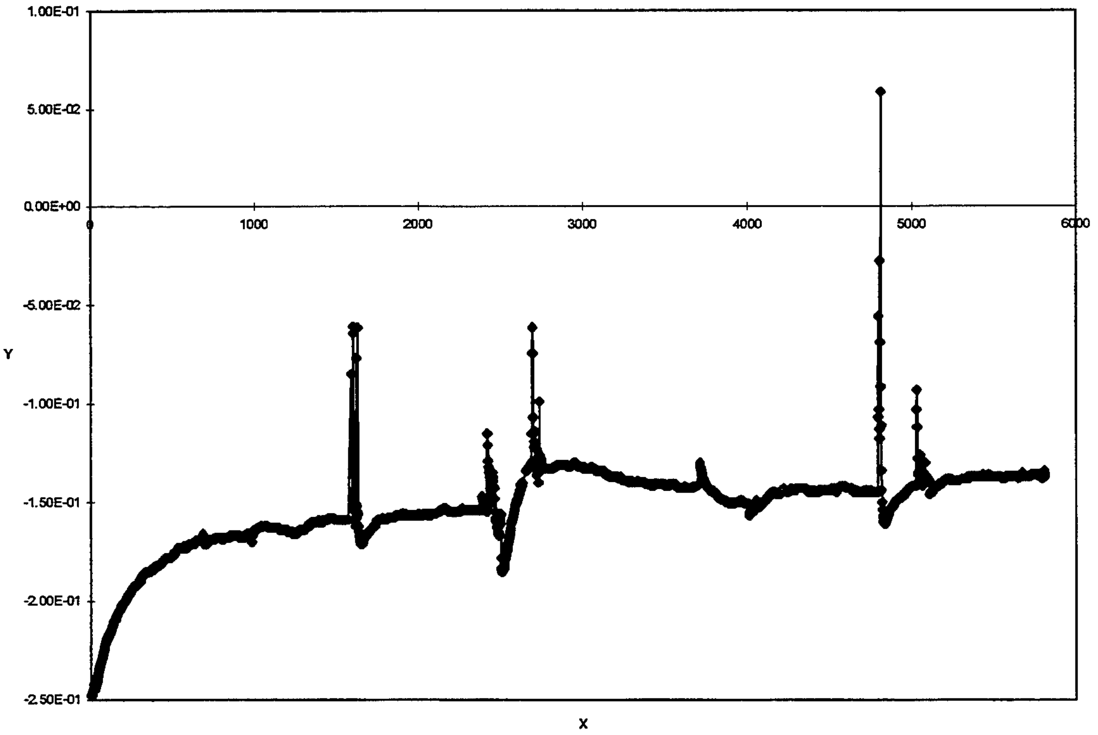


Figure I: Data series with 2817 data points.

Typically, much of the data is constant over a given time period, with intermittent deviations from this constant value. The data in Figure I is fairly steady between 500 and 1500 X. The presence of this "constant data" leads us to consider the possibility of replacing several of these non-changing points with a single point which represents the data set. The obvious solution is to replace several points, say every 10 points, with the average of those ten points. This method requires determining the Y average and the X average in the above Y vs. X plot. Using this method, it should be possible to reduce the graph down to one tenth the number of data points, or only 282 data points.

The problem with this method arises when the data does change. We can simply retain the points which are changing, and average those points which do not change. Now, how do we determine which points are changing? What is the definition of change? What happens when one point changes by itself; is it a valid point, or a wild point? And, if it is a wild point, should we average it into our data set, or discard it completely?

The following paper will outline a solution to the questions stated above, and will provide the FORTRAN code which will then be used to reduce the data in Figure I down to a more manageable data set of 95 or 97 data points without loosing any important information.

Finally, this paper will address the problems of this technique, mainly, how do you distinguish between the "real data" and the new "averaged" data? This becomes a problem when the data is presented in graphical form, where it is usually assumed that points on a graph represent actual experimental data.

WILD POINTS

Wild points are defined as those points which do not represent the experimental model. Often, these points are obtained accidentally and are random in nature. While several statistical techniques have been derived to determine wild points (Chauvenet's Criterion[22,23,24], etc.), they are tedious in nature and cannot be easily implemented into computer code.

This paper simply defines a **wild point** as any data point which changes in one direction, and then immediately changes again in the opposite direction more than half the original distance. In essence, a change in the data must contain more than one point changing in a single direction. Figure I above shows an example of a wild point at about X=4800. This point jumps above zero, and then the next point is back with the "real" trend.

Once a wild point is identified, the question arises as to what to do with it. One solution is to average the data point into the new data. Another solution simply deletes the point as though it never existed. Finally, a third option is to replace the wild point with a new data point which has a more "realistic" value. These options are described in more detail below.

Average into the sample

The first solution to the wild point problem was to average the data point into the new data. We decided above that up to ten points could be averaged together to represent one point which remains constant. The decision to average in a wild point will greatly affect this new averaged point. If the nine points which surround the wild point have an average value of 10 volts, and the wild point has jumped out to -40 volts, the new point will have a value of 5 volts. This point will appear on the graph as if the experiment had a constant value of 5 volts for the 10 hours represented by the new data point. We have managed to maintain all of our experimental data, but we have greatly sacrificed any accuracy and have potentially mis-represented our results. This problem is easily fixed by next two methods.

Delete from the sample

By the very definition of the term WILD POINT, we should be comfortable with eliminating the bad point from our data. This procedure would obviously change our new data in the above example from 5 volts to the correct value of 10 volts.

The problems with this method arise from our crude definition of a wild point. A closer look at a more classical wild point analysis technique, such as Chauvenet's Criterion, indicates that a large sample population (up to 1000 points in our ECN experiments) leaves great latitude for potentially large spreads in data (In Chauvenet's Criterion, $Z= 5$ at $N= \infty$, therefore $d_{acc} = 5*\sigma$). These techniques use the sample standard deviation to define a wild point. That is, they define a wild point as a any point which lies outside of "most" of the values in the population. Recall that for a Gaussian distribution, 99.73% of the data lies within 3σ of the mean. These techniques also theorize that given a large enough population, anything is "bound to happen" (Probability of one event in a sample is $1\text{-}1/N)^3$. The classical statistical approaches will accept every point if the population is sufficiently large. Certainly the wild point we identified at X=4800 in Figure I is within acceptable limits and should be retained if we use these classical techniques.

Replace the Wild Point

The last option is to replace the wild point with a new value that more closely represents the true value. This new value can be interpolated from the surrounding two points. An averaging of the preceeding and following points will yield a new value which simply replaces the wild point. This method is similar to deleting the point, but is not quite as drastic.

Our problem becomes one of definition. Is our purpose in presenting the data to present the data as actual points with exact values, or to show the trends in the data while retaining important changes which show a significant event? In the ECN experiments the latter definition is true, and we choose to use a loose definition of a wild point with the realization that not every point is as important as the trends of the points over time.

Of course, the logical continuation of this definition is to present the data not with points, but to simply display a curve which represents a model of the data. This extreme definition completely eliminates the need for any data compression, but is also buries any useful information such at the values of the interesting points where changes have occurred. If desired, the line graph is a simple solution and this paper does not apply, but in order to retain the important data, we will concentrate on either eliminating the wild points, replacing them, or averaging them into the new data.

SAMPLE ACCEPTABLE DEVIATION

The next important question is how to define when data is constant and when it changes. The classical definition of the standard deviation indicates that most of the data is within 3σ if the mean. This definition, however, does not indicate the rate of change expected between any two adjacent points. For this, we must create a new definition of our sample's acceptable deviation.

Our experimental goal has been to define the trends in the data as a function of time. We are interested in how the data changes from point to point. This goal leads us to define the average vertical step size between any adjacent data points. Recall that we are defining the abscissa as the Y value, and the ordinate as the X axis. Therefore, we are interested in determining the average ΔY value of the sample population. The following equation is easily implemented using a DO loop in our computer routine:

$$\Delta Y = \sqrt{\frac{\sum_{i=1}^{n-1}\left(Y_{i+1} - Y_i\right)^2}{n-1}} \qquad (1)$$

Equation 1 determines the average step size between the data. We can now define a "change" in the data as any $|Y_{n+1} - Y_n|$ which is greater than ΔY. It also allows us to determine that any $|Y_{n+1} - Y_n|$ less than ΔY is not a change.

Unfortunately, the above definition is too rigid for the needs of this paper. We want to be able to reduce a data set down to any size, limited only by our choice of the maximum number of points to be averaged. A typical graph on 8½ X 11 paper looks good with up to about 100 data points. Therefore we want to compress the data in Figure I from 397 to 100 points, not the minimum of 39 points possible by averaging every 10 points. Since the size of ΔY determines which points are going to averaged and which will be retained as changing points, a given set of data will be compressed to one size based on the value of ΔY. A slight modification uses a scaling factor, FRAC, to vary the size of ΔY to allow the desired sample size to be obtained.

$$\Delta \mathbf{Y} = \mathbf{FRAC} * \Delta \mathbf{Y} \quad \text{where} \quad 0 < \mathbf{FRAC} < \infty \qquad (2)$$

This is implemented in the code using an IF-THEN statement which compares the compressed sample size with the desired sample size (100), and then changes the value of FRAC and re-compresses the data. This loop is continued until the desired size is reached for the sample set.

This method also allows flexibility between values obtained of a single sample. For example, in the ECN experiments, five values are monitored as a function of time (Voltage, St. Dev. Voltage, Current, St. Dev. Current, and Resistance Noise). Each of these will have, for the experiment in Figure I, 397 data points over the 100 day experiment. Using equation 1 to define ΔY will results in very different values of ΔY for each of the five data sets. This will most likely compress the five data sets down to very different sizes. The technique used in equation 2 allows each of the five data sets to determine the optimum FRAC*ΔY value which will compress the data to the pre-determined size, 100 in our example.

DATA ANALYSIS

Now that we have defined a wild point, determined what a significant change is, and picked a desired population size for our data, we are ready to apply our technique to a sample using FORTRAN. This section will overview the step by step procedure used in the program to determine the ΔY value and to analyze the data for significant changes and wild points.

A simplistic data set, shown in Figure II, identifies the five possible situations which may be encountered for any given data set. These events, labeled A through E on the graph, will be explained in detail in the following sections.

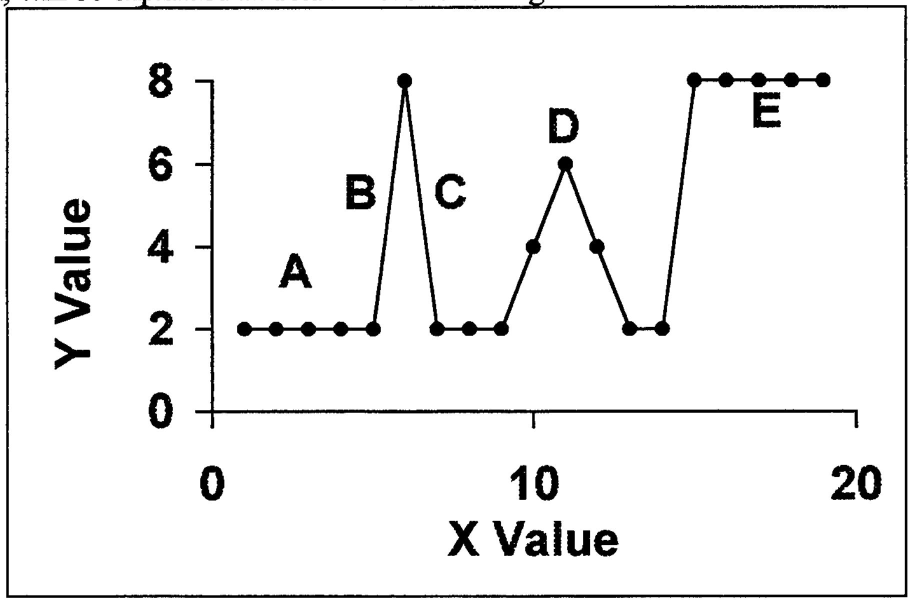


Figure II: Simplistic data set showing the possible data events. A: No change, B: First change, C: Second change, opposite slope (wild point), D: Second change, same slope (good point), E: No change following a change (step change).

Case A: Non-changing data

This situation is defined for any $Y_{n+1} - Y_n < Y_{tol}$ where $Y_{tol} = FRAC*\Delta Y$. This is the simplest situation because the data is ignored, and a counter value, K, is incremented by one. The counter value, K, is used by the program to keep track of how many values have remained constant. When the value of K reaches the maximum number of points to be averaged (10 in our example), the program stops, averages the previous ten points, averages the times corresponding to those ten values, and writes those value into new arrays labeled Y_{new} and X_{new}. After values have been averaged, the value of K is reset and the program continues on with the next points.

Case B: First data change

If the program finds a point such that $|Y_{n+1} - Y_n| > Y_{tol}$, the points are noted, by setting a flag FLAG = 1, as the beginning of a change. The program must then decide the direction and magnitude of change in order to later determine if the next change is in the same or opposite direction. This is done using a variable, SIGN1, which is given a value of $Y_{n+1} - Y_n$. The two values, FLAG and SIGN1, allow the program to "remember" what has happened previously in the set of data that it is currently analyzing. Once it has changed the flag values, the computer increments the counter, K = K + 1, and then continues on to the next point.

Case C: Second Change, opposite direction (Wild Point)

If, after finding the first change and determining the sign of the change, the next point is also a change, the program must again determine the sign of the change. In case C, the second change will have an opposite sign, and hence SIGN2 will be negative. By our earlier discussions on wild points, we can decide that since SIGN1*SIGN2 < 0, the changes must be in opposite directions, and if SIGN2/SIGN1 < -0.5 the second change is significant, and therefore the point is a wild point.

The decision to average the data is the easiest to implement, the FLAG and SIGN flags are reset to zero, and the counter K is incremented just as if there were no change at all. When an important change is found, or ten values have not changed, the wild point will simply be averaged in with the good data points.

Eliminating the wild point is more complicated. The simplest solution is to implement a DO loop beginning at the wild point which will write over the point in the array with the point following it. This is done as follows:

```
 DO 10 I = J,N-1
    Y(I) = Y(I+1)
    X(I) = T(I+1)
10 CONTINUE
```

where J is the index number of the wild point and N is the number of data points in the population. The counter is then incremented by 0 (because the point was eliminated), the flags are reset, and the next data points are checked. When the data points are averaged, the wild point will not be included because it has been erased.

Replacing the wild point is done by interpolating between the preceeding and following points.

```
Y(I) = (Y(I-1) + Y(I+1))/2
```

The wild point is replaced, and the counter K is incremented by one and the program continues. The new value is then averaged in just like it was a good point all along.

The FORTRAN program includes a prompt asking the user to specify whether the wild points should be averaged, eliminated, or replaced. The results of the experiment are given in the appendix for all cases.

Case D: Second Change, same sign

In this case FLAG = 1, indicating that there has been one change prior to this point, and SIGN = SIGN2, indicating that the change has occurred in the same direction. This is our first case of an interesting change. Below is a copy of Figure I with some of the data points labeled for reference.

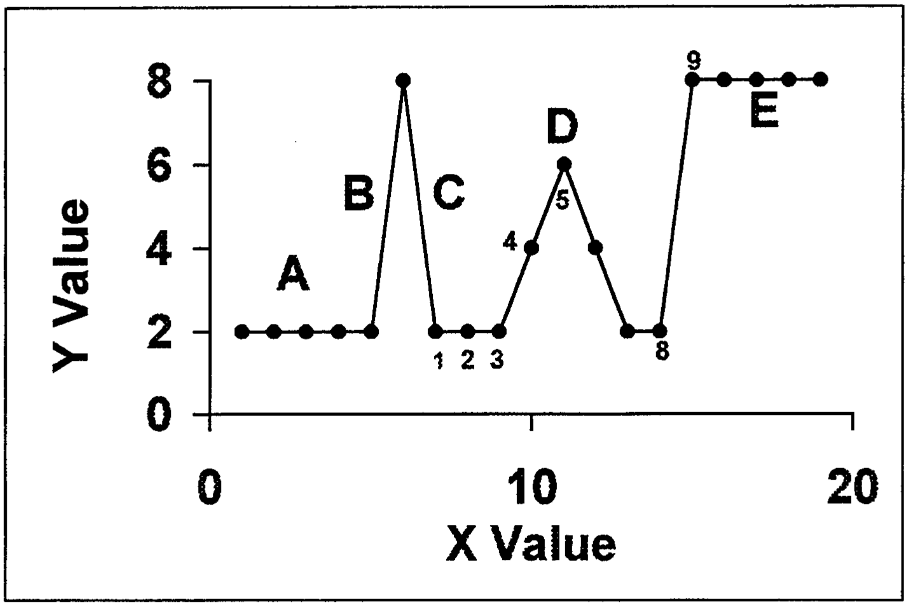


Figure III: Emphasis on case D with specific points labeled 1 - 5.

In this example, the second change was detected between points 4 and 5. Since we have defined a change as $Y_{n+1} - Y_n > Y_{tol}$, the counter value K must have been 4 for case D. This implies that the first change had to occur between points 3 and 4, or K and K-1. In order to retain the values which surround the change, we must retain the changing points, 4 and 5, but also the point which begins the change, point 3. All points prior to the change can be averaged into a new point. Therefore, the points K+1, K, K-1, and K-2 are retained and points before K-2 are averaged. Once the values have been written into the new Y and X arrays, the counter K is reset to zero and the process is restarted with the next data points.

Notice that if point 3 had been averaged, the time value of the previous points would also have been averaged and the new point would have appeared at about X=8. This would have changed the slope of the line making the data appear as if the change began at this new point. Instead, point 3 is retained so that the true start of the change can be identified.

Case E: No Change after a change (step change)

Referring to Figure II, this situation is similar to case D, except that the data after the change remains constant. For this case, we want to retain the points before after the change, points 8 and 9. Since the current point, K, would be equal to 9, we must retain points K and K-1. All the points prior to K-1 can be averaged, and the process is restarted at K=0 and the flags reset.

Cases A through E are implemented in the FORTRAN subroutine AVG as four separate cases. The information above, along with the comments in the code itself, will allow the reader to understand the code.

DEFINING THE OUTPUT SIZE AND COMPRESSION RATIO

As stated above, a graph on standard paper looks best with about 100 data points, MAX = 100. Reducing the graph for use as an insert in a document will limit this number proportionally. The use of the scaling factor FRAC allows us to pre-determine the size of the output from the compression program. Increasing the size of FRAC will increase the value of Y_{tol} and therefore reduce the number of changes which are retained. Likewise, reducing the value of Y_{tol} will retain more points and the final output will contain more numbers. The compression limit is determined by the number of values that are allowed to be averaged, a value called K_{max}. In our example $K_{max} = 10$. This means that the smallest value for the data is N/Kmax, where N is the number of original data points. Because the code must define finite step sizes for FRAC, it is usually not possible to exactly achieve a compression to the desired sample size. To alleviate this problem, a target range has been specified such that the iteration process terminates if $(MAX - 20) < N_{final} < (MAX + 20)$.

The term compression ratio, η, is defined similar to an efficiency:

$$\eta = [1-(N_{final} / N)]100\% \qquad (3)$$

where N_{final} is the number of data points after compression. This value represents the amount by which the data has been compressed. For example, if a 1000 data point sample is reduced to 200 points, it has been compressed by 80%. The maximum compression possible is $\eta_{max} = 1-1/K_{max}$, or 90% for our example.

The value of η is an indication of the amount of data in a compressed sample that is actual data. A sample with $\eta = 40\%$ contains much of the original data points. A sample that has a value of $\eta = \eta_{max}$ has been completely averaged such that every point has been modified.

PROBLEMS WITH OUTPUT

The use of η is one way to represent the amount of conditioning that a data sample has incurred. Unfortunately this method does not specifically indicate which points are original points and which ones are averages. Knowledge of the procedure used to compress the data allows the analyst to guess that those data points which precede and follow a dramatic change in the data are probably original data. That was the idea in the first place! The real problem is encountered when the new data set is presented to another person, or used as a figure in a document.

This becomes a problem of presentation, bordering on an ethical dilemma. The user of this process must state that the new chart contains values which were not explicitly obtained in the original experiment. The data points do, however, very closely represent the data that was obtained and hence the shape of the graph, or the data's trend over time, has remained constant through-out the compression process. This was discussed above: is the purpose to present the actual data points, or to present what happens to the data over a long period of time? This is an individual problem which should be addressed prior to implementing this procedure.

CONCLUSION

This paper has outlined a method for reducing a data set down to a more manageable size for presentation purposes while maintaining the points of interest such as shifts or changes in the data. Attached as an appendix is the code that achieves this process written in Watfor's FORTRAN-77. The output of this program is a text file which contains columns of the new data and new times for each variable that is input. The program is set up to read in the X and Y data in a text file. The output file will contain two columns of data, Xdata, Ydata which represent the compressed data value and the corresponding independatant data points.

Also attached is the sample input and output in text and shown graphically. The experiment was run with the following settings:

$N = 2817$
$Kmax = N/100 = 282$
$MAX = 100$
$\eta_{max} = 99.65\% \quad (1-1/282)$

using a data set containing average voltage from an ECN experiment of a coated panel. The results of the test run are:

N_{final} 97
η ....96.59 %

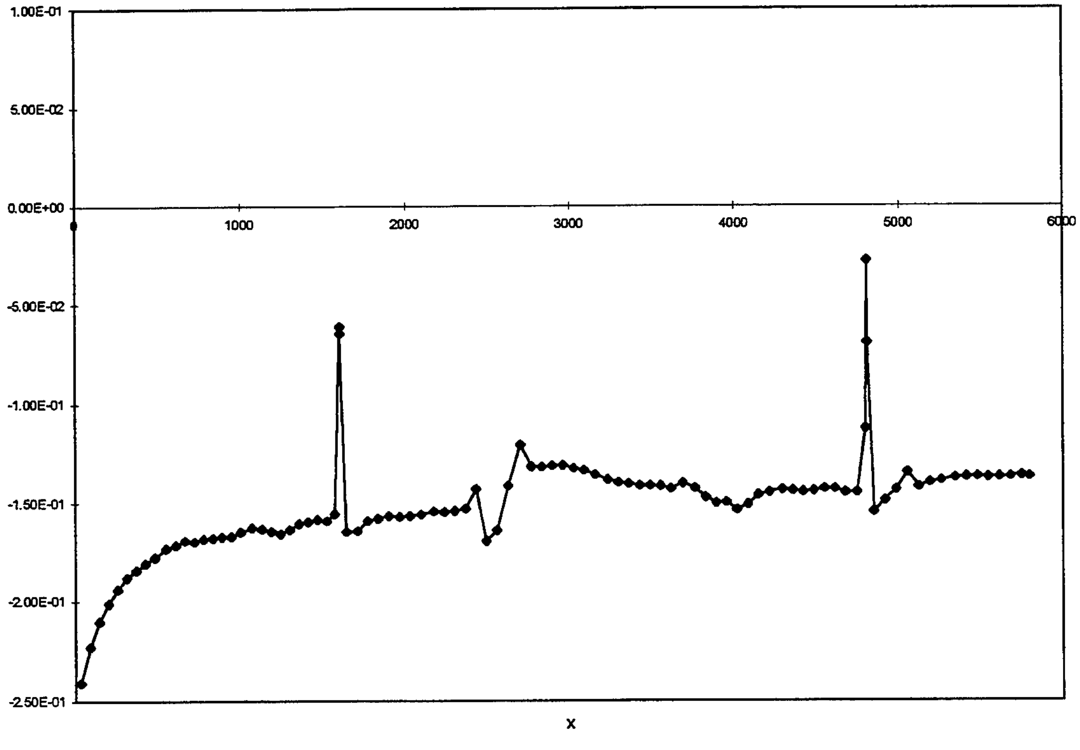


Figure IV: Reduced data set, wild points eliminated. 96 data points.

The spikes in the data set remain because each spike has failed our wild point criteria, they each contain more than one point which has changed. The wild point at X=4800 has been eliminated so that only the few points that are below zero remain. A comparison of Figures IV and I shows that while the data set has been reduced by 96%, the shape of the curve remains essentially unchanged, with the exception of the wild points. A detailed analysis of the data will reveal the the values at the beginning of the changes are infact the original data points. What is unclear, however, is which point on the graph actually represent original data, and which data points are actually an average of up to 282 data points.

Tables

Table 1A: ECN									
Specimen No.	Probe	First	Second	Total	Specimen No.	Probe	First	Second	Total
AA-06a	1b	31	52	83	BH-33a	8a	31	74	105
AA-08a	3a	23	62	85	BH-34a	6b	31	71	102
AA-12a	3b	22	64	86	BH-31b	6b	27	75	102
AA-10b	1b	30	57	87	BH-39b	8a	26	70	96
AA-11b	3b	39	47	86	BH-15c	6a	36	74	110
AA-03c	1a	24	69	93	BH-38c	8b	29	74	103
AA-05c	1a	25	58	83	BH-24d	6a	34	76	110
AA-06d	3a	29	62	91	BH-34d	8b	33	72	105
ZH-34b	4a	33	72	105	GH-10a	5a	29	57	86
ZH-35b	4b	39	83	122	GH-28a	7b	28	69	97
ZH-21c	2b	37	85	122	GH-01b	5a	34	71	105
ZH-22c	2a	35	81	116	GH-40b	7b	28	66	94
ZH-32c	4b	29	74	103	GH-08c	5b	33	57	90
ZH-33c	2a	33	84	117	GH-29c	7a	27	68	95
ZH-31d	2b	30	73	103	GH-27d	7a	23	64	87
ZH-38d	4a	30	70	100	GH-31d	5b	22	78	100

Table 1b: Salt Spray						
		Front			Back	
Specimen No.	First	Second	Total	First	Second	Total
AA-13 b/d	31	40	71	37	41	78
AA-17 a/c	35	36	71	25	42	67
AA-17 b/d	40	36	76	20	48	68
ZH-36 b/d	28	61	89	30	59	89
ZH-39 a/c	31	61	92	29	63	92
ZH-40 a/c	29	58	87	30	62	92
BH-20 a/c	28	58	86	28	54	82
BH-25 a/c	28	54	82	28	54	82
BH-29 a/c	28	52	80	30	59	89
GH-13 a/c	32	58	90	32	62	94
GH-16 a/c	28	62	90	30	56	86
GH-21 a/c	27	63	90	33	58	91

Table 1c: Hot Salt Bath						
		Front			Back	
Specimen	First	Second	Total	First	Second	Total
AA-02 a/c	32	66	98	24	76	100
AA-13 a/c	26	41	67	28	32	60
AA-18 b/d	30	39	69	29	61	90
ZH-21 b/d	41	114	155	26	64	90
ZH-37 b/d	31	66	97	27	58	85
ZH-40 b/d	25	59	84	29	56	85
BH-02 a/c	36	87	123	40	84	124
BH-04 b/d	38	102	140	42	129	171
BH-18 a/c	28	103	131	26	65	91
GH-03 b/d	31	72	103	33	72	105
GH-26 a/c	21	83	104	24	82	106
GH-30 b/d	22	79	101	22	76	98

	Table 2: Corrosion/Blistering Scale from Appearance
Value	Scratch
1	severe spread (several mm), heavy corrosion
2	severe spread in places, moderate corrosion
3	moderate spread (two mm), quite severe corrosion
4	some spread (up to 1.5 mm) in places, mod. corrosion
5	some spread (up to 1.5 mm) in places, some corrosion
6	only a little spread (1 mm or less), some corrosion
7	little spread, little corrosion
8	slight spread, (0.5 mm), slight corrosion
9	slight spread, virtually no corrosion
10	no spread, no corrosion
Value	Face
1	multiple blisters (60), rust, extensive loss of adhesion
2	lot of blisters (eg 40), some adhesion loss
3	lot of blisters but very little adhesion loss
4	several largish blisters plus some adhesion loss eg from edge
5	scattered but fairly numerous (eg 20) blisters
6	few blisters (10)
7	only a few blisters (< 5)
8	a very few isolated blisters
9	one or two isolated blisters
10	zero blisters and no corrosion or adhesion loss

Table 3 : 2 Coat Marine ENM Results
Alkyd - Alkyd System

Samples:	3c to 5c	6d to 8a	6a to 10b	11d to 12c
Type of Test	A	B	C	D
Time (Days)	88	56 (+36)	70	70
Ave. Voltage (SCE)	-0.5	-0.4	-0.3	-0.55
Voltage at end (SCE)	-0.63	-0.51	-0.47	-0.58
Ave. Current (A)	2.00E-09	6.00E-08	4.00E-09	6.00E-08
Current at end (A)	5.00E-07	2.00E-09	2.00E-09	2.00E-09
Ave. Rn (ohm)	1.00E+06	1.50E+07	2.50E+07	1.00E+06
Rn at end (ohm)	4.00E+04	2.50E+07	5.00E+07	1.50E+06
Corrosion Rating				
at end	3, 4	5, 6	6, 7	5, 5
Code for Test:				
A = July 1 - 19, Aug. 6 - Sept. 26				
B = July 1 - 19, Aug. 6 - Sept. 26				
C = July 19 - Sept. 26 (Sea Water Aug. 6 - 26)				
D = July 19 - Aug. 5, Aug. 26 - Sept. 26				

Table 4 : 2 Coat Marine ENM Results
Zinc - Haze System

Samples:	22c to 33c	34b to 38d	21c to 31d	32c to 35b
Type of Test	A	B	C	D
Time (Days)	88	56 (+36)	70	70
Ave. Voltage (SCE)	-0.92	-0.93	-0.95	-0.95
Voltage at end (SCE)	-0.95	-0.93	-0.95	-0.91
Ave. Current (A)	2.00E-09	2.00E-08	1.00E-08	1.00E-08
Current at end (A)	4.00E-09	1.00E-08	2.40E-08	1.60E-08
Ave. Rn (ohm)	4.00E+06	2.00E+06	5.00E+06	5.00E+05
Rn at end (ohm)	5.00E+05	2.50E+06	5.00E+05	5.00E+05
Corrosion Rating at end	8, 9	7, 9	10, 10	9, 9

Code for Test:
A = July 1 - 19, Aug. 6 - Sept. 26
B = July 1 - 19, Aug. 6 - Sept. 26
C = July 19 - Sept. 26 (Sea Water Aug. 6 - 26)
D = July 19 - Aug. 5, Aug. 26 - Sept. 26

Table 5 : 2 Coat Marine ENM Results
Green - Haze System

Samples:	1b to 10a	27d to 29c	8c to 31d	28a to 40b
Type of Test	A	B	C	D
Time (Days)	88	56 (+36)	70	70
Ave. Voltage (SCE)	-0.5	-0.6	-0.48	-0.65
Voltage at end (SCE)	-0.43	-0.71	-0.48	-0.6
Ave. Current (A)	2.00E-09	1.60E-08	1.20E-09	2.00E-09
Current at end (A)	8.00E-09	3.00E-08	2.00E-10	3.00E-09
Ave. Rn (ohm)	1.50E+07	2.50E+07	5.00E+07	2.50E+07
Rn at end (ohm)	1.00E+06	5.00E+06	2.50E+08	1.50E+07
Corrosion Rating at end	8, 10	7, 8	9, 9	8, 10

Code for Test:
A = July 1 - 19, Aug. 6 - Sept. 26
B = July 1 - 19, Aug. 6 - Sept. 26
C = July 19 - Sept. 26 (Sea Water Aug. 6 - 26)
D = July 19 - Aug. 5, Aug. 26 - Sept. 26

Table 6 : 2 Coat Marine ENM Results
Brown - Haze System

Samples:	15c to 24d	33a to 39b	31b to 34a	34b to 38c
Type of Test	A	B	C	D
Time (Days)	88	56 (+36)	70	70
Ave. Voltage (SCE)	-0.4	-0.5	-0.63	-0.4
Voltage at end (SCE)	-0.52	-0.63	-0.65	-0.42
Ave. Current (A)	4.00E-09	6.00E-10	4.00E-09	2.00E-09
Current at end (A)	6.00E-09	1.00E-09	1.20E-08	1.00E-09
Ave. Rn (ohm)	1.50E+07	5.00E+07	3.00E+06	3.50E+07
Rn at end (ohm)	4.00E+07	1.00E+07	1.50E+06	1.00E+07
Corrosion Rating				
at end	8, 10	7, 8	9, 9	9, 10
Code for Test:				
A = July 1 - 19, Aug. 6 - Sept. 26				
B = July 1 - 19, Aug. 6 - Sept. 26				
C = July 19 - Sept. 26 (Sea Water Aug. 6 - 26)				
D = July 19 - Aug. 5, Aug. 26 - Sept. 26				

Table 7				
System	V avg. V(SCE Scale)	I avg. (amps/cm^2)	Rn avg. ohms/cm^2)	Corrosion Rating (%)
Alkyd-Alkyd	-0.45	8.00E-07	9.00E+06	56
Zinc-Haze	-0.93	1.50E-08	3.00E+06	89
Green-Haze	-0.55	5.00E-09	3.00E+07	85
Brown-Haze	-0.47	2.00E-09	1.80E+07	87

Table 8 3 Coat Accelerated Testing

Accelerated Test Results (Cyclic Salt Spray 1050 hrs)*
- Visual Assessment & DC Resistance

Paint	Specimen	Protection Rating		DC Resistance (Ω/cm^2)	
		Face	Scratch	Face	Scratch
AAS	6a	7	3	1.0E9, 1.5E9	3.5E3
	6d	7	3	5.0E8, 4.0E8	6.0E3
	7d	6	3	1.0E9, 1.0E9	4.5E3
BHH	26c	10	6	5.0E9, >2.0E10	6.0E3
	27c	9	6	>2.0E10, >2.0E10	7.0E3
	29c	7	6	3.0E9, 3.0E10	6.0E3
BHS	1b	7	4	3.0E10, 2.0E10	4.5E3
	5b	7	4	>2.0E10, 2.0E10	7.0E3
	1c	7	3	1.0E10, 3.0E10	7.0E3
GHH	29a	9	2	1.0E9, 1.0E9	8.0E3
	20b	10	1	3.0E9, 9.0E8	7.0E3
	29d	9	2	3.0E8, 2.0E8	6.0E3
GHS	2a	5	3	2.0E7, 3.0E8	3.0E3
	2b	5	4	>7.0E10, >8.0E10	6.0E3
	1c	4	5	>7.0E10, >6.0E10	6.0E3
ZAS	2c	4	4	1.8E9, 1.0E9	8.0E3
	3c	8	4	3.0E7, 4.0E8	9.0E3
	4c	7	3	1.5E8, 4.0E8	7.0E3
ZGH	22c	9	7	>3.0E10, >4.0E10	6.0E3
	23c	9	8	4.0E10, 1.5E10	8.0E3
	24d	10	7	>2.0E10, >5.0E9	8.0E3
ZHS	1b	9	8	>3.0E10, >3.0E10	6.0E3
	16b	8	8	>1.0E10, >1.0E10	1.0E3
	17d	9	7	>2.0E10, >3.0E10	8.0E3

*The specimens were exposed to UV/humidity cycle at Coffeyville for 250 hrs

AAS: Alkyd primer, Alkyd midddle coat, Silicone Alkyd top coat

BHH: Brown Epoxy primer, Haze Gray Epoxy middle coat, Haze Gray Epoxy top coat

BHS: Brown Epoxy primer, Haze Gray Epoxy middle coat, Silicone Alkyd top coat

GHH:Green Epoxy primer, Haze Gray Epoxy middle coat, Haze Gray Epoxy top coat GHS: Green Epoxy primer, Haze Gray Epoxy middle coat, Silicone Alkyd top coat

ZAS: Zinc Silicate primer, Alkyd midddle coat, Silicone Alkyd top coat

ZGH: Zinc Silicate primer, Green Epoxy middle coat, Haze Gray Epoxy top coat

ZHS: Zinc Silicate primer, Haze Gray Epoxy middle coat, Silicone Alkyd top coat

Table 9 Accelerated Test Results 5% NaCl

Accelerated Test Results (Hot Salt Bath) In 5% NaCl solution at 55°C for 240 hrs
- Visual Assessment & DC Resistance

Paint	Specimen	Protection Rating		DC Resistance (Ω/cm^2)	
		Face	Scratch	Face	Scratch
AAS	13a	9	6	1.0E9	2.5E3
	16b	7	6	1.0E9	3.0E3
	5a	6	7	9.0E7	3.5E3
	14a	5	6	1.0E7	3.0E3
BHH	33b	9	6	1.5E10	3.5E3
	35c	9	6	1.0E10	1.1E4
	30a	5	6	>2.0E9	3.0E3
	29b	4	7	7.0E9	3.0E3
	30d	5	6	2.0E9	3.0E3
BHS	14b	10	6	4.5E7	1.0E4
	18c	7	6	3.0E9	4.0E3
	12b	9	7	>2.0E9	4.0E3
GHH	24a	9	6	2.0E9	3.0E3
	24d	8	6	2.0E9	4.0E3
GHS	4c	10	6	4.0E9	4.0E3
	8b	10	6	1.5E10	4.0E3
	9b	5	7	2.0E9	3.5E3
ZAS	12b	7	6	1.5E8	6.0E3
	13d	5	7	1.5E9	5.0E3
	8a	5	8	8.0E6	5.0E3
ZGH	30d	8	10	3.0E9	5.0E3
	33d	6	9	2.0E9	5.0E3
	25c	10	10	2.0E9	5.5E3
ZHS	2b	10	10	2.0E9	6.0E3
	4b	10	10	3.0E9	8.0E3
	9b	10	10	2.0E9	9.0E3

AAS: Alkyd primer, Alkyd midddle coat, Silicone Alkyd top coat
BHH: Brown Epoxy primer, Haze Gray Epoxy middle coat, Haze Gray Epoxy top coat
BHS: Brown Epoxy primer, Haze Gray Epoxy middle coat, Silicone Alkyd top coat
GHH:Green Epoxy primer, Haze Gray Epoxy middle coat, Haze Gray Epoxy top coat GHS: Green Epoxy primer, Haze Gray Epoxy middle coat, Silicone Alkyd top coat
ZAS: Zinc Silicate primer, Alkyd midddle coat, Silicone Alkyd top coat
ZGH: Zinc Silicate primer, Green Epoxy middle coat, Haze Gray Epoxy top coat
ZHS: Zinc Silicate primer, Haze Gray Epoxy middle coat, Silicone Alkyd top coat

Table 10 Accelerated Testing 3 Coat Systems in Sea water

Accelerated Test Results (Hot Salt Bath)* - Visual Assessment & DC Resistance

Paint	Specimen	Protection Rating		DC Resistance (Ω/cm^2)	
		Face	Scratch	Face	Scratch
AAS	13a	9	6	1.0E9	2.5E3
	16b	7	6	1.0E9	3.0E3
	5a	6	7	9.0E7	3.5E3
	14a	5	6	1.0E7	3.0E3
BHH	33b	9	6	1.5E10	3.5E3
	35c	9	6	1.0E10	1.1E4
	30a	5	6	>2.0E9	3.0E3
	29b	4	7	7.0E9	3.0E3
	30d	5	6	2.0E9	3.0E3
BHS	14b	10	6	4.5E7	1.0E4
	18c	7	6	3.0E9	4.0E3
	12b	9	7	>2.0E9	4.0E3
GHH	24a	9	6	2.0E9	3.0E3
	24d	8	6	2.0E9	4.0E3
GHS	4c	10	6	4.0E9	4.0E3
	8b	10	6	1.5E10	4.0E3
	9b	5	7	2.0E9	3.5E3
ZAS	12b	7	6	1.5E8	6.0E3
	13d	5	7	1.5E9	5.0E3
	8a	5	8	8.0E6	5.0E3
ZGH	30d	8	10	3.0E9	5.0E3
	33d	6	9	2.0E9	5.0E3
	25c	10	10	2.0E9	5.5E3
ZHS	2b	10	10	2.0E9	6.0E3
	4b	10	10	3.0E9	8.0E3
	9b	10	10	2.0E9	9.0E3

*In 5% NaCl solution at 55°C for 240 hrs

AAS: Alkyd primer, Alkyd midddle coat, Silicone Alkyd top coat

BHH: Brown Epoxy primer, Haze Gray Epoxy middle coat, Haze Gray Epoxy top coat

BHS: Brown Epoxy primer, Haze Gray Epoxy middle coat, Silicone Alkyd top coat

GHH:Green Epoxy primer, Haze Gray Epoxy middle coat, Haze Gray Epoxy top coat GHS: Green Epoxy primer, Haze Gray Epoxy middle coat, Silicone Alkyd top coat

ZAS: Zinc Silicate primer, Alkyd midddle coat, Silicone Alkyd top coat

ZGH: Zinc Silicate primer, Green Epoxy middle coat, Haze Gray Epoxy top coat

ZHS: Zinc Silicate primer, Haze Gray Epoxy middle coat, Silicone Alkyd top coat

Table 11

Comparison of R_{dc}, Noise and AC Impedance

Probe #			R_{dc}	R_n	R_l	$R_{dc}\|\|$
1	ZHS	7C	2.00E+4	1.85E+5	1.15E+3	1.97E+4
		8C	1.20E+6		3.69E+5	
2	BHH	33A	5.00E+8	1.57E+8	5.50E+8	4.17E+8
		36B	2.50E+9		1.00E+9	
3	BHS	6C	2.00E+8	3.46E+7	1.52E+8	1.43E+8
		7B	5.00E+8		2.02E+8	
4	BHS	2D	5.00E+8	5.62E+7	4.06E+8	8.33E+7
		4B	1.00E+8		8.97E+7	
5	ZHS	7D	2.00E+4	7.30E+5	2.00E+3	1.33E+4
		8D	4.00E+4		1.20E+4	
6	GHS	13D	5.00E+8	3.27E+8	4.00E+8	2.50E+8
		14C	5.00E+8		4.00E+8	
7	GHS	9C	1.50E+9	7.02E+7	4.90E+8	3.75E+8
		13C	5.00E+8		2.00E+8	
8	BHH	34A	1.50E+9	3.70E+8	4.10E+8	7.50E+8
		37D	1.50E+9		4.50E+8	
9	AAS	8B	4.00E+6	9.19E+6	4.56E+6	2.40E+6
		11D	6.00E+6		6.77E+6	
10	AAS	12C	5.00E+6	2.39E+6	5.92E+6	1.88E+6
		13D	3.00E+6		6.55E+6	
11	AAS	15C	8.00E+6	9.31E+6	8.68E+6	4.00E+6
		17D	8.00E+6		8.16E+6	
12	AAS	1A	2.00E+7	1.08E+7	1.82E+7	6.67E+6
		5D	1.00E+7		1.22E+7	

Figures

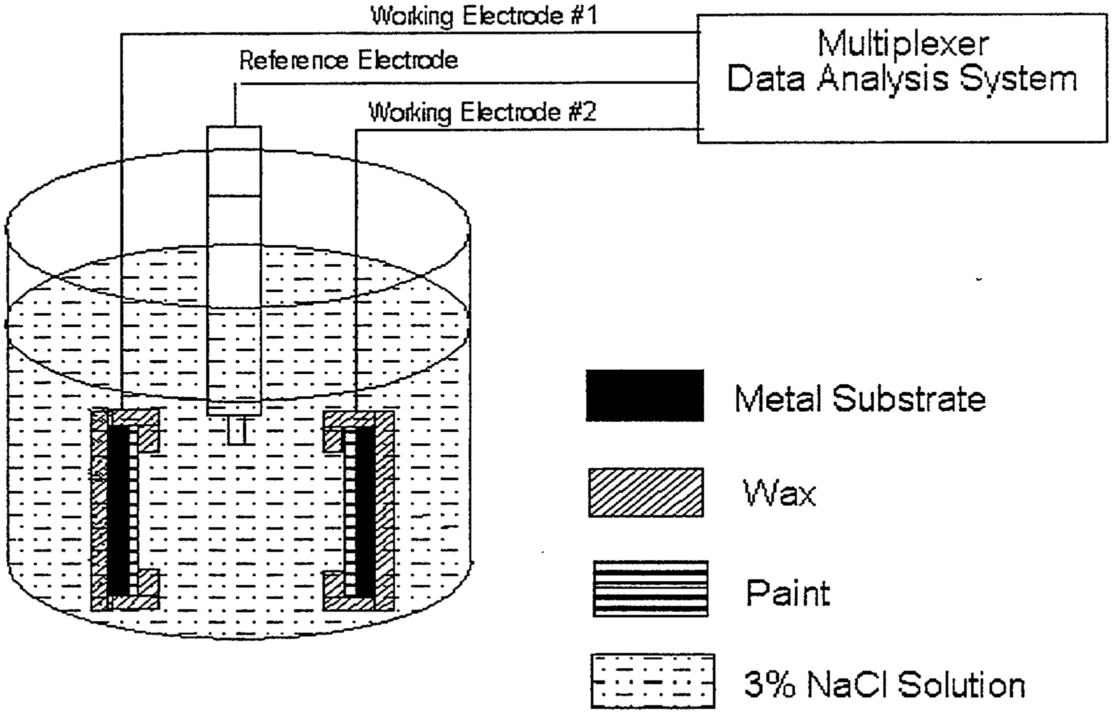


Figure 1

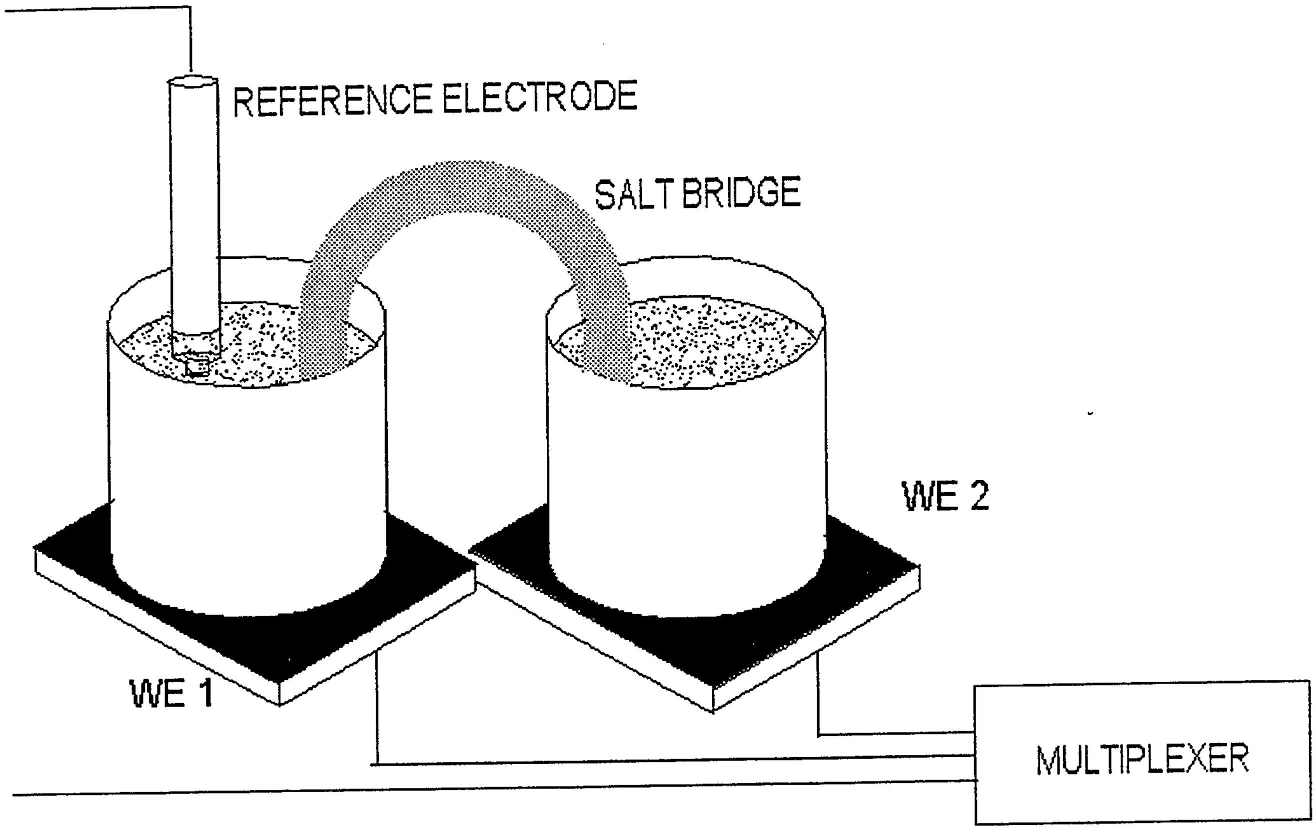
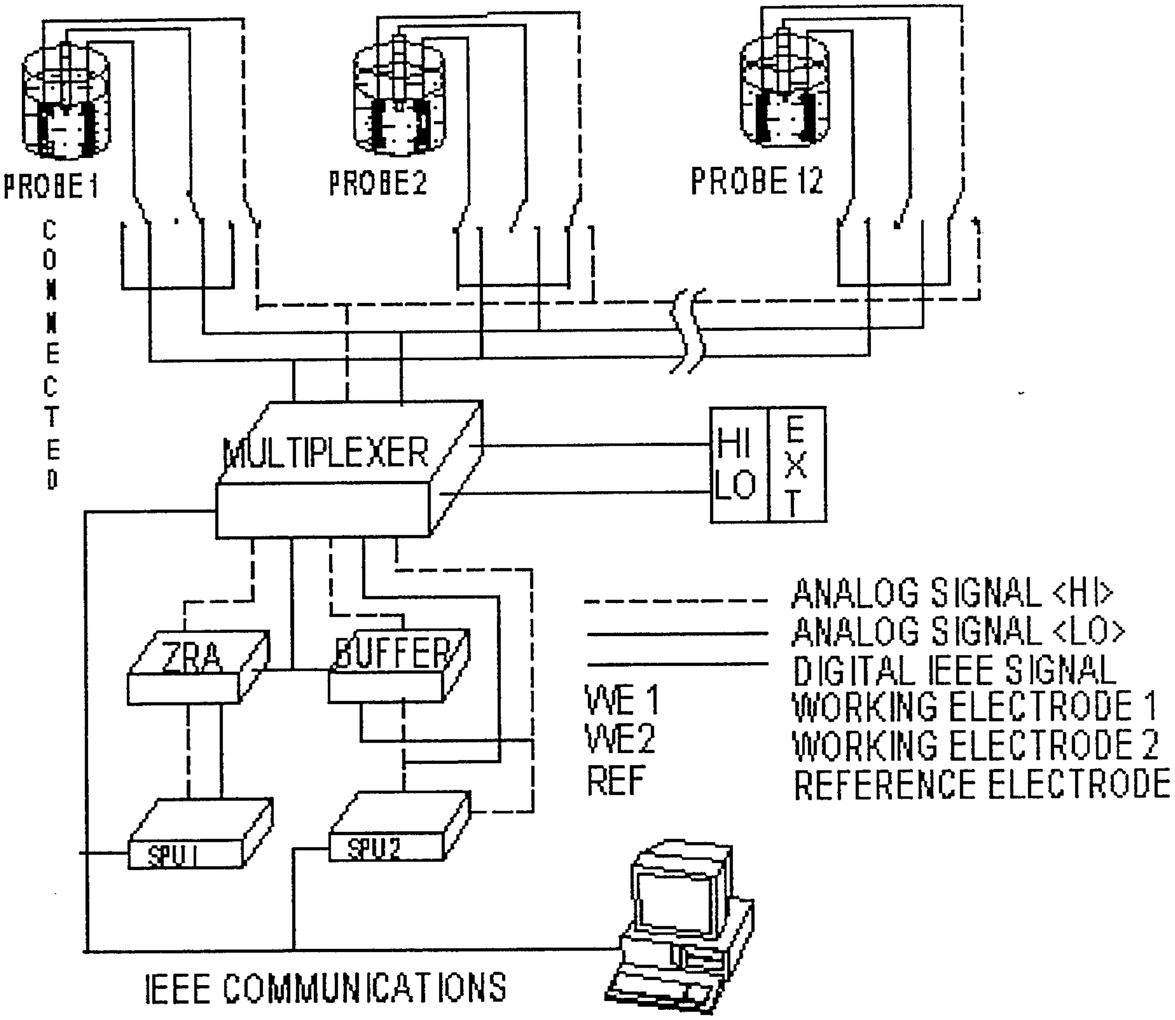


Figure 2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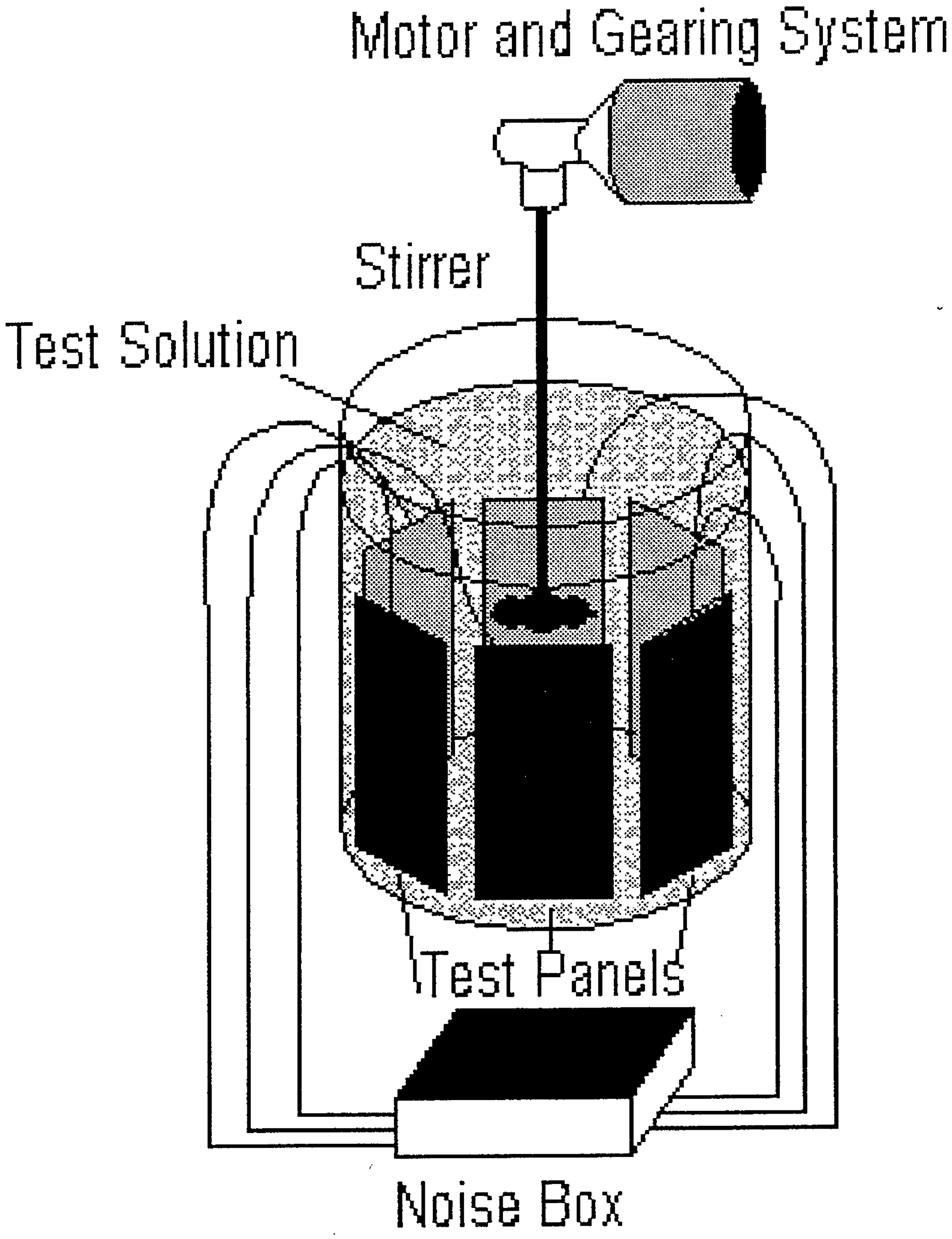
WE2 WORKING ELECTRODE 2
REF REFERENCE ELECTRODE

Figure 3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Stirrer
Test Solution
Test Panels
Noise Box

Figure 5
Reduced Average Voltage GHS (6B)

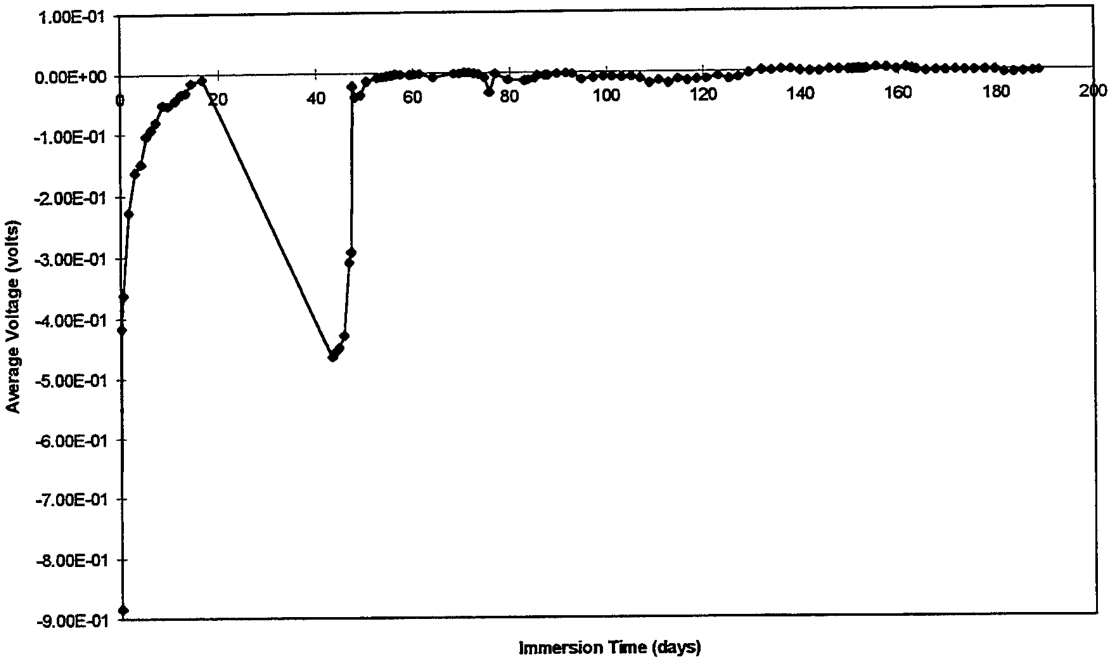


Figure 6
Reduced Average Current GHS(2B)

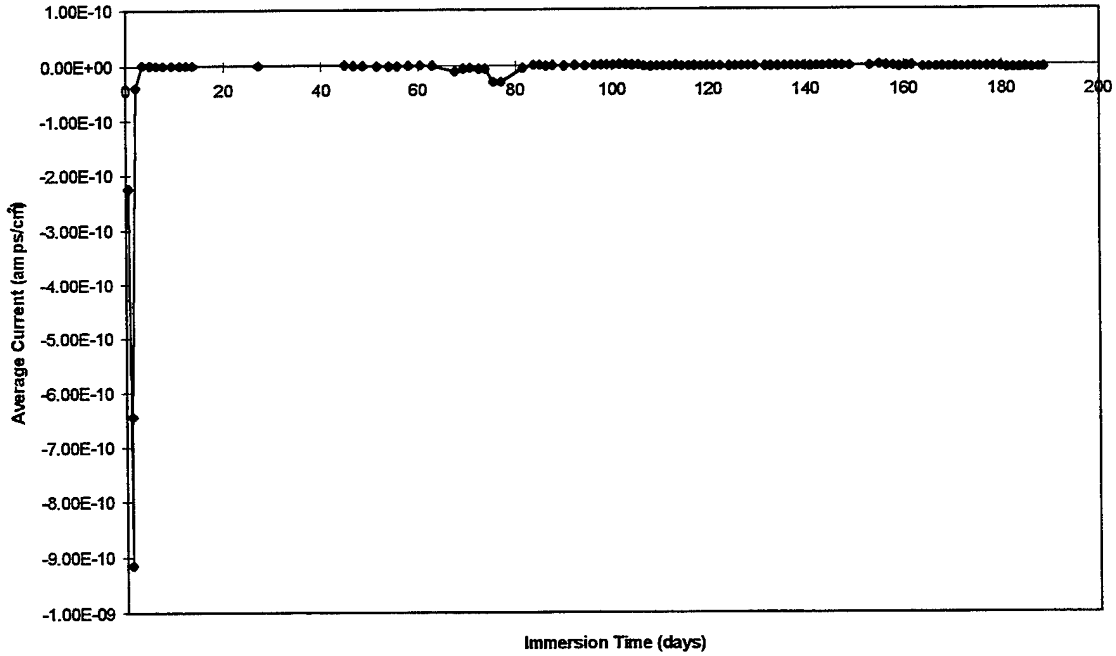


Figure 7
Reduced Resistance Noise GHS (6B)

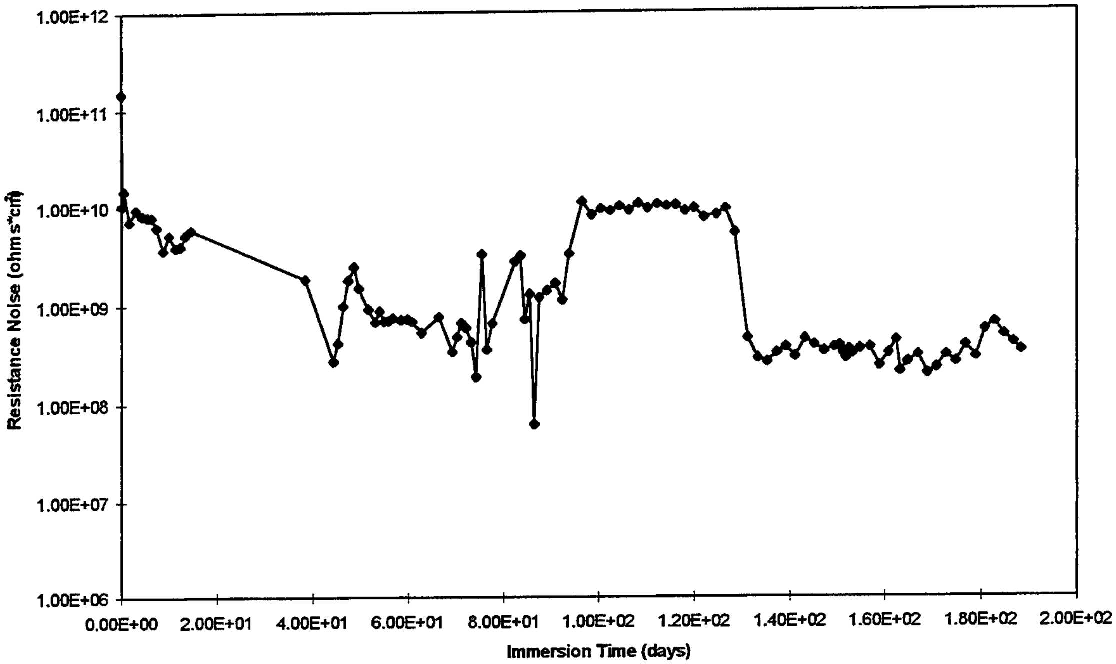


Figure 8
Reduced Average Voltage ZHS (5B)

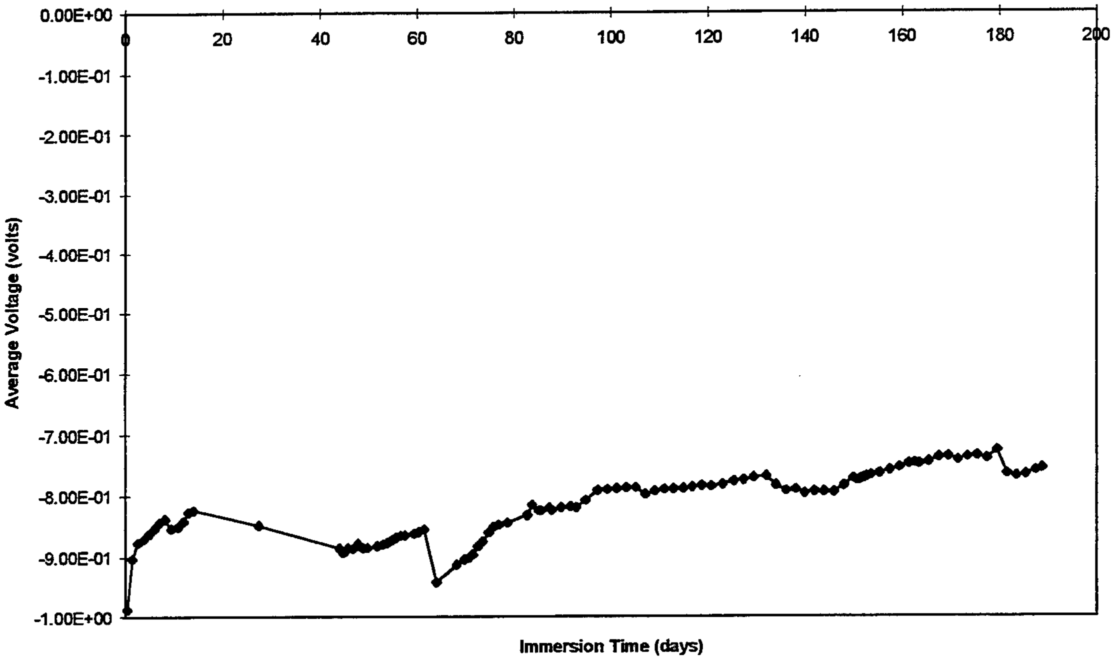


Figure 9
Reduced Average Current ZHS (1B)

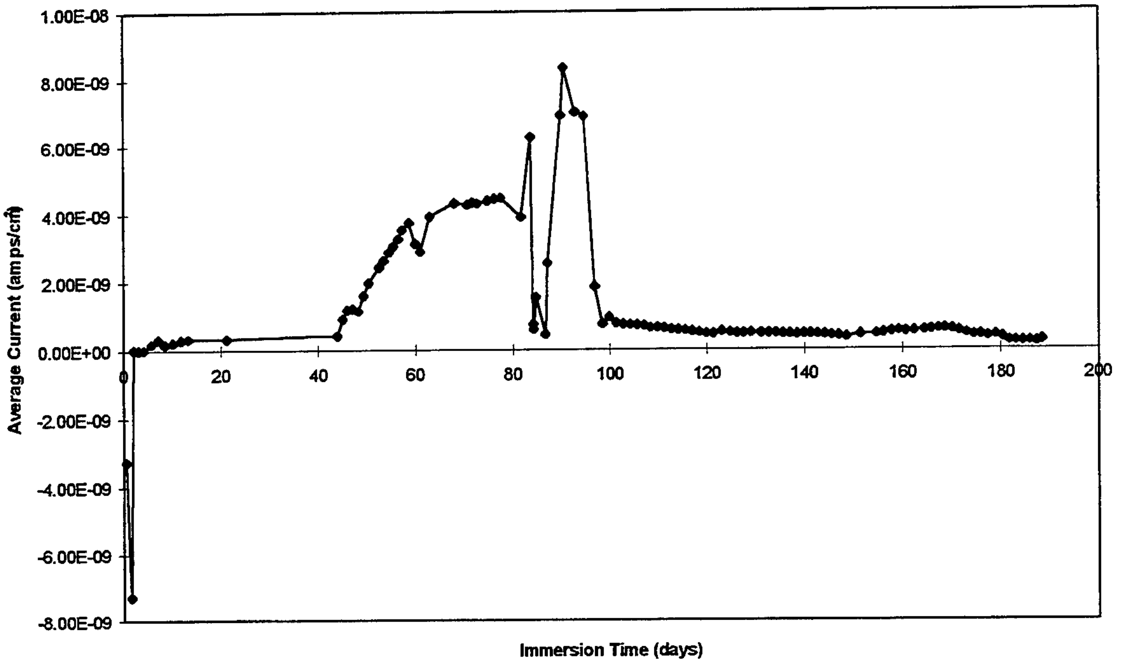


Figure 10
Reduced Resistance Noise ZHS (1B)

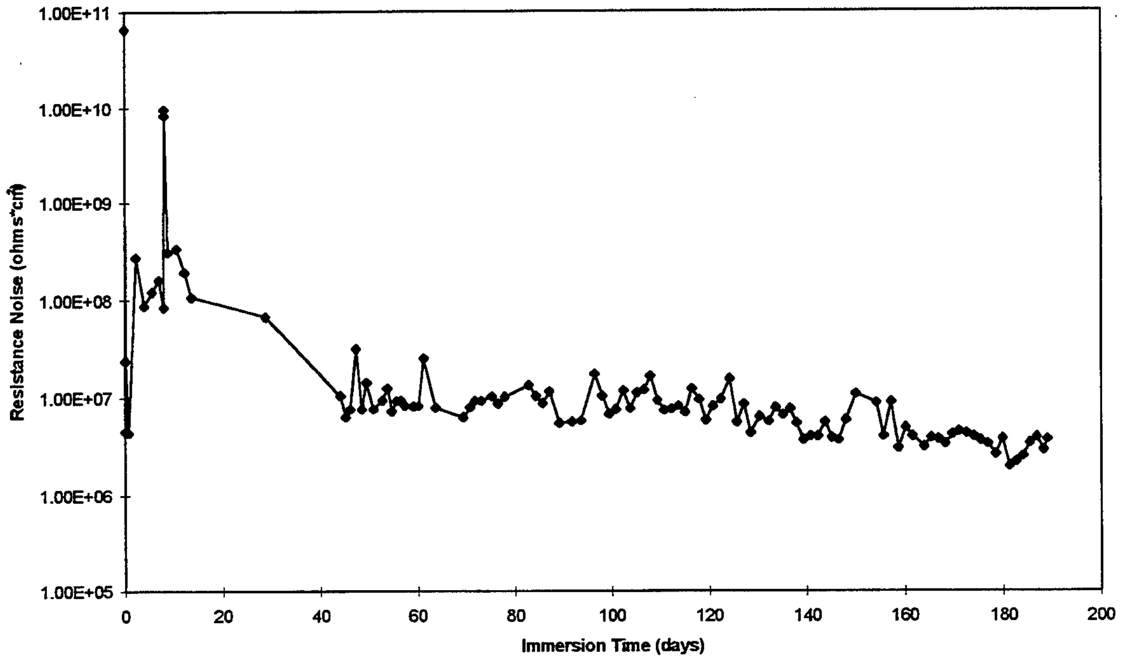


Figure 11
Reduced Average Voltage ZAS (6A)

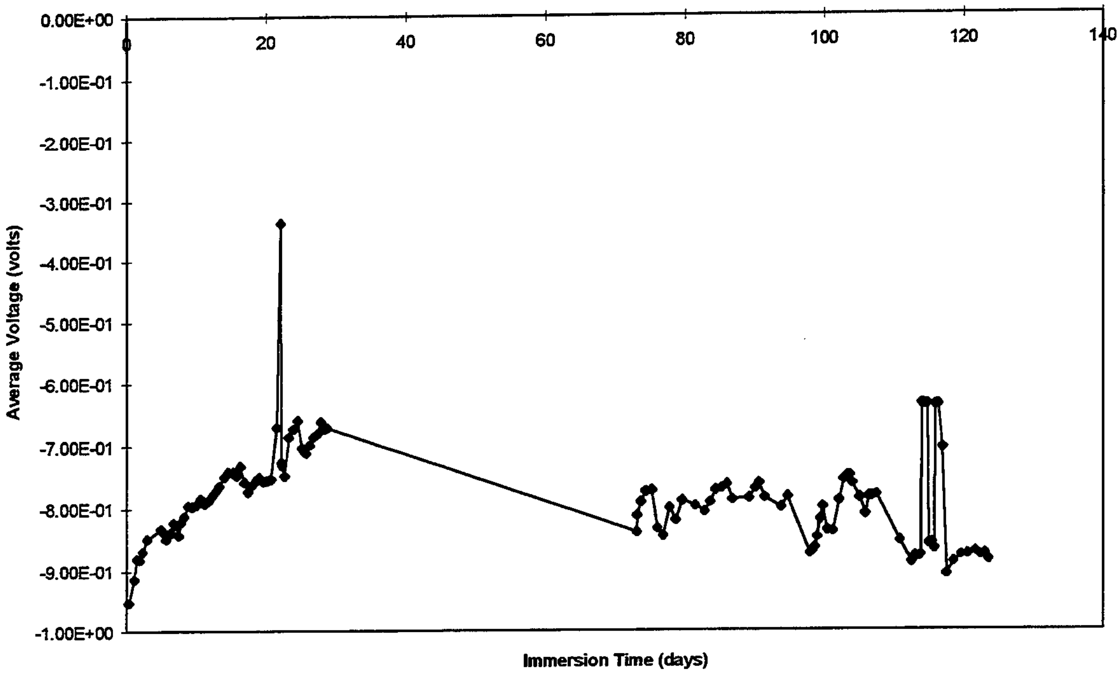


Figure 12
Reduced Average Current ZAS (6A)

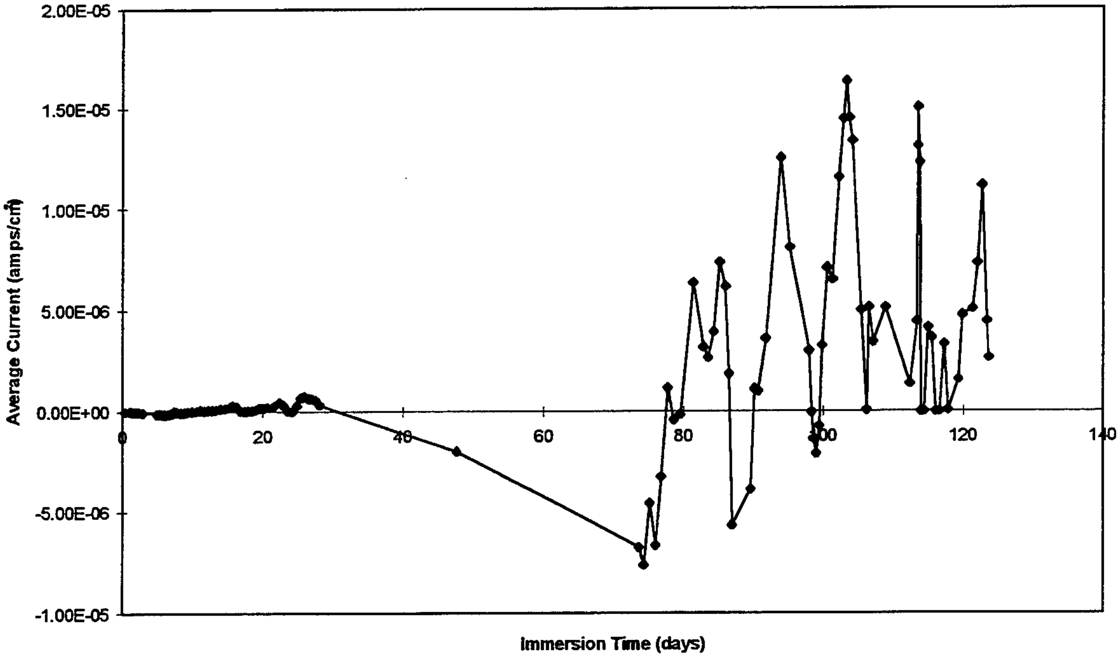


Figure 13
Reduced Resistance Noise ZAS (2A)

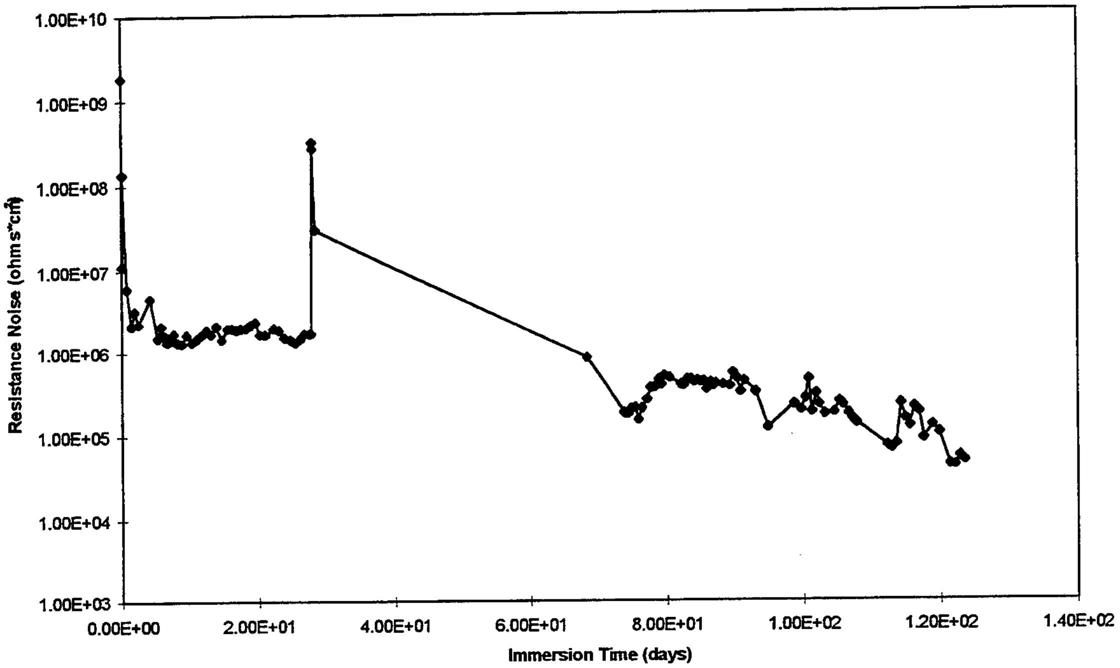


Figure 14
Effect of Agitaiton on Resistance Noise (Gamry)

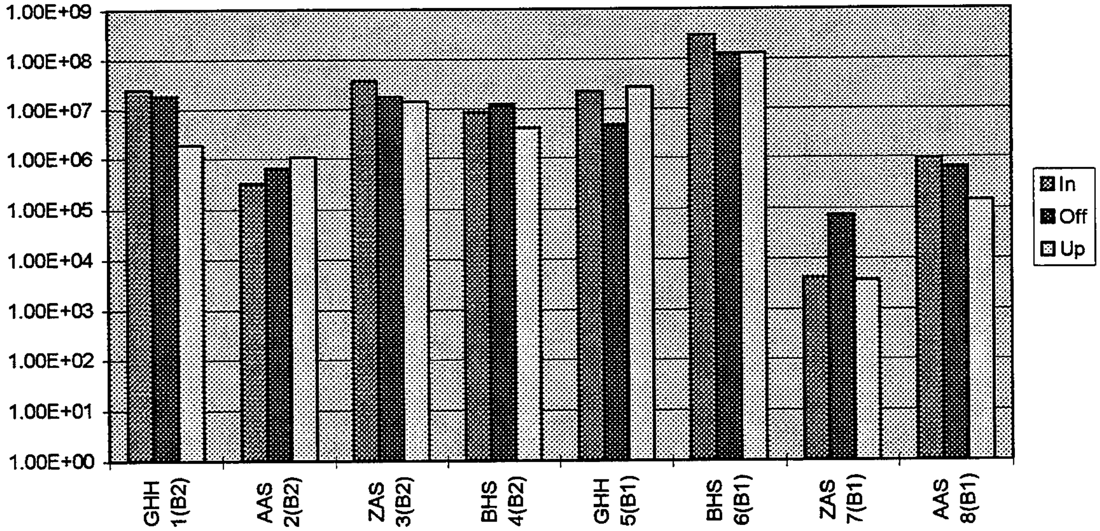


Figure 15

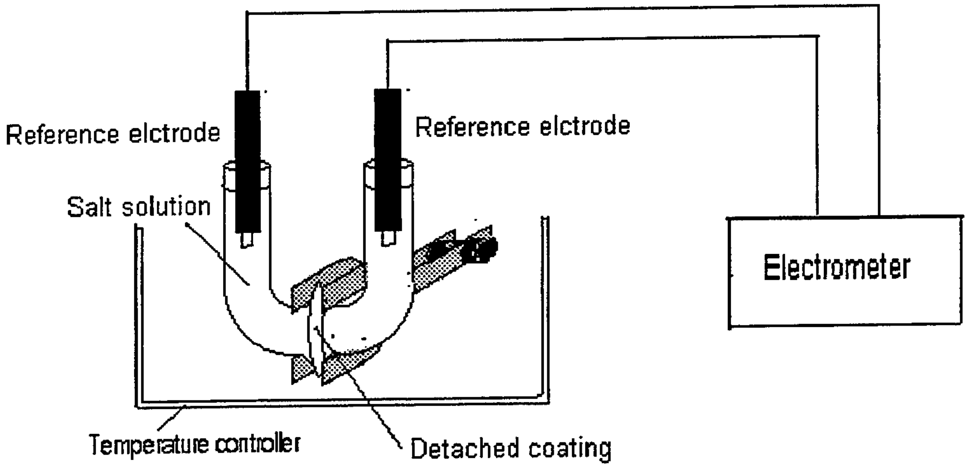


Figure 16

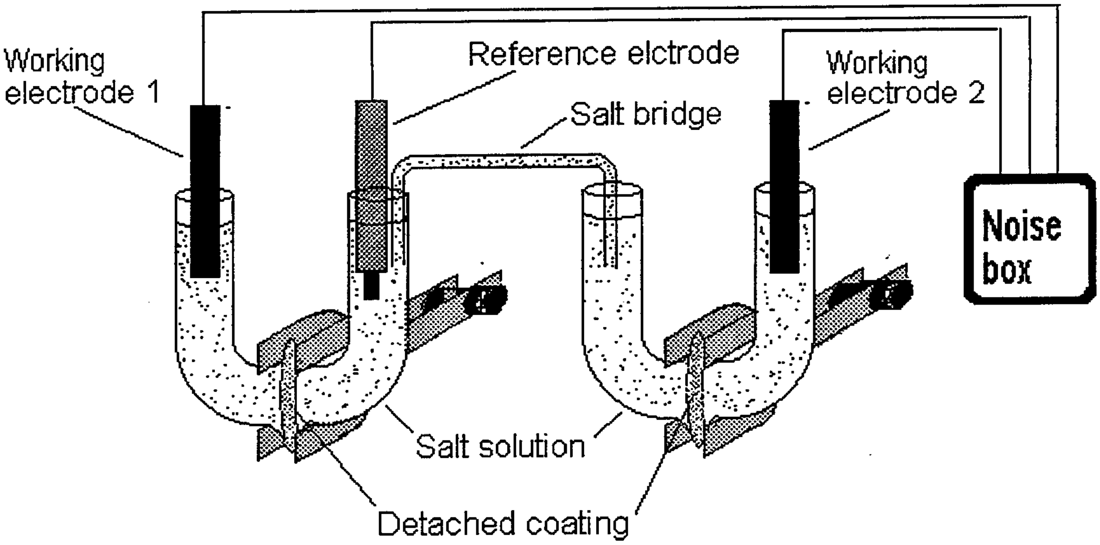
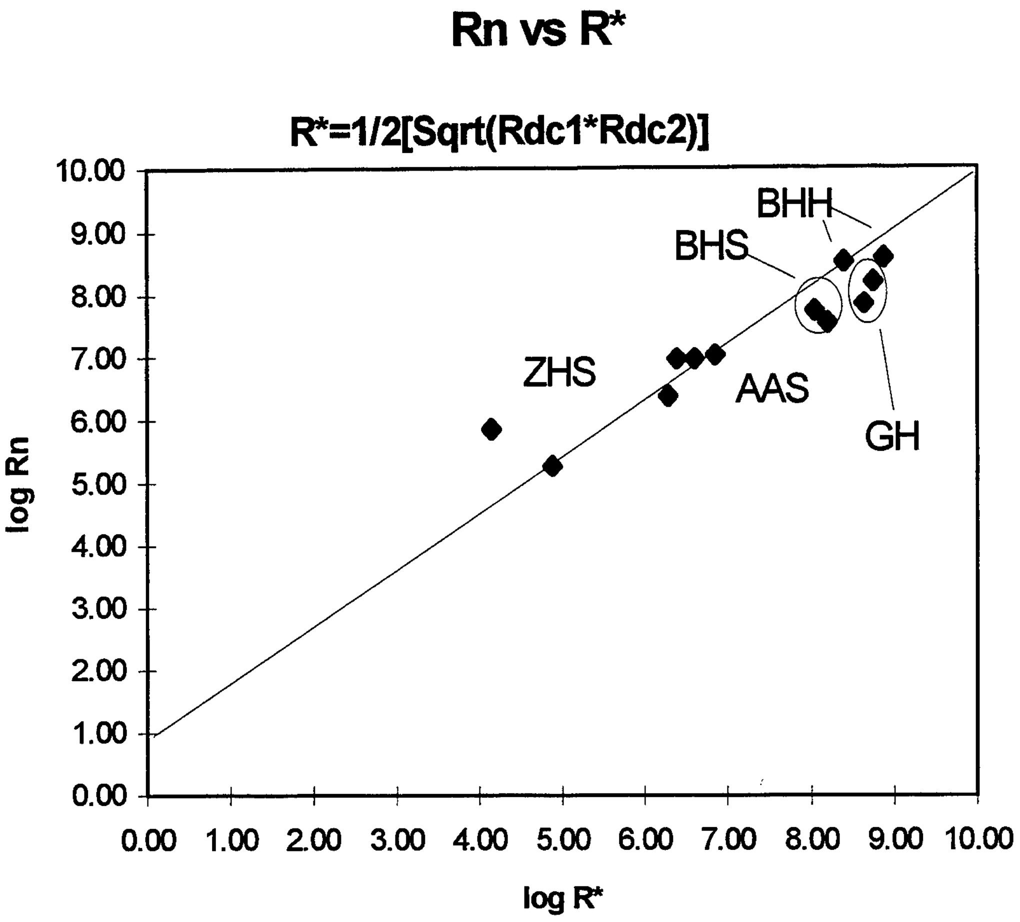


Figure 17



References

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[1] B.S.Skerry & D.A.Eden "Electrochemical testing to assess corrosion protective coatings" Prog. Org. Coatings 15 269-285 (1987).

[2] B.S.Skerry & D.A.Eden "Characterization of coatings performance using electrochemical noise analysis" Prog. Org. Coatings 19 379-396 (1991).

[3] C.T.Chen and B.S.Skerry "Assessment of the corrosion resistance of painted steel by AC impedance and electrochemical noise techniques" Corrosion 47 598-611 (1991).

[4] D.J.Mills, G.P.Bierwagen, B.S.Skerry and D.Tallman "Characterization of Marine Coatings by the Electrochemical Noise method" Proceedings of *12th international Corrosion Congress* Houston Texas Sept 1993 Vol 1 p 184.

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[5] G P Bierwagen, D J Mills, D Talman "Extensions of Electrochemical noise Methods as a possible in-situ corrosion sensing technique" Proceedings of *12th International Corrosion Congress* Houston Texas Sept 1993 Vol 6 p 4206.

[6] D.J. Mills, G.P.Bierwagen, B.Skerry and D.Tallman "Investigation of coatings using electrochemical noise method" accepted for publication in **Materials Performance** Jan 1995.

[7] G.P.Bierwagen, D.J. Mills, B.S. Skerry, and D. Tallman "Statistical Analysis of Electrochemical Noise Data for Coated Metal Systems," **ASTM Special Technical Publication (STP)** *Proc. of Symposium on Electrochemical Noise Measurement for Corrosion Applications,* Montreal Canada, May 1994.

[8] G. P. Bierwagen "Calculation of Noise Resistance from Simultaneous Electrochemical Voltage and Current Noise Data"'**J. Electrochemical Soc. 141,** L155-157 (N ov. 1994).

[9] G. P. Bierwagen, V. Balbyshev, D. J. Mills, & D.E. Tallman, "Fundamental Considerations on Electrochemical Noise Methods to Examine Corrosion under Organic Coatings," Proceedings of International Conference on *Advances in Corrosion Prevention by Organic Coatings,* Christ's College, Cambridge (Sept 1994) to be published by Electrochmical society 1995.

[10] G. P. Bierwagen, D. J. Mills, D. E. Tallman, & B. S. Skerry, "Assessment of the Protective Properties of Marine Coatings By Electrochemical Noise Techniques," Proceedings of Symposium *Corrosion and Corrosion Prevention in Seawater Environments* at the 184th Meeting of the Electrochemical Society in New Orleans, LA, Oct, 1993 Abstract No 81.

[11] D.J. Mills "A comparison of noise measurements using Sherwin-Williams and CML equipment" Internal report P&C Dept NDSU Nov 1993

[12] D.J.. Mills, S. Berg, & G.P. Bierwagen, "Characterization of The Corrosion Control Properties of Organic Electrodeposition Coatings," Proc. of the Symposium on Advances in Corrosion Protection by Organic Coatings II, Special Publication of The Electrochemical Society, Proceedings Volume 95-13, D.Scantlebury & M.Kendig, editors, (1995) 82-97

[13] D.J. Mills, Y. Pae and G. P. Bierwagen "The effect of the substrate on electrochemical measurements on coated metal""' - in preparation (to be submitted to Surface Coatings International).

[14] D.J. Mills, Y. Pae and G. P. Bierwagen "The effect of the substrate on electrochemical measurements on coated metal""' - in preparation (to be submitted to Surface Coatings International).

[15] Gordon P. Bierwagen, " Corrosion Studies on Coated Metals," submitted to **Prog. Organic Coatings,** October 1994 in conjunction with a Festschrift Volume in honor of Prof. W. Funke.

[16] R.C.Bacon, J.J.Smith and E.M.Rugg, **Ind.Eng.Chem. 40,** 161 (1948)

[17] F. Huet Reply to G.P.Bierwagen's letter to JES to be published in Journal of the Electrochemical Society

[18] U. Bertocci and F. Huet "Noise Analysis Applied to Electrochemical Systems" **Corrosion, 51,** 131-144

---

[19] D.J.Mills, P.J.Boden "A Novel Method of Testing and Monitoring Anti-Corrosive Organic Coatings" **Corrosion Science 35** (5-8) 1311-1318 (1993)

[20] P. Elliot, G P Bierwagen and D J Mills "Assessment of Coatings Degradation and Corrosion by Digital Image Analysis" Paper submitted for Young Author's prize Jnl. Coat. Tech July 1994.

[21] D.J.Mills and J.E.O.Mayne, "Corrosion Control By Coatings" Ed By H.Leidheiser Jr Pub. NACE 1981 p12

[22] Chauvenet's Criterion for two dimensional data is applied as follows (from [2], page 2-13):

1. Determine the Least Squares line of the data.
2. Determine the deviations (d_i) for each of the points.
3. Determine the standard deviation (s) of d_i. (Check that the mean is 0).
4. Determine the acceptable range of di as ± s * Z, where z is the Gaussian normal error function defined by:

$$erf(Z) = \frac{1}{\sqrt{\pi}} \int_{-Z}^{+Z} e^{-\eta^2} d\eta$$

The value of Z is determined from a standard table of Z by determining the area under the curve such that:

$$A = (1-1/2N)/2$$

where N is the number of data points in the sample.

5. Check whether all of the deviations are within the acceptable range. Those points which are outside of the range may be rejected as wild points. After rejecting any wild points, a new equation for the line has to be obtained.

[23] Mehta, Sudhir. MEAM 412 Engineering Measurements Notes. North Dakota State University Department of Mechanical Engineering and Applied Mechanics, 1994.

[24] Meyer, Stuart L. Data Analysis for Scientists and Engineers. John Wiley and Sons, Inc. New York, NY, 1976. Chapter 6.

Invited Presentations

D J Mills, G P Bierwagen, B Skerry and D Tallman Characteriztion of Marine Coatings by the Electrochemical Noise method *Corrosion Control for Low Cost reliability* 12th international Corrosion Congress Houston Texas Sept ember 22 1993

G P Bierwagen, D J Mills, D Talman Extensions of Electrochemical noise Methods as a possible in-situ Corrosion sensing technique *Corrosion control for Low Cost reliability* 12th International Corrosion Congress Houston Texas Sept ember 22 1993

D J Mills Assessment of protective Pro perties of marine Coatings by the Electrochemical noise method Workshop on *Quantitative Methods for evaluation of Paint Coating performance* NSWC Carderock Annapolis October 1993

Gordon P. Bierwagen, Douglas J. Mills, Dennis E. Tallman, & Brian S. Skerry, "Assessment of the Protective Properties of Marine Coatings By Electrochemical Noise Techniques," Symposium

Corrosion and Corrosion Prevention in Seawater Environments at the 184th Meeting of the Electrochemical Society in New Orleans, LA, October 11, 1993.

Gordon P. Bierwagen, Douglas J. Mills, Dennis E. Tallman, & Brian S. Skerry, "Assessment of the Protective Properties of Coatings By Electrochemical Noise Techniques," ESD1993 Advanced Coatings Technology meeting, Nov 1993 Dearborn, MI

D J Mills Aspects of The electrochemical noise technique as appled to organically coated substrates NACE Meeting *Corrosion '94* Workshop on Electrochemical noise Baltimore March 1994

G.P.Bierwagen, D.J. Mills, B.S. Skerry, and D. Tallman, "Statistical Analysis of Electrochemical Nosie Data for Coated Metal Systems," *ASTM Symposium on Electrochemical Noise Measurement for Corrosion Applications,* Montreal Canada, May 22 1994

Gordon P. Bierwagen, "Electrochemical Noise Methods for the Study of Corrosion Protection by Organic Coatings,' Los Alamos National Laboratory, Los Alamos, NM, August 15, 1994

Gordon P. Bierwagen, "Electrochemical Noise Methods for the Characterization of Corrosion in Coated Metal Systems," Sandia National Laboratory, Albuquerque, NM August 16, 1994

Gordon P. Bierwagen, "Reflections on Corrosion Control by Coatings," Tess Award Symposium, *American Chemical Society Fall 1994 National Meeting,* Washington D.C. August 22, 1994 (paper 151, PMSE Div. abstract published in PMSE Preprints, Vol. 154, August 1994)

D J Mills Application of Electrochemical noise for Evaluating Coated metal substrates Rockwell International, Thousand Oaks California August 1994

Gordon P. Bierwagen, "Electrochemical Noise Methods for the Study of Organic Coatings," University of Trento, Trento. Italy September 16, 1994,

Gordon P. Bierwagen, "Electrochemical Noise Methods for the Prediction of the Corrosion Protective Lifetimes of Organic Coatings," Invi the 60th Annual Meeting of the "APi"Group of the German Chemical Society (GDCh), , Weimar Germany Sept. 21, 1994

Dennis E. Tallman, Douglas J. Mills and Gordon P. Bierwagen, "Electrochemical Noise Measurements of Coating systems FACSS (Federation of Analytical Chemistry and Spectroscopy Societies) meeting.*in "Electrochemistry of Coatings and Membranes"* (part of the Novel Materials) Symposium in St. Louis MO October 2-7, 1994

* contributed

Publications from this Project

D. J. Mills, G. P. Bierwagen, D.E. Tallman, & B.S.Skerry, "Characterization of Corrosion under Marine Coatings by Electrochemical Noise Methods, " *Proc. 12th International Corrosion Congress*, Vol. 1, p. 182-193, (paper 486), Houston, TX (Sept. 1993)

Bierwagen, G.P., D.J.Mills, & D.E.Tallman, "Electrochemical Noise Methods as a Possible *In Situ* Corrosion Sensing Technique," *Proc. 12th International Corrosion Congress,* Vol.. 6, p. 4208-4218 (paper 576) Houston, TX (Sept. 1993)

G. P. Bierwagen, "Calculation of Noise Resistance from Simultaneous Electrochemical Voltage & Current Noise Data," **J. Electrochem. Soc.,141**(1994) L155-L157

G.P. Bierwagen, Vsevolod Balbyshev, Douglas Mills, & Dennis Tallman, "Fundamental Considerations on Electrochemical Noise Methods to Examine Corrosion under Organic Coatings," Proc. of the Symposium on Advances in Corrosion Protection by Organic Coatings II, Special Publication of The Electrochemical Society, Proceedings Volume 95-13, D.Scantlebury & M.Kendig, editors, (1995) 69-81

D.J.. Mills, S. Berg, & G.P. Bierwagen, "Characterization of The corrosion control Properties of Organic Electrodeposition Coatings," Proc. of the Symposium on Advances in Corrosion Protection by Organic Coatings II, Special Publication of The Electrochemical Society, Proceedings Volume 95-13, D.Scantlebury & M.Kendig, editors, (1995) 82-97

D. J. Mills, G. P. Bierwagen, D.E. Tallman, & B.S.Skerry, "Investigation of Corrosion Anticorrosive Coatings by the Electrochemical Noise Method," **Material Perf., 34,** (1995) 33

G.P. Bierwagen, "Reflections on Corrosion Control by Coatings," accepted for publication, **Prog. Organic Coatings**, to be published fall 1995

G. P. Bierwagen, DJ Mills, D.E.Tallman,and B.S.Skerry, "Reproducibility Analysis of Electrochemical Noise Data For Coated Metal Systems," to be published in ASTM **Special Technical Publication** from the 1st International Symposium on Electrochemical Noise Meaqsurment for Corrosion Applications, May 17, 1994 Montreal, Quebec Canada