A Review and Development of Accelerated Test Methods for Anti-Corrosive Organic Coatings

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Abstract

To enable improvements in the development of anti-corrosive coatings quick methods of evaluation are required and several are available which are both qualitative and quantitative. This investigation reviews both types of method, the first in the form of traditional salt spray exposure and the second in the form of electrochemical techniques. The emphasis in the experimental work reported here is on the Electrochemical Noise Measurement (ENM). ENM has been used to monitor coatings under immersion conditions, the aim being to assist a paint company develop a set of more environmentally friendly coatings. The immersion test has also incorporated a temperature cycle which proved effective at separating 'good' coatings within a short timeframe. Results showed good correlation between ENM and salt spray testing.

Work is also reported which was done with the aim of making the ENM method more practically useful. The standard configuration ('Bridge') requires two separate specimens which is unattractive for site work. The Single Substrate (SS) arrangement was developed to get around this problem but this still requires the metal to be connected to the measuring instrument. This is avoided in the most recent development which needs No Connection to Substrate (NOCS). Results are given for immersed samples monitored using the ENM NOCS arrangement and compared with the standard 'Bridge' method and DC resistance. Results are also presented using sets of different electrodes (platinum, calomel and silver/silver chloride). This preliminary work has shown that the NOCS method holds great promise.

In the laboratory Electrochemical Impedance Spectroscopy (EIS) is also commonly employed to assess the performance of anti-corrosive coatings. Concluding this work a comparison of the ENM and EIS techniques was undertaken on a set of laboratory samples. Results showed that both methods had the ability to rank the performance of coatings. However ENM's advantages (as outlined above) were confirmed.

Glossary of Abbreviations

Abbreviation	Definition
ENM	Electrochemical Noise Measurement
EIS	Electrochemical Impedance Spectroscopy
DC	Direct Current
R_n	Noise resistance
R_{dc}	DC resistance
R_{sn}	Spectral noise resistance
R_p	Polarisation resistance
R_{po}	Pore resistance

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1.1 Introduction and Background

The intention in this first chapter is to review the field of paint technology in a general way stressing both the scientific approach of the modern paint chemist and the importance of the contribution made by science to the development of organic coatings with the appropriate associated testing.

The requirement for this body of work became evident after several driving forces were identified for the development of current, industrially available, organic coatings and the subsequent need for their performance testing. Several influences initiated the programme of work, including the Mass Reduction Scheme (MRS) and Process Guidance Notes (in particular PG6/23), issued by the Secretary of State. It was in response to the legislative requirements laid out in these documents which stated the manufacturers of coatings should dutifully attempt to reduce the amount of Volatile Organic Compounds (VOC) released to the atmosphere that formulation and testing of low VOC coatings was required. The body of work combined both requirements identified. The formulation of more environmentally friendly coatings i.e. ones with lower VOCs, was undertaken at Pronto Industrial Paints Limited, an industrial coatings manufacturers, and the subsequent test work was split between the coating manufacturers and the University of Northampton. The programme of work was undertaken under the support of, what was known then as, a Teaching Company Scheme (TCS) and ran over a two year period - 2002 - 2004. These programmes allow for Small/Medium Enterprises (SME's), categorised by having less than 250 employees, to utilise the services of a post-graduate and the facilities of a nearby university. These programmes recently (2005) changed title to now be known as Knowledge Transfer Partnerships (KTPs).

The reason the testwork was carried out over two different sites was due to each facility only having access to test equipment necessary for their interests. The coating manufacturer only had access to the test equipment which is standard to the industry and is historically referenced – salt fog/humidity test chamber; this will be discussed in more detail in chapter two and throughout this work. Whilst the university had access to several pieces of test equipment useful for the evaluation of coating performance, a salt fog/humidity chamber was not one of them. The test equipment of most relevance to this investigation was Electrochemical Noise Measurement (ENM) equipment which again will be discussed in more detail in chapter two and throughout this work. The goal was to advance the test programme at the coating manufacturers and introduce more qualitative methods to assist in coating formulation. As Bierwagen states (2000), 'In many ways, failure "lies in the eye of the beholder". The user of the coating really defines when the coating fails to satisfy his needs and its designed purpose. One of the problems of testing of the corrosion protection by coatings is to convert 'failure' as observed by the user in practice to a measurable quantity. This is where ENM has been proven to be useful (Mills & Mabbutt, 1998; Mabbutt & Mills, 1998; Mabbutt *et al.*, 2002).

1.2 Introduction to Volatile Organic Compounds

VOCs are an important class of air pollutants, commonly found in the atmosphere at ground level in all urban and industrial environments. The sources of VOCs are both anthropogenic and natural. It is therefore important to control anthropogenic emissions of VOCs. Their presence leads to photochemical oxidation causing increased smog episodes, ground level ozone concentrations whilst also being harmful to the ecosystem.

There are many hundreds of compounds which fall within the category of VOC and the situation is yet further complicated by different definitions and nomenclature. Strictly speaking, the term volatile organic compounds refers to those organic compounds which are present in the atmosphere as gases, but which under normal conditions of temperature and pressure would be liquids or solids. A volatile organic compound is by definition a organic compound whose vapour pressure at 20°C is less than 760 torr (101.3 kPa) and greater than 1 torr (0.13 kPa). This is a strict definition for VOCs, VOCs can also be taken to mean any carbon-containing compound found in the atmosphere, excluding elemental carbon, carbon monoxide, and carbon dioxide.

1.3 Performance Testing

There are a number of methods available to aid development of more effect organic coatings by predicting the performance and service life. The predictive nature of these tests is often open to debate as extrapolation can often lead to spurious results. The information given in this chapter will be useful in preparing the ground for the more detailed discussion in later chapters.

1.4 Paint Technology

The technology of paint rests today on a vast and ever expanding fund of practical and theoretical knowledge. Scientific principle has developed to such an extent over the years that control of the delicate operations of paint manufacture can no longer be left to personal judgement but demands the attention of professional chemists and engineers.

Paints are surface coatings that are designed to fulfil a protective and/or decorative function for the substrate. While inorganic paints are known, organic coatings predominate in paint technology and development. The formulation of a paint in respect of its major components, the resinous binder and the pigments, is largely dictated by the intended application i.e. by the combined requirements of the substrate and the service environment. The raw materials of a coating typically consist of the binder (including any added plasticiser), the pigments (as well as any extender material), a solvent or blend of solvents, and various other additives added at low levels which may be added at relatively low levels but have a marked effect on the paint. Amongst these auxiliary additives can be included rheological agents, driers, anti-skinning agents, surface-active agents, biocides as well as numerous others. In the following sections we will consider the components of a paint in more detail.

1.4.1 Polymers

The polymeric or resin binder of a paint is the film-forming component of the formulation. Without it, continuous coatings would not be possible. A large variety of polymers and polymer precursors are used in paints. Furthermore, the chemical nature of the material dictates its mode of use and, indeed, the overall formulation of paints based on the resin. Paint binders can be subdivided into two broad categories: convertible and non-convertible types. The former are materials that are used in an unpolymerised or partially polymerised state and which, following application to the substrate, undergo polymerisation to form a solid film. Non-convertible paints are based on polymerised binders dispersed or dissolved in a medium which evaporates after the coating has been applied, to leave a coherent film on the substrate. Some examples of convertible binders include oils, alkyd, amino, epoxy, phenolic, polyurethane and silicone resins. Non-convertible binders include cellulose, chlorinated rubber, acrylic and vinyl resins. A brief discussion on the more important types used in the experimental work in this thesis follows.

1.4.2 Alkyd

Alkyds, introduced into the paint industry around 1930, were at first regarded as experimental products. They are now established as essential components of high class decorative and industrial paints. Alkyd resins constitute the most widely used paint binders and are synthetic polyesters. They are produced by the interaction of a polycarboxylic or fatty acid or its anhydride (phthalic anhydride), a polyhydric alcohol (glycerol) and a vegetable oil or its fatty acid. Two manufacturing methods are used in the preparation of alkyd resins: the alcoholysis (or monoglyceride) process, by which oil-modified alkyds are produced and the fatty acid process which is used to prepare fatty-acid-modified alkyd resins. Both processes yield oil-modified alkyds which are classified on the basis of oil length and the oil used.

1.4.3 Epoxy

Epoxy resins are produced by condensation polymerisation reactions between epichlorohydrin and diphenylol-propane (bisphenol-A), usually in the presence of sodium hydroxide and under reflux. The reaction conditions and the proportions of the two constituents determine the properties of the final film, a linear polymer of low solubility in (non-polar) solvents but soluble in highly polar solvents such as ketones.

The epoxy resins have glycidyl ether or oxirane terminations and these cyclic epoxides can open so that the resin can undergo cross-linkage. This converts them from linear thermoplastic materials to three-dimensional thermosetting resins. This reaction is slow, even with heat, but a number of reagents, particularly tertiary amines, accelerate ring opening and promote cross-linking without heating.

1.4.3.1 Zero VOC aqueous epoxy emulsions

The most useful epoxy resins used for conventional solvent-based ambient cure two-component epoxy resin binders contain epoxy resins where *n*, the repeating value, lies between 1.1 and 3 (Klein, 1988). Most standard epoxy resins are based on the reaction products of epichlorohydrin and bisphenol-A. In solvent-based coatings, the epoxy molecules are entangled and fully interpenetrating as they are applied to the surface. Solvent evaporation then leaves what is expected to be a uniform film of low permeability. In straight bisphenol-A-based epoxy resin dispersion coatings, the epoxy molecules are packaged in discrete particles which must coalesce during drying and subsequent ageing to form a protective film. Improperly coalesced films are more permeable, especially to moisture, than corresponding solvent-based films. This is why the formulator adds organic solvents to such dispersions to aid film formation at temperatures as low as 0°C. Therefore, at least some of the more rigid bisphenol-A in epoxy resin dispersions has to be substituted with plasticising monomers if the epoxy resins are to have an impact on coatings technology for stricter regulation of VOC emissions.

1.4.4 Acrylic

Acrylic resins are poly(vinylidene) compounds. The resins are derived from the esters of acrylic and methacrylic acid which are polymerised by a vinyl-type process. Acrylic resins are hard and rigid thermoplastic polymers that form somewhat inflexible films but which have good optical properties and excellent chemical resistance. Co-polymerisation of methyl (and other) methacrylates with monomers such as styrene yields thermosetting resins.

1.4.5 Water-borne binders

There is a need for aqueous coating binders for heavy-duty application which have attractive formulating flexibility, good film formation at ambient temperature without co-solvent demand and to give heavy-duty performance properties whilst meeting modern health and safety requirements as well as environmental legislation standards.

1.5 Pigments

Pigments are particulate solids that are dispersed in paints to confer certain characteristics upon them. These characteristics include colour, opacity, durability, mechanical strength and corrosion protection for metallic substrates. Most pigments are crystalline and the crystal form often affects the characteristics of the pigment. The size and shape of the pigment particles are an important consideration since they affect the agglomeration or packing within the paint binder or matrix. Pigments have to be dispersed in the binder and, in order to have the desired effect, they must remain in suspension or be easily dispersed again should settling occur.

1.5.1 Corrosion-inhibitory pigments

Pigments used to protect metallic substrates against corrosion fall into two broad classes - metals and salts. Of the former, magnesium and zinc are the most important, although powdered aluminium and stainless steel have some application. Corrosion-inhibitory salts contain water-leachable anions which can passivate the metal or affect the corrosion process. With these pigments, the mechanism of protection differs from that of metals.

Various inorganic salts function as corrosion-inhibitors when incorporated in paints, usually primer coats. Historically, lead- and chromate- containing compounds were the main inhibitory pigments but the toxicity and pollution problems associated with such materials has resulted in the use of less environmentally impacting pigments as an alternative. Although currently used inhibitive pigments such as zinc phosphate are less effective than some of the traditional materials, they still are able to confer considerable protection upon the substrate. Zinc phosphate containing coatings have been found to deposit considerable quantities of zinc salt on the metal surface which precipitates zinc hydroxide once corrosion has started (Camina *et al.*, 1990). This slows the cathodic reaction and gave typical cathodic inhibition characteristics when subjected to electrochemical impedance spectroscopy. Both chromate and phosphate also exhibit some degree of ionic barrier effect in addition to chemical inhibition. This was demonstrated by higher DC resistance values for the pigmented alkyd films compared to clear films.

1.5.2 Pigment Volume Concentration

It is well known that the physio-chemical properties of a paint are affected by its pigment volume concentration (PVC). Further there is a critical pigment volume concentration (CPVC) above which, many such properties change abruptly (Asbeck & Van Loo, 1949). These authors demonstrated that blistering is more likely to occur and gloss decrease markedly as the CPVC is approached, whereas permeability and rusting increase dramatically at or above the CPVC.

1.6 Mechanism of Protection

1.6.1 Ionic Resistance as Corrosion Protection

Coating systems which block or act as a barrier slow down the passage and consequent migration of ions to the substrate. Mendoza & Sykes (1990) showed that intact barrier coatings on a clean and well prepared substrate can give good, and even improved, performance compared with soluble inhibitive pigments. The electrical resistance of a coating relates to the ionic transport rate of the coating and is used as an indicator for the ability of a coating to protect against corrosion. Bacon *et al.* (1948) showed that coatings with electrical resistance values $>1\times10^8$ ohm-cm^2 provided good protection against corrosion. Where electrical resistance was $<1\times10^6$ ohm-cm^2 the corrosion protection was poor and at intermediate values of resistance the protection was borderline.

Although a good organic coating should form a barrier against diffusion of ions, water and oxygen are considerably more permeable and, therefore, are able to be present at the metal/coating interface. Under some circumstances, this can lead to substrate corrosion and coating delamination.

Organic coatings can be effective in protecting steel in corrosive environments – their aim being to isolate the material from aggressive environments. Research in the polymer field has resulted in the development of many organic coatings which can offer protection such as epoxy, polyurethane and alkyds and many others.

The protection against corrosion provided by organic coatings is determined by a complex mechanism which includes many different factors. As more variables become involved, the more difficult it is to understand the process. Kendig &

Scully (1997) proposed three mechanisms in order to explain the anti-corrosive properties afforded by organic coatings:

1. Anodic inhibition: the anodic reaction is retarded by means of the addition of a pigment
2. Cathodic inhibition: the coating acts as a barrier preventing contact of oxygen and water with the metallic substrate
3. Ohmic inhibition: the high electrical resistance of the coating impedes the current flow between metal and environment.

1.6.2 Chemical Inhibition

As discussed above corrosive inhibitive pigments work in various ways but the most effective of them (e.g. chromate) works to strengthen the thin oxide (passive) film on the metal surface.

1.7 Durability testing

Durability may be defined as the capacity of a paint to endure; that is, to remain unchanged by environment and events. The events we are concerned with are those that impose stresses and strains on the paint system. Effects of environmental conditions have an enormous effect on durability; therefore, test methods for developing and monitoring the performance of paint systems are always designed to simulate conditions in final application. They are usually designed to accelerate the degradative processes to which paints are subjected. The need for this acceleration of the degradation processes is to provide early warning of paint failure.

The extent and range of tests that may be applied vary according to a number of circumstances. In the industrial paint markets the paint manufacturer may have to meet specifications laid down by the end-user. Test method specifications have been drawn up by a number of national and international organisations such as the British Standards Institution (BSI), the American Society for Testing Materials (ASTM), Deutsche Industrie Normal (DIN) and the International Standards Organisation (ISO). In the United Kingdom other organisation have developed and are responsible for maintaining certain standard test specifications. An example of this is the Ministry of Defence (MOD DEF Specifications).

Establishments such as the Building Research Station and the Paint Research Association have contributed to the development of test methods and influence the standardisation of test methods through representation on technical panels of the national and international standards organisations.

1.7.1 Chemical resistance

There is a general need to be able to predict how any system that is being used for anti-corrosive protection will perform over time. Developing test methods for the assessment of anti-corrosive coatings is hindered by the fact that a total understanding of the mechanism of action of anti-corrosive paints has not been reached.

The purpose of accelerated testing is to duplicate, in the laboratory, as closely as possible the ageing of a coating in real outdoor environments but in a much shorter time. In real-life environments, the ageing process leading to coating failure can generally be described as follows. Primarily there is weakening of the coating by significant amounts of bond breakage within the polymer matrix. This causes the overall barrier properties to be decreased i.e. transportation of water, oxygen and ions through the coating increases. This leads to even more transportation of water, oxygen and ions through the coating causing deterioration of coating-metal adhesion at this interface. This may be followed by the development of an aqueous phase at the coating/metal interface. Activation of the metal surface for the anodic and cathodic reactions particularly if ions are present, and finally corrosion, and delamination of the coating. Unfortunately for coating formulators, specifiers, and other workers in the field, all of this takes several years to happen in the field, if the coating and substrate are good. This makes testing and developing of new coatings impossible; unless accelerated testing methods are used.

The factors that affect coatings and are candidates for acceleration include:
Solar radiation and ozone, water and moisture and ion uptake, chemical damage (e.g., from pollutants), elevated temperatures and thermal changes, abrasion or other mechanical stresses.

The major weathering stresses which cause degradation of organic coatings are: UV radiation, water and ions and temperature changes. The first of these weathering factors is unique to organic coatings; the latter two are also major causes of corrosion of bare metals. An electrolyte (usually sodium chloride (NaCl) or ammonium sulphate or both) is frequently included in the accelerating test.

Cycling tests are now common. There are a large number of accelerated corrosion or weathering tests. Several of them are widely used, such as salt spray or QUV weathering. Amongst workers in the field there seems to be a general consensus that the following tests yield relevant data:

1.7.1.1 Resistance to salt spray

Salt spray tests are probably the most common tests applicable to corrosion resistance – and the most controversial. It is well established that salts such as sodium chloride can cause rapid corrosion of ferrous substrates. Therefore, it is useful to have information on the behaviour of a coating system in protecting such substrate from corrosion both with intact and damaged paint films. Controversy arises largely from the interpretation of the data because of the poor predictability of the tests. However, they are well established, and are given credit as being a useful tool in guidance towards performance properties in the absence of longer term corrosion data. Therefore, they are unlikely to be replaced completely. They are considered to be unrealistic by some workers (Lyon *et al.*,1989; Howard *et al.*, 1999, Parts I & II) because of the degree of acceleration of the corrosion process that they achieve and the variability of the extent of 'damage' which is inflicted in some of the tests. Considering this, the test may be useful in assessing the quality of a coating on a control basis and highlight any deviation in performance from standards under accelerated conditions.
Two salt spray tests are common: the continuous salt spray and the intermittent (Prohesion cycle).

1.7.1.2 Corrosion

ASTM D5894 (modified Prohesion or Prohesion/UV)
This is a promising test receiving more and more attention. Its cycle is 2-weeks long, and is typically run for 6 cycles (i.e. 12 weeks total). During the first week of each cycle, samples are in a UV/condensation chamber for 4 hours of UV-light at 60°C, alternating with 4 hours of condensation at 50°C. During the second week of the cycle, samples are moved to a salt-spray chamber where they undergo one hour of salt spray (0.5% NaCl + 0.35% ammonium sulphate pH 5.0-

5.4) at 24°C alternating with one hour of drying at 35°C. There are warnings in the literature, however, about too-rapid corrosion of zinc in this test; it perhaps should be avoided for galvanised substrates and zinc-pigmented coatings. Another item to note is that this test often gives strange results when used on pre-painted materials.

1.7.1.3 Constant condensation or humidity testing

Condensation rates are higher in condensation testing than humidity testing, because in constant condensation chambers the back sides of the panels are at room temperature, and the painted side faces water vapour at 40°C. This slight temperature differential leads to higher water condensation on the panel. If there is no such temperature differential, you have humidity testing, also called a 'tropical chamber'. The Cleveland chamber is condensation testing; a salt spray chamber with the salt fog turned off, the heater turned on, and water in the bottom (to generate vapour) is a humidity test. Constant condensation or humidity testing can be useful where it is suspected that pre-treatment of the substrate before painting has been less than ideal. Contaminants under the paint in these conditions can attract water, leading to rapid blistering of the coating. Various standard test methods using constant condensation or humidity testing include ISO 6270, ISO 11503, BS 3900, ASTM D2247, ASTM D4585, and DIN 50017.

The continuous salt spray BS117 (also known as salt fog) test is still commonly used but has come in for criticism. Lyon *et al.* (1999) have provided a particularly strong criticism of this technique showing results utilising the cyclic test and ammonium sulphate/sodium chloride mixtures to be more representative of externally exposed weathered panels.

1.8 Weathering

1.8.1 QUV weathering

This test method alternates condensation with UV-exposure. The QUV chamber is used for studying the effect of UV light on organic coatings. The temperature, amount of UV radiation, length (time) of UV radiation, and length (time) of condensation cycles in the chamber are programmable. Some recommended practices are described in the standard ASTM G-53.

1.9 Electrochemical Testing

There are several methods of electrochemical evaluation which can be used to evaluate the corrosion resistance of organic coatings, a brief discussion of some of the more accepted methods follows.

1.9.1 D.C. Resistance

Bacon, Smith and Rugg (1948) pioneered the use of electrochemical evaluation for assessing the anti-corrosive properties of coatings. They used DC resistance to indicate which coatings had good anti-corrosive properties and which coatings did not. The DC resistance method has been given less attention over recent years but still finds use for assessing coatings. However, the method has the disadvantage that to indicate a resistance a current must pass through the coating. This may be considered as partially destructive testing as passing a current requires a high impressed voltage that can be in excess of 1V and this can induce paths of conduction in the system which then act to allow aggressive ions through, accelerating degradation of the coating. Hence this method of evaluation does not lend itself towards continuous monitoring of the coating.

1.9.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy has developed over the past twenty five years as a useful laboratory technique for assessing the anti-corrosive properties of organic coatings. EIS is considered useful as the technique can give mechanistic information on processes of corrosion and coating degradation. Despite finding majority recognition the technique has some negative points which should be considered when being compared with alternative techniques for assessing corrosion protection. Firstly, the technique can take up to 40 minutes per reading depending on the frequency range used, typically 0.05 Hz – 50 kHz. As well as being restricting with regard to test time periods, the test period may also encounter changes in corrosion rate kinetics which are important in the early stages of testing. Secondly, EIS imposes an external voltage on the test samples and is therefore not truly non-intrustive. Finally, interpretation of the data can be problematic.

1.9.3 Electrochemical Noise Method (ENM)

The Electrochemical Noise Method has found use in the anti-corrosive assessment of organic coatings since the late eighties (Skerry *et al.*, 1987; 1988). Electrochemical noise can be described as fluctuations in potential and current around a mean value in an electrochemical cell. The fluctuations in potential and consequently current are natural phenomena which can be monitored using the Electrochemical Noise Method. Previous studies have established ENM as a useful technique for investigating the corrosion resistance of organic coatings, both intact and scribed with an artificial defect, on steel substrates (Skerry *et al.*, 1987; 1988; Mills *et al.*, 1998; 2000; 2003; Woodcock & Mills, 2003). This work will report the use of ENM to assess the anti-corrosive properties of organic coatings as previously described (Skerry *et al.*, 1987; 1988; Mills *et al.*, 1998; 2000; 2003) and introduce developments of the technique in chapter seven.

2.1 Predicting the Performance of Organic Coatings

Organic coatings have long been used to protect metals and alloys against corrosion and represent one of the most widespread methods of providing protection to improve the durability of coated structures. Despite such extensive usage and heavy reliance of organic coatings to protect structures/substrates, no single acceptable method exists for assessing the corrosion protection performance capability of paints. Instead, several different standards are used and it is down to the qualitative judgement of the operator to determine the predicted life of the coating. This is a problem which challenges research and development work for new products, whether they be conventional or show reduced environmentally impacting properties. The challenge is due to the difficulties in attempting to model the complex processes of degradation and failure of paint systems in a meaningful way by the use of accelerated test methods. In the laboratory the industry standard (continuous salt spray) is very much the preferred method by which commercial coating development is measured. These test methods are undertaken to designated test methods i.e. ASTM B117, even after known problems of interpretation of data and lack of correlation with practical experience has been reported (Lyon & Guest, 1989; Howard et al., 1999). Since metallic corrosion is an electrochemical phenomenon, it is reasonable to suggest that electrochemical test methods may be useful in assessing the ability of a coating to prevent corrosion. Quantitative and objective information is obtainable by such methods. This has been shown in many studies reporting electrical and electrochemical measurements of resistance, capacitance and polarisation phenomena on coated electrodes (Skerry *et al.*, 1987; 1988; Murry, 1997; Bierwagen *et al.*, 1996; 2000; 2003; Mills *et al.*, 1998; 2000; 2003; Fedrizzi *et al.*, 2003; 2006).

A good accelerated test method is very difficult to obtain because for a test procedure to truly be an 'accelerated test method', it must only shorten the time to failure, but not change the failure mechanism. This is a very difficult requirement to satisfy, because many ways in which one might accelerate failure e.g. by increasing the stress that causes the failure, often introduces new failure modes. For organic coatings, a clear example of this is attempting to accelerate exposure failure as a result of solar radiation at a high intensity exposure to radiation that contains significant UV energy in wavelengths below 360nm. The shorter UV wavelengths cause bond breakage that will not occur in outdoor exposure, thus giving a failure that will not occur in normal practice. Thus, to accelerate failure requires an understanding of the failure mechanism in order to ensure that this mechanism indeed drives the failure under investigation and does not introduce a new failure mode which would not be encountered naturally.

2.2 Exposure conditions

Standard accelerated tests employ a continuous 5% Sodium chloride spray solution, such as that used to date in the ASTM B117 and similar standards. However, in the 1960's, Harrison and Tickle recognised the benefit of including ammonium sulphate for improved prediction of outdoor performance over sodium chloride solution. As a result a solution of 0.5% NaCl and 3.5% $(NH_4)_2SO_4$ is known as Harrison's solution and is used in some predictive test work (Woodcock & Mills, 2003). Timmins employed a diluted solution based on Harrison's solution (0.4% $(NH_4)_2SO_4$ and 0.05% NaCl) in a cyclic test (3 h wet/1 h dry) to provide improved prediction over the salt spray test. Later, Lyon and co-workers used an artificial acid rain solution, shallow specimen incline angles (5-15°) and wet/dry cycles with an atmospheric test cabinet to determine the performance of coatings.

Work by Howard et al. (1999) showed that comparisons with outdoor exposure samples reveal that the ASTM B117 test showed unrealistic corrosion morphology and that over 1000 hrs test time the standard Prohesion test appears to show the best combination of realism and acceleration.

2.3 Combination testing

An ongoing issue with respect to the testing of the corrosion protection properties of organic coatings over metal substrates is the predictability associated with experimental test results. Use of a single test method like continuous salt fog testing for corrosion protection predictive lifetimes for coatings is no longer considered acceptable. Modern corrosion testing of coatings performance now emphasises on multiple test methods, including cyclic salt fog testing, EIS measurements, subjective visual analysis of exposed panels, corrosion and UV exposure testing and direct exposure testing of multiple panels in known corrosive environments (Skerry *et al.*, 1988; Simpson *et al.*, 1991; Yang *et al.*, 2001; 2002; 2003; Bierwagen *et al.*, 2003).

The most crucial elements of a meaningful laboratory test are that it should simulate the relative performance ranking of materials in service and that it should produce failure modes consistent with field experience. It is also a requirement of modern testing that it is reasonable quick, reproducible and be sensitive enough to differentiate changes made to coating systems, perhaps including, paint pre-treatments, primer and topcoat modifications.

2.4 Thermal Exposure and Cyclic Testing

The success of cyclic corrosion tests has revolved around the cyclic conditions of temperature fluctuation, UV exposure and degree of wet and dry exposure throughout the test, rather than the static conditions as used in continuous salt fog exposure. Exposure conditions used in cyclic testing impart a more realistic stress onto the coating system in an accelerated manner.

A typical consideration in procedure for accelerated weathering is the making of a controlled scribe onto the coating test panel to expose the underlying substrate. The scribe is required to represent a defect area where the subsequent onset of corrosion may be witnessed, this being the principle mode of failure measured in this type of testing. This mode of failure manifests itself during test in the form of blistering at the scribed area as the corrosion develops at the coating/substrate interface. Some of the blisters formed may fail further by cracking. This blistering mode of failure is commonly seen in field exposed test panels which have been scribed therefore reproducing a mode of failure which is assumed to be common to the coating under accelerated and external exposure testing conditions. Differences in performance may well be observed for a given coating type when comparing between test protocols i.e. ISO 20340 (draft) which has a thermal temperature gradient of -20°C - +60°C in comparison to ASTM D5894 which has a smaller temperature gradient of +23°C - +60°C and does not include low temperature freeze.

Incorporating a thermal cycle into test procedures would further accelerate the degradation of the coating by imparting stresses on the polymer matrix and allow for reduced exposure periods. Bierwagen *et al.* (2000) stated that accelerating methods such as hot salt spray or Prohesion methods require as much as 2000hrs exposure to qualitatively differentiate high performance samples whilst room temperature immersion electrochemical measurements such as EIS and ENM may take up to ten weeks to differentiate high performance samples. Therefore, they employed thermal cycling methods which showed that corrosion resistance results could be differentiated within a week using a cycle of three days of thermal cycling followed by three days of room temperature exposure, both under immersion conditions.

Valentinelli *et al*. (2002) also incorporated a thermal cycle to evaluate the performance of coatings, in this instance barrier coatings. It was concluded that the thermal cycling of immersed samples showed to be an effective test for identifying coating degradation. In addition to this work Fedrizzi et al. (2003) showed that thermal cycling allowed for the ranking of a variety of materials in a short time while remaining objective and reliable.

2.5 Electrochemical Methods

Bacon, Smith and Rugg (1948) reported some of the first work using electrochemical methods to evaluate the protection afforded to the substrate by marine coatings. In the work 300 coating systems were exposed to artificial sea water and monitored using DC resistance. The DC resistance technique is still useful in today's research as a method of finding a final resistance value. However, it has the disadvantage that to indicate resistance a significant current must be passed through the coating. Passing a current requires a high impressed voltage that can be in excess of 1V which can induce paths of conduction in the coating. This can leave areas of weakness allowing for the passage of aggressive ions, accelerating degradation of the coating. Mabbutt & Mills (1997) also reported inconsistencies with the technique with DC resistance where values were low but little or no corrosion evident.

2.5.1 Electrochemical Noise Measurement

Electrochemical potential noise is the fluctuation in the electrochemical potential of an electrode relative to a reference electrode, whereas electrochemical current noise is the fluctuation in an electrochemical current (Cottis & Turgoose, 1999). The advantage of this technique is that it can be considered non-intrusive as it monitors the naturally occurring fluctuations in potential and current. It can also be automated with relative ease to monitor up to twelve samples, as has been done by the author. To date the most useful parameter obtained has been resistance noise (R_n) which is relatively easy to calculate from the standard deviation of potential divided by the standard deviation of current. Typical voltage and current plots are shown in figures 1 and 2. These were taken from a solvent based alkyd under investigation in this work. Because this is the main technique being used in the work being reported in this thesis it will be discussed further in a later chapter.

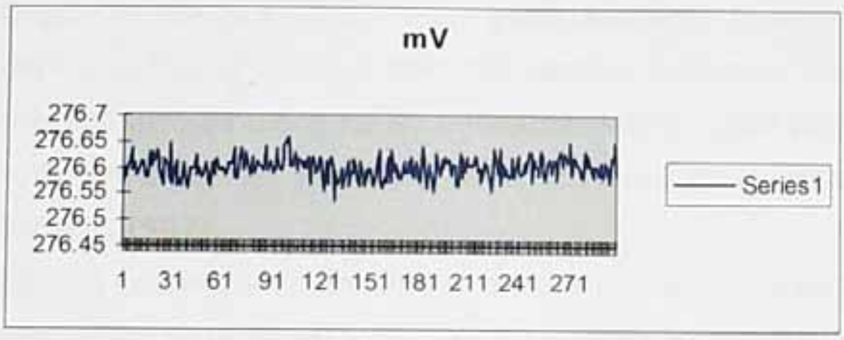


Figure 1. Typical voltage plot

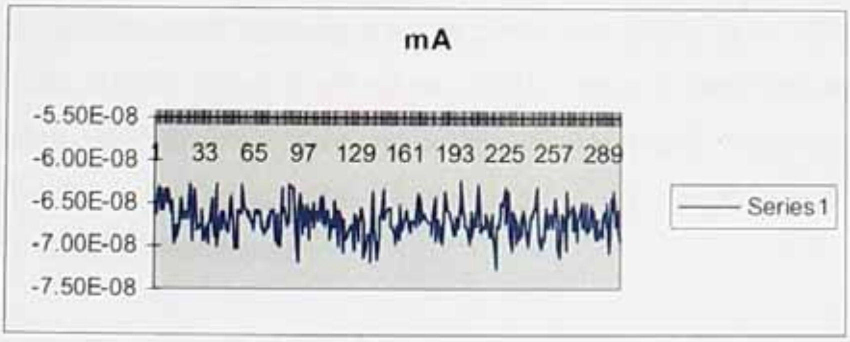


Figure 2. Typical current plot

2.5.2 Electrochemical Impedance Spectroscopy

EIS uses an AC signal which is applied to an electrode, usually a corroding metal, and the response is measured. Usually a small voltage signal is applied and the resulting current measured. The measuring equipment processes the current-time and the voltage-time measurements to provide the impedance at different frequencies, giving the impedance spectrum (Cottis & Turgoose, 1999).

This technique is now a well used method for corrosion rate determination. A small alternating signal, typically of 20 or 40 mV peak to peak, is applied to the corrosion cell. The frequency of the signal is varied, usually between 10 kHz and

100 mHz for metallic systems, and impedance measurements are plotted in a Nyquist or Bode format. From this data, a value of the charge transfer resistance can be estimated and a corrosion rate can be deduced. Electrochemical Impedance Spectroscopy has developed over the past twenty five years as a useful laboratory technique in the analysis of corrosion mechanisms and corrosion rate (Skully, 2000). Work by Skully (2000) validated the use of EIS derived values of polarisation resistance and shown correlation with other techniques. The technique has found applications for assessing protection afforded by anti-corrosive coatings in several works (Fedrizzi *et al.*, 2003; 2006; Bos & Homborg, 2006).

Organic coatings generally have good resistance to ionic conduction and offer a barrier to the diffusion of chemical species. However, it may be impossible to prevent such diffusion for an unlimited time as paint films cannot prevent corrosion over vast periods of time, but can help by reducing its progress (Skerry & Eden, 1987).

When a coating is exposed to an aqueous solution, water absorption processes occur. One of the most sensitive methods available for monitoring the absorption of water by a coating is based on electrochemical measurements. The evaluation of water uptake by organic coatings can be undertaken by means of electrochemical impedance spectroscopy (EIS). A number of papers (Skerry & Eden, 1987; Valentinelli *et al.*, 2002) have shown the application of EIS to the evaluation of protective properties of polymeric coatings when exposed to corrosive environments, demonstrating its use as a tool for the assessment of coating performance.

2.5.3 Assessment of performance properties using electrochemical techniques

Skerry and Eden's (1987) original work focused on measuring and analysing ENM voltage and current data for painted metal substrates in order to assess the corrosion resistance provided by different coatings. This work was continued and developed over the years (Eden *et al.*, 1986) and showed ENM to be a useful tool in the monitoring of anti-corrosive properties of organic coatings.

Moon & Skerry extended the work (1993) when ENM was collected in the form of time records or sets of consecutive voltage or current observations. The analysis methods of this data included statistical techniques and visual inspection of the time records. These studies suggested that the ENM time records contain valuable information about corrosion control by coatings. However, the statistical and visual methods of analysis did not reveal information about the specific mechanisms of corrosion inhibition.

Moon & Skerry (1993) also showed that information about mechanisms of corrosion and corrosion inhibition could be extracted from ENM data for painted metal. The structure of the time record was described in terms of its 'colour', in analogy to the colour of visible light – white light and noise contained equal contributions of components at all frequencies.

Taking into account that no test can duplicate all of the variables associated with a coatings degradation and its environment, Valentinelli *et al*. (2002) looked at two modern accelerated tests to investigate their potential capabilities. The tests were the Norwegian Norsok M 501 and thermal cycling in electrolyte immersion. The first test highlighted the adhesion performances of coatings and the importance of priming for scratch protection. The thermal cycling test led to a rapid loss of film properties allowing for ranking of the coatings.

Dehri *et al*. (1996) used EIS to investigate the cut edge corrosion of polyester coated galvanised steel. Measurements were taken on specimens which had been tested in an accelerated atmospheric corrosion test. The results indicated that the coating performance varies from the cut edge into the sheet. The work also showed that different electrode configurations produced the same results. It confirmed that a two electrode configuration using platinum as both a reference and counter electrode produced expected results for the coating tested and the results were therefore not due to artefacts associated with a particular electrode configuration. The use of alternative electrodes is of interest and is investigated in the experimental section of this work and results given in chapter five.

Electrochemical Noise and AC Impedance data where collected for two polymer coatings on cold-rolled steel during immersion in 0.5% NaCl for five months by Mansfeld & Xiao (1996). The two types of measurements clearly distinguished between the relatively poor performance of the alkyd system and the excellent performance of the epoxy polyamide system. Similar trends with exposure time were highlighted for the pore resistance, Rpo, and the noise resistance. Rn. However, the numerical values of the parameters obtained with EIS were different from those obtained with ENM. Mansfeld (1996) suggests that this might be the possible effect of an inhomogeneous dry film which is in agreement with work reported by Bierwagen *et al*. (1996).

Two main features of a protective organic coating are its adhesion and corrosion protection. In order to improve both, chemical pretreatments can be used. The use of chromates was very popular, but they are highly restricted because of their toxicity, so chromate-free pretreatments have been developed as an alternative i.e. thin layers of zirconia. Electrochemical impedance spectroscopy (EIS) was used in sodium sulphate solutions to evaluate adhesion and the corrosion behaviour of these materials by Fedrizzi *et al.* (2001). No barrier properties of the zirconia films were reported. Resistance to delamination was reported and the information obtained by EIS was in good agreement with the data obtained by salt fog chamber tests.

Miszczyk & Darowicki (2001; 2003) showed the effect of environmental temperature variations and thermal treatment on the protective properties of organic coatings. Observed changes were interpreted as a protective coating system degraded and explained on the basis of analysis of stresses within the coating system. It was concluded that the procedure allows to distinguish the performance of different coatings in a relatively short period of time. The effect of temperature cycling between 20-55°C and -20-20°C was investigated using EIS. EIS results showed that these temperature variations reduced the coatings protective properties. Temperature incursions as a means of acceleration have also been included in this work, results are given in chapter four.

Spengler *et al.* (1997) concluded on work undertaken assessing the corrosion protection of low toxicity paints that the contribution of electrochemical impedance was useful, showing a good correlation between EIS and the deterioration of the coatings observed for the majority of the cases evaluated. Nevertheless, some limitations were verified when under film corrosion occurred in the reference system and EIS did not detect it. This could be a result of two possible factors: (i) different local variations in film thickness leading to local structure variation, and/or (ii) difference in the rate of permeability of the coatings.

Mojica *et al.* (2004) assessed three industrial coating systems using salt fog exposure in accordance with ASTM B 117 and assessed the coatings visually using ASTM D 714 (blistering) and ASTM D 610 (rust) before evaluating the corrosion protection via EIS and ENM. It was noted that electrochemical noise provided an alternative means for the study of the protective properties of the coatings, allowing corrosion to be monitored under thick coatings (280-760μm).

2.6 Standardisation of Electrochemical Measurements and Electrodes

The increase in use of electrochemical noise measurement in corrosion research and industrial process monitoring prompted the formation of an ASTM task group in 1991. Task group activities focused exclusively on measurements to be made in the laboratory. The initial goal was to develop a consensus on:

1. Terminology
2. Specifications and configurations for laboratory instrumentation
3. Laboratory apparatus
4. Data analysis methods

A round robin was also organised to develop a body of data on different material/environment systems using a variety of instrument configurations and data analysis techniques (Kearns et al., 1996). Regarding EIS, currently there is a standard being developed (ISO 16773) specifically on the use of AC impedance to examine organically coated substrates. This is in four parts, of which two parts have already been published. It is possible that this committee (ISO TC35 SC9WG29) could extend its work to focus on developing a similar Electrochemical Noise standard using the ASTM task group information and the model provided by ISO 16773 (Mills, private communication).

2.7 Developments in the ENM arrangement

A novel configuration for gathering data using ENM was first reported by Mabbutt & Mills (1998). The new configuration was the electrical equivalent to the traditional method used by Skerry & Eden (1987) but eliminated the requirement for two isolated specimens and a conducting bridge. The technique was named the Single Substrate technique. The technique was further used by Mabbutt *et al.* (2002) to assess the anti-corrosive properties of organic coating systems intended for marine application. Good agreement was shown between values of R_n obtained from the traditional method and the single substrate technique over differing resistances. A further development known as the NOCS method will be discussed in chapter five.

Chapter Three – Experimental – Methodology for Accelerated Weathering and General Electrochemical Experiments

3.1 General experimental work – discussion of test methods

This chapter will discuss the main techniques which were used to obtain the results given in chapters four, five and six.

3.2 Salt spray

There are several manufacturers of the test equipment which all conform to the same standards and test conditions. However, these test conditions can be modified by the operating systems used on the cabinets to create bespoke test procedures as required. The weathering cabinet used in this investigation was manufactured by C & W, see Figure1.

The technique used in this investigation utilised an atomised salt fog onto an exposed panel. The panels were housed within racking inside the salt spray cabinet at a 45° angle. The geometry of the panel was set at 45° to replicate exposure conditions where any precipitation which is gathered upon the surface of the sample will run off and does not pond, resulting in immersion conditions. These exposure conditions are akin to those of rainwater droplets which come into contact with coated surfaces, carrying various ionic species and pollutants, before leaving the surface dry again through evaporation or run off.
The technique is somewhat traditional within the coatings industry and has been used in excess of 50 years.

3.2.1 Prohesion cabinet

The 'Prohesion cabinet' is essentially the weathering cabinet with the Prohesion test cycle programme entered when using the C & W equipment. Prohesion includes exposure conditions consisting of a 0.05% sodium chloride and 0.35% ammonium sulphate electrolyte solution, the solution acidity should be between pH 5.0 – 5.4. The exposure cycle is one hour salt fog exposure at 25°C (or ambient) and one hour 'dry-off' at 35°C (the 'dry-off' is achieved by purging the chamber with fresh air, such that within 45 minutes all visible droplets are dried off from the specimen). The cycle is repeated in this fashion for the desired exposure period.

Figure 1 Accelerated weathering cabinet for both Prohesion testing and continuous salt fog exposure (ASTM B117)

3.3 Electrochemical Measurements

3.3.1 DC Resistance using Keithley Electrometer

This is a high impedance electrometer which will accept resistances from sources with impedance up to 10^{13}ohms. It is an analogue manual machine. There is a digital equivalent available. However, the latter instrument is difficult to use if there is a source of voltage in the test cell.

3.3.2 Electrochemical Impedance Spectroscopy (EIS)

These measurements were performed using the Gill AC which was supplied by ACM (using its integral frequency response analyser). The equipment is fully isolated from mains earth.

A typical experiment sweeps from 10 kHz to 0.1 Hz with a 10 mV perturbation around the rest potential. The usual result is a Nyquist Impedance plot of half a semi-circle with the high frequency part giving the solution resistance and the width of the semi-circle giving the corrosion rate. The analysis of this data is performed by circle fitting with the point where the semi-circle can be extrapolated to intersect the x-axis being the resistance of the coating. Alternatively, a Bode plot of log frequency against log impedance can be generated. The intersection with the y axis is the 0.1Hz measurement.

At each frequency a sine wave is generated and fed into the potentiostat. This wave is then imposed on the cell and its potential and current flow measured. The measured values of current and voltage are compared for amplitude and phase and an impedance calculated. This is repeated for the rest of the frequencies and a plot generated. The standard starting point for an equivalent circuit with AC impedance is the basic Randles circuit.

3.3.3 Electrochemical Noise Measurement (ENM)

Electrochemical Noise is appealing because it is one of the more simple tests and can be conducted at open circuit potential without perturbing the corroding system. Currently, no real consensus exists as to the test details with regards to time intervals between data points gathered. Test parameters used in this investigation are those used by Mabbutt & Mills (1998) as they reported reproducible results.

Attempts have been made to find a relationship between uniform corrosion rate and measured electrochemical noise. An equation has recently been identified showing the equivalence of R_n to R_p. However, no ASTM standard yet exists for ENM testing.

3.4 Methodology and Equipment for ENM

3.4.1 Preparation of corrosion cells

Samples were prepared with the appropriate coating applied for testing. After curing under ambient conditions for a minimum of seven days the samples had PVC tubing sections attached to generate a corrosion cell. The tubing was cut into sections of approximately 60mm in length with a diameter of 40mm. these were attached to the samples by clear silicone sealant. This sealant was selected in view of having no influence on the anti-corrosive performance of the coating, only contributing towards eliminating water loss from the base of the attached section. The sealant was applied to the bottom of the tubing sections in a 3mm bead and applied to the surface of the samples with reasonable force (pressure with the palm of the hand) to achieve a water-tight seal. The applied tubing was then allowed to 'set' for an appropriate length of time, dependant on ambient conditions, to ensure the sample was water-tight and free from any leaks. To ensure a water-tight seal is achieved the attached tube was filled with de-ionised water for a 10-20 min period. This allowed for areas of water permeation to be identified and eliminated or repaired appropriately. Any leak, in particular, those with slow water release, would influence the performance of the coating by increasing the ionic concentration of the immersion test solution.

3.4.2 Salt-bridge

A conductive connection is required between the prepared samples to complete the corrosion cell. The ENM test configuration dictates the connection required. Test configurations used in this investigation will be discussed in further detail in later chapters. The use of a 'salt-bridge' is only a necessity when undertaking the 'standard' ENM bridge configuration.

The 'salt-bridge' comprises of a suspension or matrix, dependant on the 'salt-bridge' used, of the test solution. There were two different 'salt-bridges' used in this investigation dependant upon resources available. One comprised of malleable plastic tubing with a conductive solution whilst the other comprised of glass tubing with a conductive agarose matrix. Both 'salt-bridges' were assumed to behave in a similar fashion with regard to conductivity, however, no direct comparison of the bridges was undertaken in this investigation. The preparation of the 'salt-bridges' is detailed as follows:

3.4.2.1 Flexible 'salt-bridge' (plastic tubing)

The bridge was assembled from a 10cm length of flexible plastic tubing with a bore diameter of approximately 7mm, this varied with different plastic tubing available. The tubing was 'bunged' at one end with a rolled piece of saturated filter paper. The bung was saturated in the test solution. The tubing was then filled with test solution with a pipette, ensuring that no air bubbles where present. The tubing was then 'bunged' at the opposite end in the same manner as earlier, again, ensuring not to generate air bubbles through displacement. Due to the ends of the 'salt-bridges' relying on the saturation of the filter paper bungs, the bridges were looped and the ends stored in the test solution to ensure the concentration of the bridge solution did not fluctuate.

3.4.2.2 Rigid 'salt-bridge' (glass tubing)

The bridge was assembled from a linear glass tube, ~12cm in length. The tube was heated 4cm from either end of the tube in order to soften the glass to allow for the manipulation of ~50° angles. The angles create a shape which allows the bridge to be placed into the nominally identical cells without the samples being too close together, therefore, samples remain electrically isolated. The inflexibility of the angle joints can be restricting during experimentation as samples can vary in their dimensions.

The conductive material within the bridge was not of wet-state as with the flexible bridge but as a solid-state material upon setting. A 3% agarose dry powder was mixed with the test solution to give a translucent gel. The gel was injected into the glass tubing by syringe with particular attention being paid to prevent the formation of any air bubbles which would 'set-up' in the matrix formation. The setting of the agarose gel resulted in a polysaccharide/test solution matrix which allowed for conduction through the bridge.

3.4.3 ZRA supplied by ACM

The ACM Zero Resistance Ammeter (ZRA) was used for the initial and majority parts of test work undertaken in this investigation. The test arrangement and equipment can be seen in Figures 2 and 3 respectively. Latter work was undertaken using Gill 12 supplied by ACM. Results obtained from both sources of test equipment can be compared directly as there were no discernible difference with regard to reproducibility. Samples were measured on both sources of equipment using the same Calomel electrodes giving comparable results within the limits of experimental error.

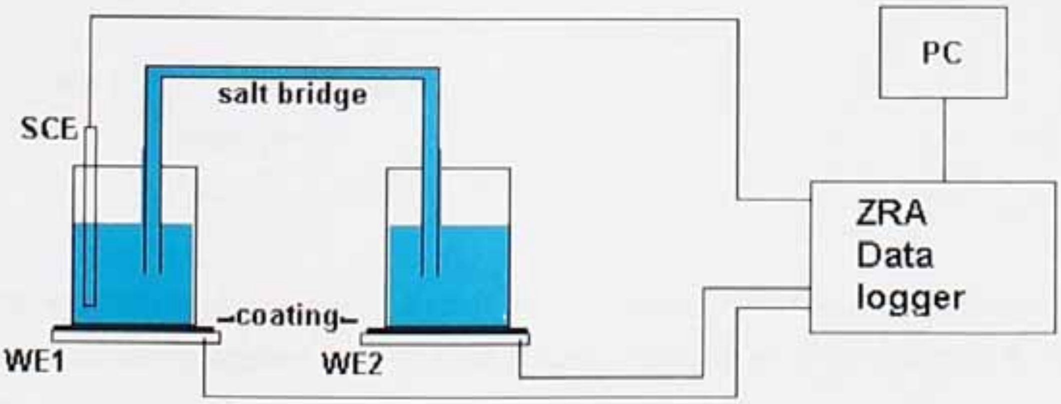


Figure 2 Standard Electrochemical Noise Method ('Bridge' method with 2 specimens)

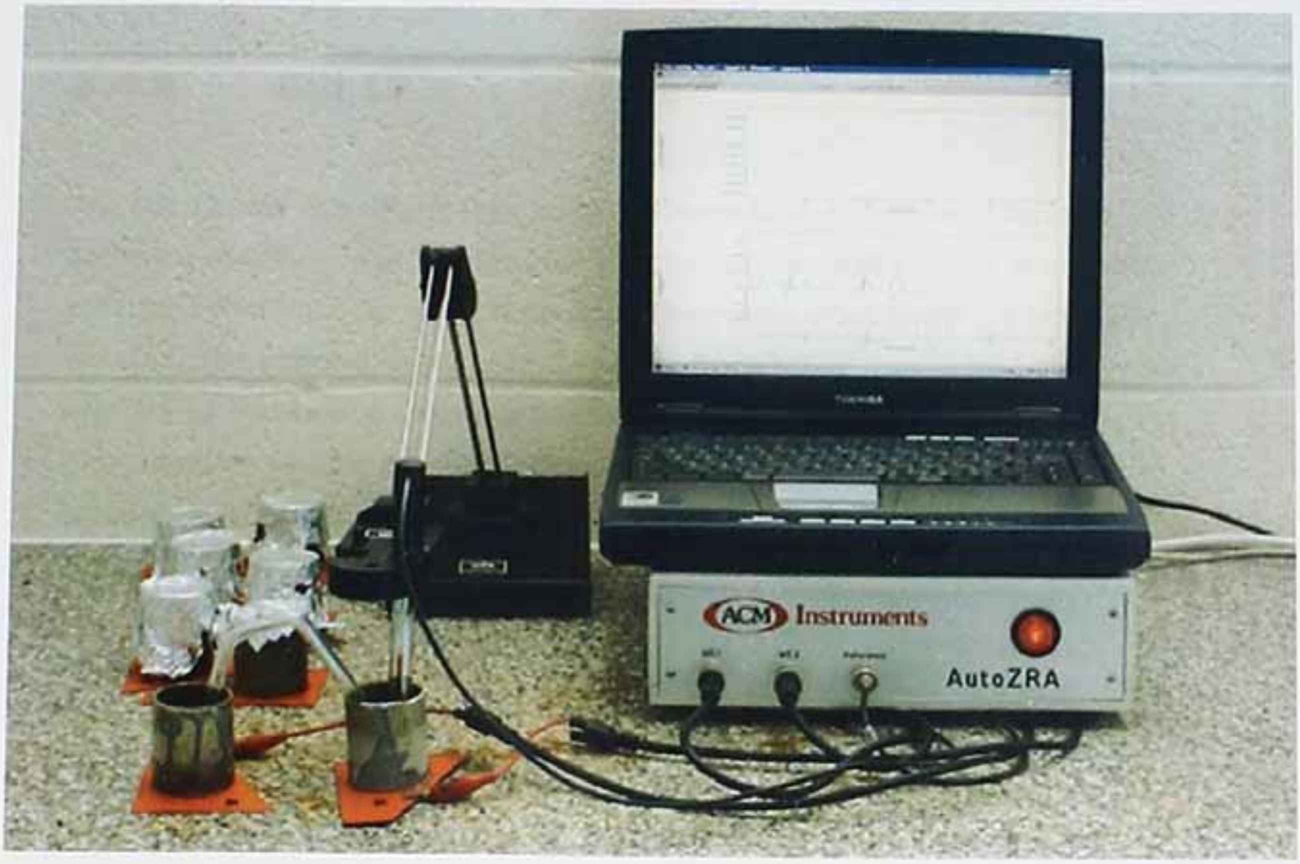


Figure 3 Equipment arrangement for ENM testing utilising the 'bridge' method

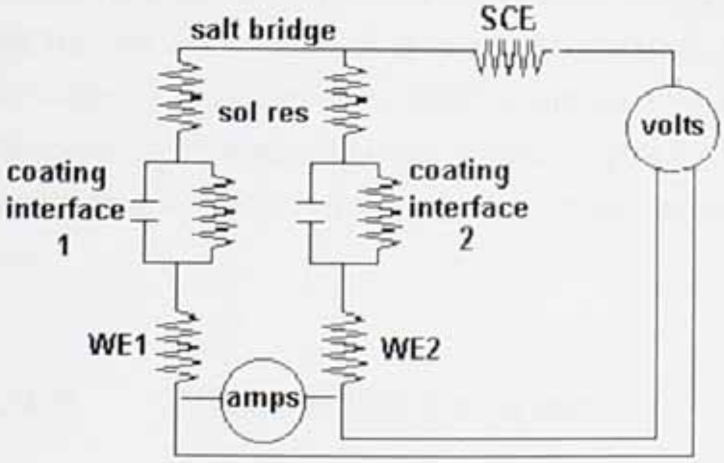


Figure 4 Schematic equivalent circuit for Standard ENM Method (2 separate specimens) when applied to a coated metal (reproduced from Mabbutt & Mills, 1998)

3.4.4 Gill 12

The Gill 12 was in a robust fully screened metallic case with an internally screened mains supply. The internal circuit is a one double-sided board with minimum wire links for noise reduction. The mains input earth is electrically isolated. The internal board is also isolated from 'noisy' computer interference. The Gill 12 had twelve channels available which could be activated for testing depending on sample numbers. The equipment would multiplex between the samples in accordance to the software programming. The test parameters were the same as those used for the ZRA.

3.4.5 Electrodes

A three electrode set-up was used for ENM throughout this investigation. In normal electrochemical noise monitoring configurations the two working electrodes consist of two separate specimens. Potential is measured in all tests using a reference electrode relative to the coupled working electrodes. Due to monitoring of potential fluctuations (noise) being the aim of the test, is important that the reference electrode is relatively noiseless. It has been suggested that the Saturated Calomel Electrode (SCE) is the least 'noisy'.
The electrode configuration was altered to give a new test arrangement which was devised as part of this body of work; further information is given in chapter five.

3.4.6 Electrolyte solution

Some of the preliminary ENM test work used 0.5% ammonium sulphate to give an indication of performance. This solution was considered to be the equivalent of Harrison's solution ionically, considering the absence of sodium chloride. Harrison's solution was originally developed following investigations of atmospheric pollution and contamination found in atmosphere close to railway operations (Harrison, 1970). Samples taken from the environment showed that the coatings were encountering much higher levels of ammonium sulphate than sodium chloride. From Harrison's work (1970) the recommended test solution for

the evaluation of coatings was 3.5% ammonium sulphate and 0.5% sodium chloride. This was said to be more representative of service conditions.
In later work on immersed samples 0.35% ammonium sulphate and 0.05% sodium chloride solution was used. This dilute equivalent of Harrison's solution was used as it is the test solution recommended for the Prohesion test cycle in accordance with ASTM G-85.

Chapter Four – Developments in organic coating formulations and the subsequent testing

4.1 Introduction

In accordance with growing environmental and duty of care pressures, a change in direction in traditional coating formulating is required. Emphasis now lies with coating manufacturers to reduce the VOC content of final application products. This emphasis has led to the development of coatings based upon waterbased technologies and high solid solvent based products. As with all advancements in technology the assumption that the technology is always improved with development can not always be made. With the introduction of waterbased technology doubts were raised as to its ability to perform in the same environments as solvent based technologies to the same level.

Throughout developments there is a requirement to test the coating and to accelerate the external environment. The acceleration of testing allows the formulator to respond to undesirable properties at an earlier stage.

As mentioned in chapter two the traditional method of accelerating exposure/corrosive environments i.e. the hot salt spray test ASTM B117, is somewhat subjective and does not always accord with practice.

The aim of developments in coating formulations was to reduce the VOC content of the company's products without having any adverse effects on performance properties. Traditional salt spray testing and evaluation with ENM on immersed samples were compared as methods of assessing the anti-corrosive properties of the coatings. Comparison with external exposure panels was also included.

The test programme was designed to allow monitoring of the performance of the coating using both qualitative and quantitative methods. Traditional accelerated weathering methods and external exposure panels produce qualitative results whereas ENM on immersed samples gave quantitative results. The investigation also allowed conclusions to be made regarding a comparison between the methods of testing in relation to coating performance and any relationship between the results to be drawn.

Similar investigations have been undertaken previously (Lyon *et al.*, 1989), designed to draw conclusions on the merits of accelerated testing and its relationship to natural life-time exposure conditions. However, these investigations were only looking at the comparative performance of the test methods employed and did not investigate the development of the coating technology and performance. Results given in this chapter show how the test methods employed allowed for the 'ranking' of performance properties of the developed coatings and subsequent further developments.

The method of 'ranking' used a similar method to that devised by Bacon *et al.* 1948, with coatings expected to show good anti-corrosive properties above 10^8 ohms/cm^2, between 10^6 and 10^8 ohms/cm^2 giving moderate protection and anything below 10^6 ohms/cm^2 giving questionable protection of the substrate.

A standard as to where developments are to be made from was required. The standard was set in the form of the current products the company produce for the appropriate technology i.e. solvent or waterbased. These are called the 'baseline' set.

4.2 Experimental

4.2.1 Surface Preparation

The method of preparation of the substrate surface can have a large impact on the subsequent performance of the applied coating.

Where ENM on immersed samples was used all samples were applied to a degreased panel with no other surface preparation. Abrading was undertaken in the preparation of panels for accelerated weathering exposure.

It is known that application of coatings over shot or grit blasted steel (SA2.5 recommended) can lead to differences in performance for both intact and scribed areas. However, it is not considered practical to use this type of preparation and the 'as received and degreased' panels should enable valid comparisons to be made.

4.2.2 Film thickness (dry/wet)

As with surface preparation controlling the wet/dry film thickness of the coating is critical. The performance of the coating hinges heavily on the final dry film thickness as accelerated tests are only undertaken on dry state materials. The application of the coating in wet state can also impact on the final performance of the coating. If the coating is applied above the recommended film thickness the coating may not fully cure due to the drying process being retarded, this is dependent on the curing mechanism of the coating in question. For instance when considering the curing mechanism of alkyd based coatings, their primary mechanism for curing is oxidation, catalysed by heavy metals (generally referred to as 'driers' within the coatings industry). To achieve a suitable dry film thickness at recommended coverage rates, two independent coating applications may be required.

4.2.3 Sample application

Samples which were tested are listed in Table 1, along with a brief description of the coatings and the dry film thickness.

The samples were evaluated on cold-rolled mild steel panels (Q-panels) as supplied by Q-LAB. Panels to be exposed to accelerated and external weathering were degreased with MEK to remove any surface contamination and abraded with 60-grit abrasive paper.

Samples prepared for evaluation via ENM immersion were degreased only with MEK, no abrasive preparation was undertaken. When undertaking comparative evaluation one would prefer to keep all possible variables to a minimum. However, in the case of ENM samples not undergoing identical preparation, i.e. surface abrasion, it should be noted that in view of the subsequent profile developed a contribution towards improving adhesion will be made. Any improvement in adhesion is known to impact on the performance of a coating with regard to anti-corrosive properties. The improved adhesion can prevent the transport of water underneath the coating at the coating-substrate interface, primarily reducing the effects of blistering and its onset whilst reducing the movement of aggressive ionic species between the coating/substrate interface. Secondly, the introduction of a profile to the metal surface may contribute towards a false R_n value which may be more indicative of pitting corrosion.

After the Q-panels had been degreased and abraded appropriately the samples were applied at recommended film thickness, as per the technical data sheets, using the appropriate drawdown bar as supplied by Sheen instruments. Samples were then left to dry for seven days at ambient temperature (18 ± 2°C/50% rh) for conditioning purposes. Samples were then prepared for the appropriate test as outlined in chapter three.

Samples prepared for exposure to accelerated weathering were placed in the salt spray cabinet at 45° to horizontal angle in the racking to replicate exposure to precipitation which is designed to 'run-off' instead of 'ponding', the latter would cause an immersion environment.

Samples prepared for external weathering exposure were placed on a south-west facing external wall to emulate anticipated exposure conditions with maximum exposure to UV radiation.

Samples prepared for ENM immersion testing were, firstly, checked for cell 'leakage' for a 4-8 hour period before being exposed to full immersion conditions. The cells were filled to a ~2cm depth with 0.5% ammonium sulphate as it is approximately the same concentration ionically as dilute Harrison's solution. The cells were subsequently 'topped-up' with distilled water to maintain the 2cm depth to avoid any shift in electrolyte concentration.

4.2.4 Scribed samples

Part of the work undertaken in this chapter included samples containing scribes. The scribe is introduced to the sample to replicate any damage and subsequent break in film integrity which may be experienced by a coating system in service.

4.2.4.1 Scribe production

The mechanical scribe made into the coating required the use of a special tool designed by Mabbutt (Ph.D. thesis, 2000). This was designed to remove the area of coating rather than displace it by plastic/elastic deformation. The tool lifts the coating and shears the edges to give a square section scribe. This scribing tool is preferred to a standard blade scribe as it gives closer control of the scribed area, making it more reproducible with a width of 0.5mm and a length of 5cm.

4.2.5 Parameters of the coatings assessed

Paint	Type of paint/description	Number of coats	Dry film thickness (μm)
D	WB blended coating with water thinnable alkyd and styrene-butadiene co-polymer, with zinc phosphate	One	70-75
E	Modified short oil alkyd with phenolic chain attached with zinc phosphate	One	60
F	Modified short oil alkyd (acrylic modified) with zinc phosphate	One	70
G	Vinyl-chloride acetate co-polymer with chlorinated paraffin, zinc phosphate	One	70
H	Low VOC with increased solids content	One	70
J	Low VOC with alternative blended extenders	One	70
R	Low VOC using alternative resin	One	70
S	Low VOC with blended extenders using lamellar pigment	One	70
N	Paint D as a two coat system with a water thinnable topcoat	Two	135
P	Paint D-Modified with reduced levels of ammonia and rheological agents	One	80

Table 1 Description of coating system and film thickness

4.3 Results

Four 'baseline' paints were first investigated to set a standard for the subsequent testing of reformulated and/or newly develop paints. Initially, the paints were tested over a period of 150hrs for scribed samples and 700hrs for intact samples. Results for individual samples of the 'baseline' paints D and F are given below, figures 5 and 6 for scribed samples, and figures 7 and 8 for intact samples. The individual R_n values for the other two baseline paints (E and G) are not given here but the average R_n value of all four 'baseline' paints (D, E, F and G) are provided in figure 9 (intact samples) and figure 10 (scribed samples). Paint E is investigated with high temperature 24hrs exposure cycles in figure 11.

The reader should note that in all of the graphs throughout this thesis where Rn has been plotted on the ordinate (y axis), it has been plotted on a log scale. This is a necessary way of plotting the data because of the large variations in resistance commonly seen.

4.3.1 Investigation of coating performance

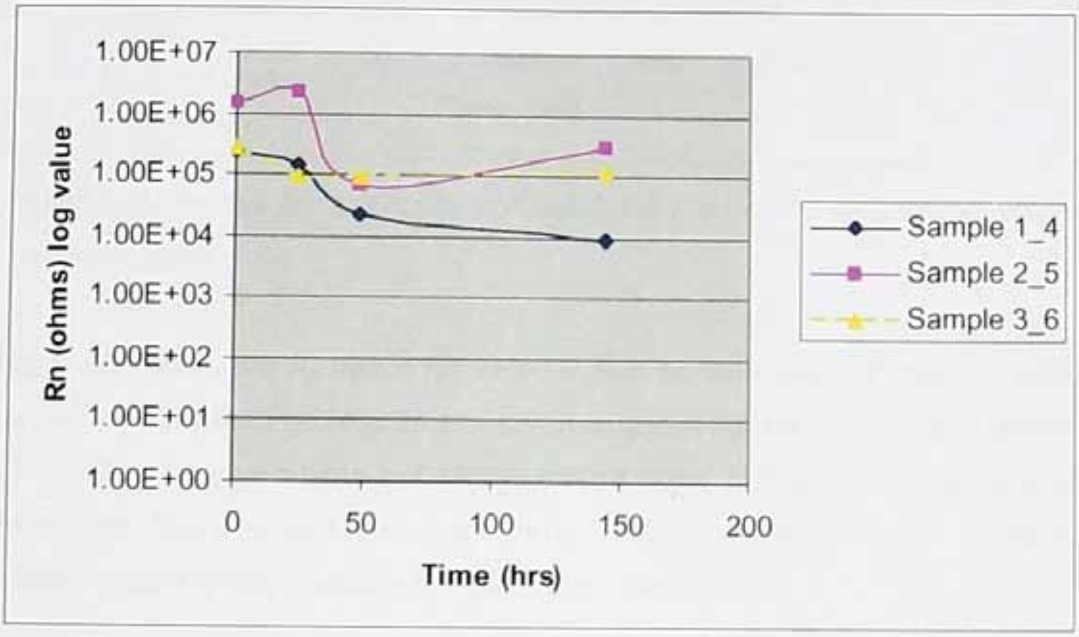


Figure 5 *R_n values for triplicate scribed Paint D samples in 0.5% Ammonium Sulphate at RT*

Figure 5 shows the R_n value for Paint D as a scribed sample over an exposure period of 150hrs. The results are given in triplicate for Paint D and show variation of results at a given time but highlight the trend consistently over the period of exposure. The average R_n value can be taken from the triplicate samples and plotted against the average of the other coatings.

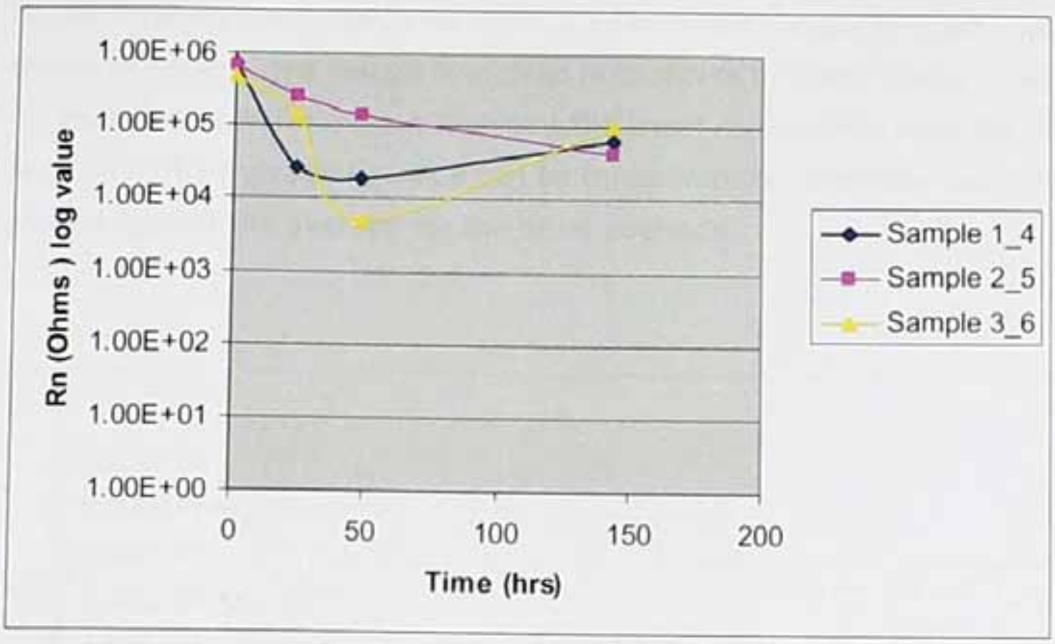


Figure 6 *R_n values for triplicate scribed Paint F samples in 0.5% Ammonium Sulphate at RT*

Figure 6 shows the R_n value for Paint F as a scribed sample over an exposure period of 150hrs. The results are given in triplicate for Paint F and show variation of results at a given time but highlight the trend consistently over the period of exposure. The average R_n value can be taken from the triplicate samples and plotted against the average for the other coatings.

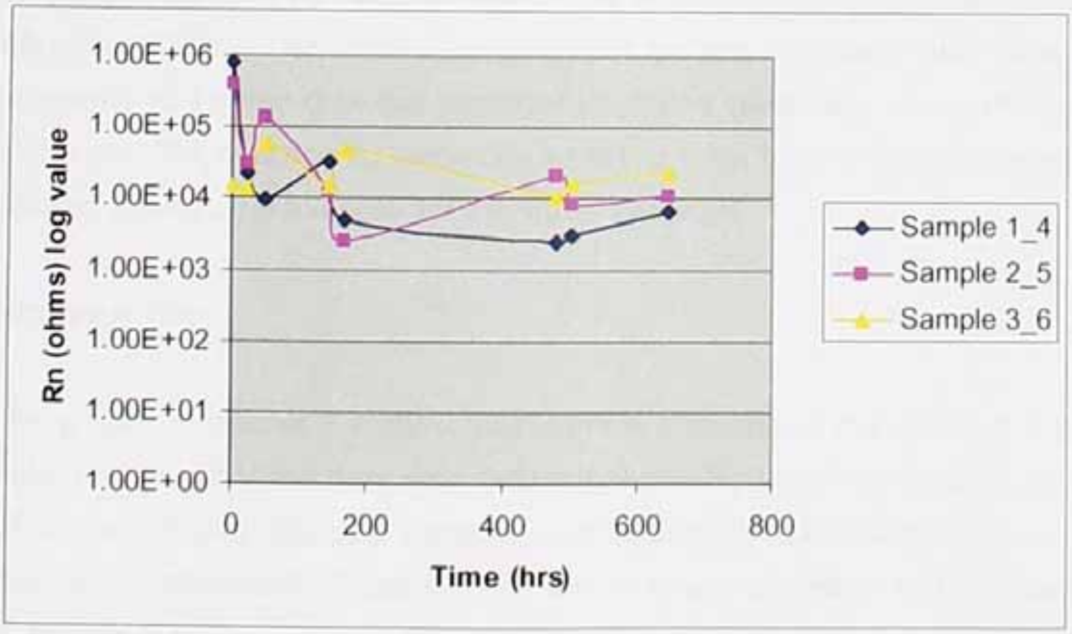


Figure 7 *R_n values for triplicate intact Paint D samples in 0.5% Ammonium Sulphate at RT*

Figure 7 shows the R_n value for Paint D as an intact sample over an exposure period of 700hrs. The results are given in triplicate for Paint D and show variation of results at a given time but highlight the trend consistently over the period of exposure. The average R_n value can be taken from the triplicate samples and plotted against the average for the other coatings.

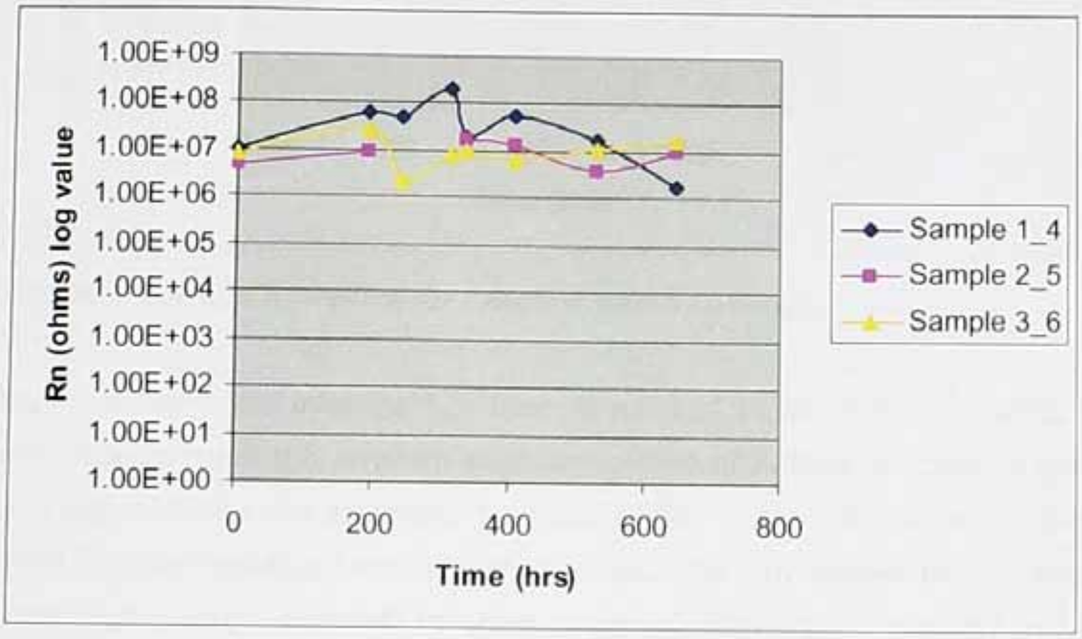


Figure 8 *R_n values for triplicate intact Paint F samples in 0.5% Ammonium Sulphate at RT*

Figure 8 shows the R_n value for Paint F as an intact sample over an exposure period of 700hrs. The results are given in triplicate for Paint F and show variation of results at a given time but highlight the trend consistently over the period of exposure. The average R_n value can be taken from the triplicate samples and plotted against the average for the other coatings.

Scatter in data

The graphs in figures 5-8 show that there is a scatter in the order of ± 0.3 (log value) for most of the data with occasional greater variation (± 0.5). Unless otherwise stated, triplicate samples were examined in all subsequent experiments reported in this work. These showed similar levels of scatter to the graphs shown in figures 5-8.

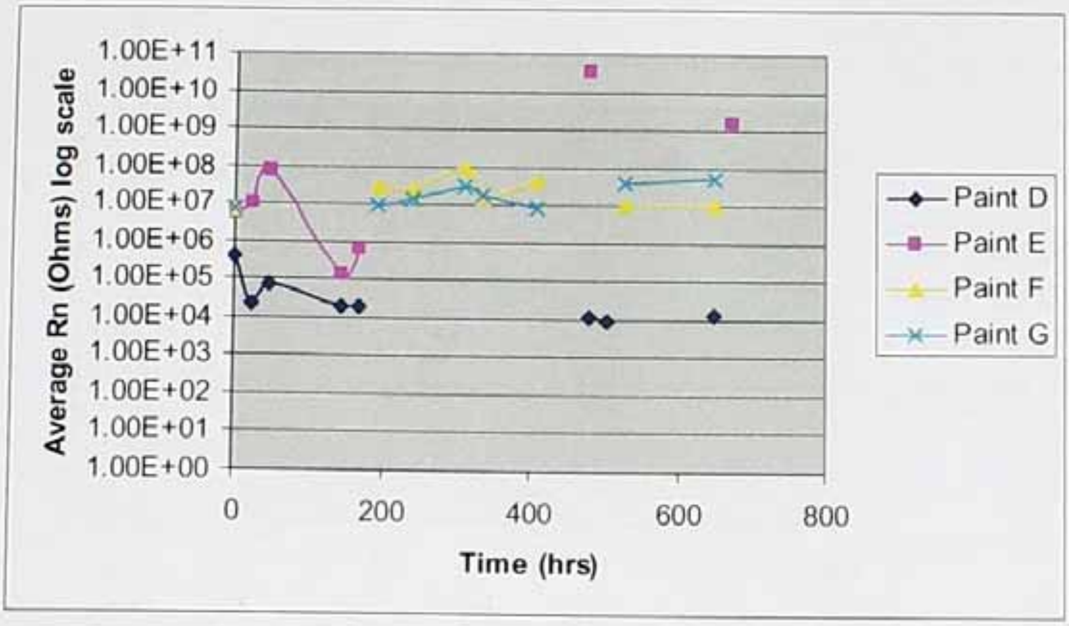


Figure 9 Average R_n values for baseline intact coatings

Figure 9 shows the average R_n values of a set of 'baseline' intact paints. The R_n was taken periodically over an exposure period of 700hrs. All coatings were intact and exposed to 0.5% ammonium sulphate. The line graph shows a reasonable level of differentiation between the samples. The only waterbased coating investigated in the baseline samples, Paint D, shows the largest fall in R_n which then remains at a similar level throughout the remaining period of the test. Both Paints F and G display a similar R_n throughout the period of the investigation with little deviation from the original R_n value taken at the onset of the test. Paint E displays a drop in R_n of almost two orders of magnitude within the first 200hrs of exposure but then shows an increase in R_n for the remainder of the test period.

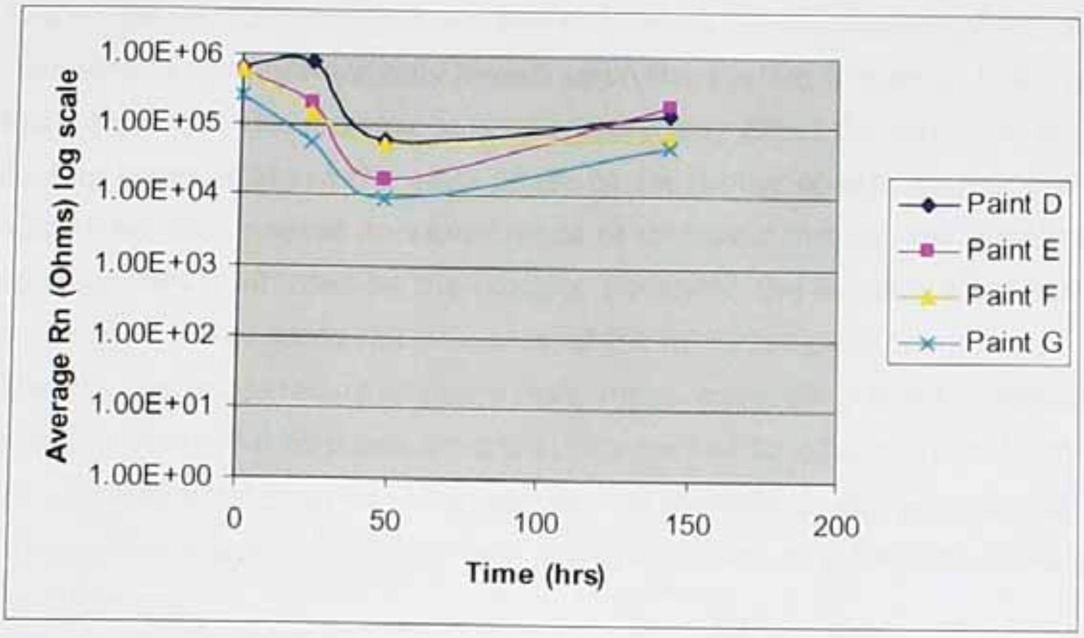


Figure 10 Average R_n values for baseline scribed coatings

Figure 10 shows the average R_n values for the same set of 'baseline' paints shown in Figure 9. The 'baseline' paints are scribed samples and therefore under exposure conditions for a shorter period of time. All paints display a similar trend, with R_n values dropping after initial exposure (50hrs) and then increasing towards the end of the 150hr exposure period.

4.3.2 High temperature exposure

A development in methods used previously has been the incorporation of a high temperature exposure for immersed specimens (Cherry & Mayne, 1963). Thermal cycles have since been used by other workers (Bierwagen *et al.*, 2000; Valentinelli *et al.*, 2002; Fedrizzi *et al.*, 2003).

After initial periods of immersion exposure samples were exposed to high temperatures to help further differentiate coatings on the basis of their anti-corrosive properties. The procedure was as follows: all test paraphernalia i.e. SCE and salt bridges where applicable, were removed from the test samples. The attached PVC cells were covered with tin foil to reduce the amount of evaporation of the test solution. The samples were then placed into a 70°C incubator for 24hrs. After the period of exposure samples were removed from the incubator and allowed to climatise under ambient conditions for a further two hours. Samples were then configured accordingly to the ENM apparatus as described in chapter three and readings taken. This high temperature exposure was undertaken at various intervals throughout the investigation in an attempt to further differentiate the coatings and accelerate the mechanism of degradation. Exposure to temperature may impact upon the coating in one, or both, of the following ways. The increase in temperature may affect the structure of the coating taking it above the glass phase to the rubber phase allowing any aggressive ions present an easier mode of transport through the 'protective' polymer matrix afforded by the coating. Secondly, the increased temperature may contribute towards the efficiency of the inhibitive pigments present in the coating. The temperature increase may improve solubility of the inhibitive pigment allowing it to passivate the substrate due to it having higher reactivity on the electrochemical series. Alternatively, the increase in temperature may catalyse the reaction allowing for a protective film being formed on the surface of the substrate.

Figure 11 illustrates what happened to three individual intact samples when two 24 hr 70°C high temperature exposure cycles were incorporated, these are indicated by arrows. High temperature exposure took place at 168 and 336hrs (one and two weeks after testing began). Exposure appears to increase R_n values for a short period followed by a slight drop which then displays a degree of stabilising. Figure 12 shows the average R_n values which were obtained by determining the geometrical mean from triplicate samples.

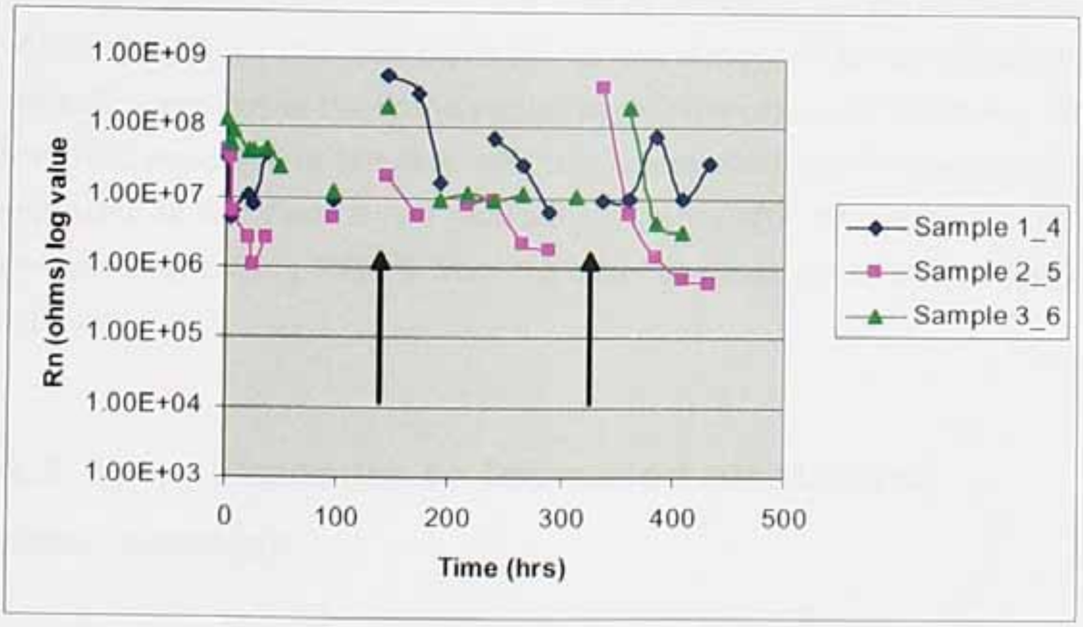


Figure 11. R_n values for triplicate intact Paint E samples in 0.5% Ammonium Sulphate at RT

Figure 11 shows R_n values in triplicate for Paint E. It shows an acceptable and expected amount of scatter amongst the three nominally identical samples for Paint E. The other paints exhibited similar or less scatter. Exposure appears to increase resistance for a short period with a slight drop after the increase but then stabilising at high 10^6.

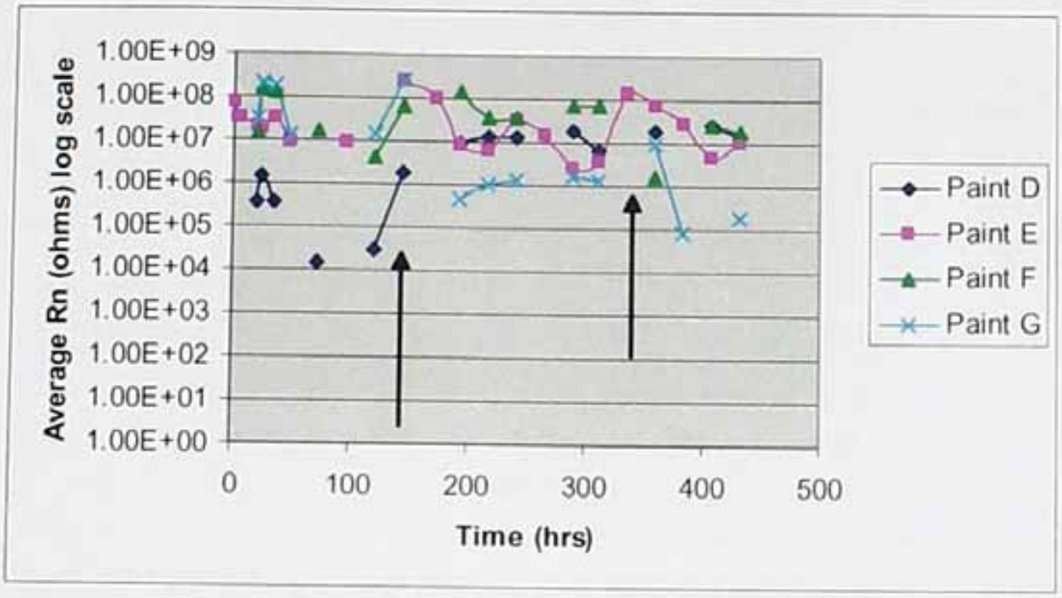


Figure 12. Intact coatings in 0.5% Ammonium Sulphate with a high temperature exposure incorporated

Figure 12 shows the average R_n values for all four baseline coatings up to 450 hrs at RT. The black arrows indicate the time of exposure to temperature for periods of 24hrs at 70 °C: this took place at 168 and 336hrs (1 and 2 weeks after testing began). Three out of the four samples show an increase in resistance after the first 70°C exposure to temperature; this is less obvious after the second exposure. In fact Paint G had reduced resistance after the second exposure and therefore separating Paint G from the other coatings after 70°C temperature exposure.

4.3.3 Exposure to increased electrolyte concentration

Samples of the same coatings (scribe prepared as described earlier in the chapter) were exposed to different conditions and the R_n value recorded. The initial period of exposure was to the usual concentration of test solution (0.5% ammonium sulphate). After the initial exposure period the concentration of the test solution was increased by a multiplication factor of 10 to 5% ammonium sulphate to assess the affect upon corrosion protection afforded by the coating.

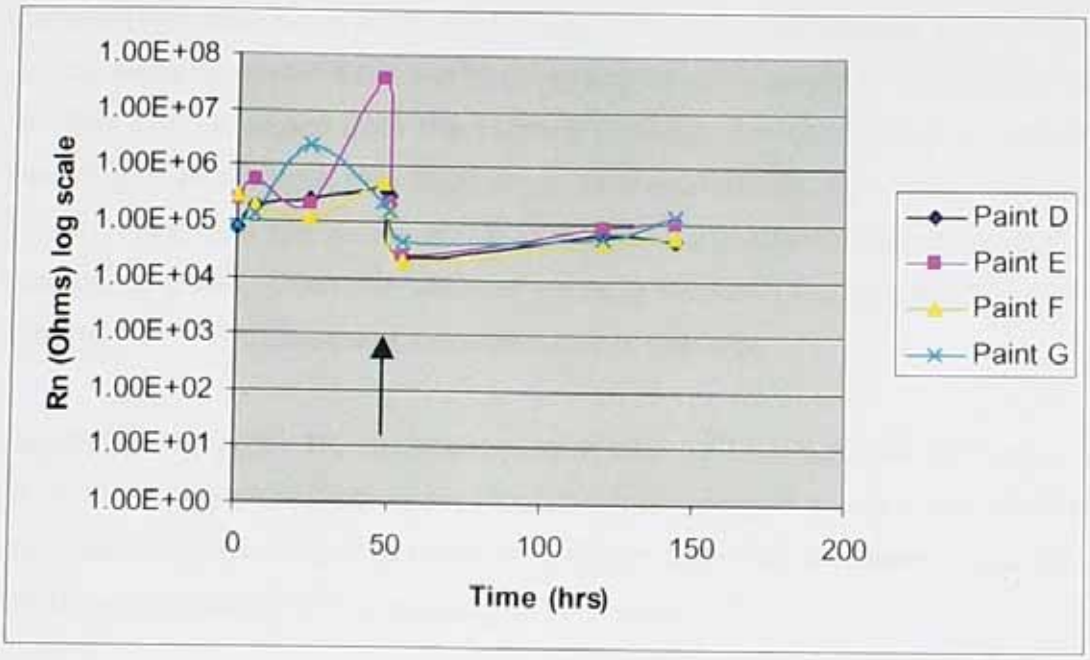


Figure 13 Average R_n values for baseline scribed coatings exposed to increased electrolyte concentration

Figure 13 shows the average R_n values for all four baseline coatings up to 150 hrs under immersion conditions at RT. The black arrows indicate the time of exposure to the increase concentration of electrolyte test solution (5% ammonium sulphate); this took place 48hrs after initial exposure. All resistances drop as a result of exposure to the increase concentration of electrolyte.

4.3.4 Salt Spray Results on 'Baseline' Coatings

Detailed Salt Spray results are not given here as the focus of the work is electrochemical evaluation. They can be found in Mills *et al.* 2002 (CD-ROM). ENM and DC resistance results were found to show good correlation with salt spray results.

4.3.4.1 DC Resistance after Salt Spray Exposure

The DC resistance measurement was made using the high impedance Keithley electrometer described in chapter three. At the end of the salt spray test the panels were removed from the cabinet and small aliquots of the diluted Harrison's solution were dropped onto the surface (4 drops per specimen). A calomel electrode was inserted into each drop. This was electrically connected to the high on the meter and the panel to the low (this is a quicker measurement to make than using ENM). Once the value of voltage between the two electrodes has been allowed for, the instrument becomes direct reading.

Figure 14 shows the DC resistance results for all four baseline coating systems (D, E, F and G) after 500hrs modified Prohesion™ salt spray exposure. The DC resistance approximated to the visual appearance i.e. the paints with lower DC resistance showed more evidence of corrosion.

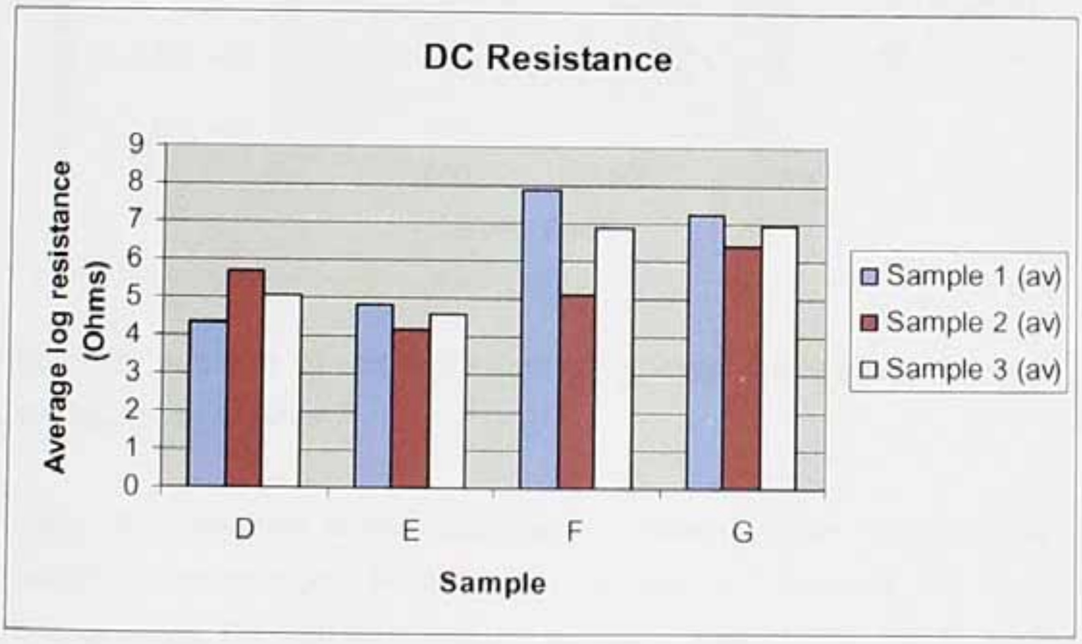


Figure 14. Average log DC resistance for 'Baseline' coatings after salt spray exposure

Figure 14 shows the average log DC resistance of 'baseline' coatings after 500hrs exposure to modified Prohesion.

4.3.5 Electrochemical Noise on immersed samples to aid development work

Plots of Log R_n against time are given for different groups of coatings in Figures 15 and 16. The values for R_n are not corrected for area. (Note that these plots use the E method for designating powers of ten i.e. $1E8 = 1 \times 10^8$). All data shown was gathered using methods described previously (Mabbutt & Mills, 2001). Figures 15 and 16 show average R_n values which is obtained by determining the geometrical mean from triplicate samples.

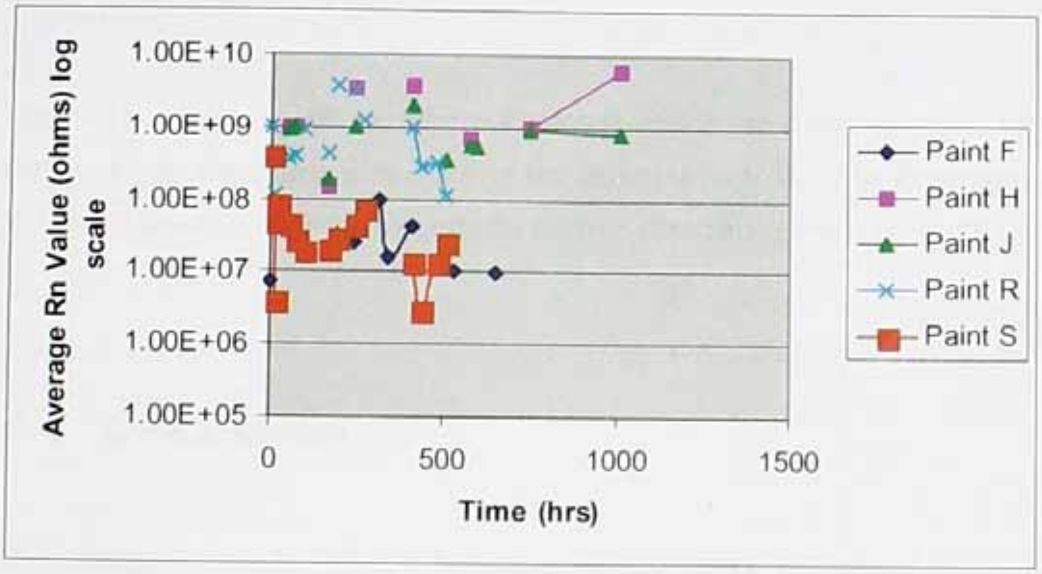


Figure 15. Average R_n values for Compliant intact coatings which are developments of Paint F

Figure 15 shows ENM being used, using R_n values, in the development of a compliant coating where Paint F is the baseline and Paints H, J, R and S are developments. No high temperature exposure was used in the assessment of these coatings. Paint S was similar to Paint F, with acceptable R_n value after 700 hr but Paints H, J and R all had even higher resistance.

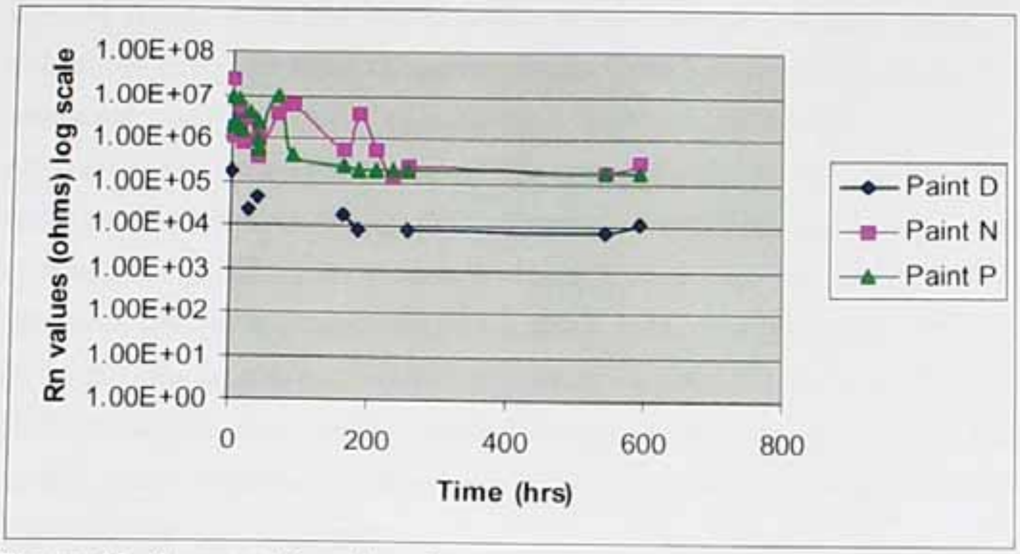


Figure 16. Average R_n values for current intact waterborne coatings which are developments of Paint D

Figure 16 shows R_n values where Paints N and P are developments of D. No high temperature exposure was used in the assessment of these coatings. Both Paints N and P had an order of magnitude higher resistance than paint D.

4.4 Discussion

The results shown in Figures 5-9 have already been discussed in section 4.3.1. Hence this discussion section focuses on the results obtained in section 4.3.3 through 4.3.5. Time line results of ENM with exposure to temperature are for baseline coatings that include both solvent and waterborne systems are shown in Figures 11 and 12. The R_n values started to fall before visible corrosion was observed. Figure 11 shows the scatter of R_n values for triplicate samples and is typical of data collected for R_n values for baseline coatings. Figure 12 shows that the solvent borne coatings (Paints E, F and G) had a much higher initial resistance than the waterborne coating (Paint D). The results show that Paint D had a low initial resistance (below values which indicate corrosion protection) but after exposure to temperature the resistance increased by almost three orders of magnitude. This increase could be attributed to increased solubility of the anti-corrosive pigment as a result of the increase in temperature. This in turn leads to lower conductivity in the coating and thus (in theory at least) it should afford increased protection of the substrate. Figure 12 also shows all four samples increasing in resistance after the first 70°C exposure before dropping again at varying rates Note that paint E increases in resistance again after the second exposure, whereas Paint G rapidly drops. This indicates that high temperature exposure can be useful in ranking high resistance coatings.

Figure 13 presents an increase in the concentration of the electrolyte. All resistances eventually drop after exposure. Initial exposure shows a sharp increase in resistance by paints E, F and G, this may be the result of active anti-corrosive pigments protecting the scribed area. The fall in resistance corresponded to signs of visible corrosion within the test cells. The resistance of all four coatings then showed a slight increase as corrosion product blocked the scribe. It would appear that none of these systems are protective at a scribe in 0.5% ammonium sulphate.

The DC resistance results in Figure 14 however showed Paint D was significantly worse than the other three 'baseline' samples with Paint E being the second worst and Paints F and G showing good corrosion resistance at similar levels of protection.

The DC resistance values duplicated the final R_n values (see Figure 9) within a reasonable degree of error but as they were only recorded at the end of salt spray exposure they are less responsive to changes in the coating systems.

Time line results of ENM for developments of compliant organic coatings based on baseline paint F are shown in Figure 15. The results show an overall steadying of R_n values, with Paints H, J and R showing high resistance in the order of 5×10^8 and Paints F and S showing somewhat lower resistance in the order of 1×10^8. All of these values are above values which should offer corrosion protection. Using these values the coatings can be ranked giving an indication of the corrosion protection qualities for each coating, such as, H=J>R>>S=F.

R_n values as a function of time for developments in waterborne coatings ("baseline" paint D) are shown in Figure 16. Whereas R_n values started to fall (and subsequently visible corrosion was observed) for Paint D, R_n values for Paints N and P are almost two orders of magnitude higher indicating improved anti corrosive properties. This correlates with no observed visible corrosion for Paints N and P after the test was complete.

The R_n values also indicate a very close relationship between Paints N and P, this can be attributed to the fact that both paints use the same two coat primer system, the only difference being Paint P has a topcoat.

4.5 Conclusions

Using ENM has proved promising in the area of formulating and assessing performance of anti-corrosive coatings. It allows the formulator the ability to rank organic coatings in order of anti-corrosive protection afforded. The performance of most intact coatings can be tracked using measurement of R_n. ENM can be used to assess the ability of a coating to protect both when nominally intact and when integrity is broken (scribe). The non-intrusive nature of the measurement allows for almost continuous monitoring.
ENM on immersed samples when used alongside traditional methods of accelerated weathering assessment can give a reasonably comprehensive predicted life service estimate, giving coatings manufacturers confidence in marketing products assessed using these methods.

The success of the high temperature incursions work here explains why temperature cycling is popular and occurs in a number of modern accelerated test regimes. The high temperature incursion has been useful in separating out similar coatings. Following previous work (Cherry & Mayne, 1963; Miszczyk & Darowicki, 2003) a low temperature exposure (e.g. in a freezer at -20°C) of the "immersed" specimens might be usefully incorporated to further separate out good coatings.

Although ENM does not directly detect visual defects in the coating, such as might arise as a result of exposure to light or UV, nonetheless these 'stresses' in the polymer structure which could be detected by ENM. However, a straight immersion test will not form a test for light fastness or UV resistance. This is because the assessment is carried out under immersion conditions which are not as severe as artificial accelerated weathering chambers (QUV testing).

Chapter Five – Developments of ENM to enable it to be used *in-situ* (on-site)

5.1 Introduction/Previous work

Murray (1997) reviewed the developments in the assessment of organic coatings using electrochemical test methods. It was a three-part publication and reviewed papers evaluating organic coated metals using electrochemical means for the period of 1988 – 1994. It stated that the last review article was written six years prior to that by Leidheiser (1991). Murray stated that commercially available electrochemical and electronic measurement instrumentation have been improved considerably since that review, and at least two electrochemical test systems are available that can be considered to be truly field portable. The two test systems he refers to are EIS and ENM. He claimed that Gamry Instruments Incorporated had demonstrated the capability for an ENM field test system. The electrometer portions of their units allowed correct ENM measurements of the coated panel potentials relative to an appropriate reference electrode without disturbing the natural sub-film processes (note that lightweight, field portable EIS units are commercially available from ACM Instruments).

Despite these statements made in Murray's review, field evaluation of existing coatings offers several challenges, especially if the evaluation technique requires an aqueous electrolyte and the coated substrate is of awkward dimensions i.e. is not (reasonably) horizontal. One approach for a field cell would involve the use of a porous, flexible, absorbent material to contain the test solution by capillary forces. The wetted 'attachment' is then sandwiched between the coated surface and an appropriate counter electrode. A flat reference cell could also be positioned on the attachment adjacent to the counter electrode. As the wetting electrolyte should penetrate into coating pores or defects, this approach may be considered better than the use of conductive gels or ion exchange membrane electrolytes. There are various possibilities for attaching the attachment cell to the coating/substrate, including the use of a magnetic clamp for painted steel structures. An alternative technique has been proposed/developed by Broster & Mills (2006) which involves a filter paper pad, consisting of several pieces of filter paper, soaked in test solution and attached to a copper sheet electrode.

5.2 Single Substrate technique

The Single Substrate technique is a re-configuration of the original ENM arrangement (Skerry & Eden, 1987) and was first proposed by Mabbutt & Mills (1998). It has subsequently been used by other workers (Bierwagen *et al.*, 2000) to evaluate and monitor the performance of anti-corrosive coatings. There has been extensive work carried out on the validation of the technique mainly by Mabbutt in his PhD thesis (2001) and several publications (Mabbutt 1997; 2002). The Single Substrate technique was not the main ENM arrangement used during this investigation, but was used during comparison work using electrochemical techniques for monitoring the anti-corrosive properties of organic coatings.

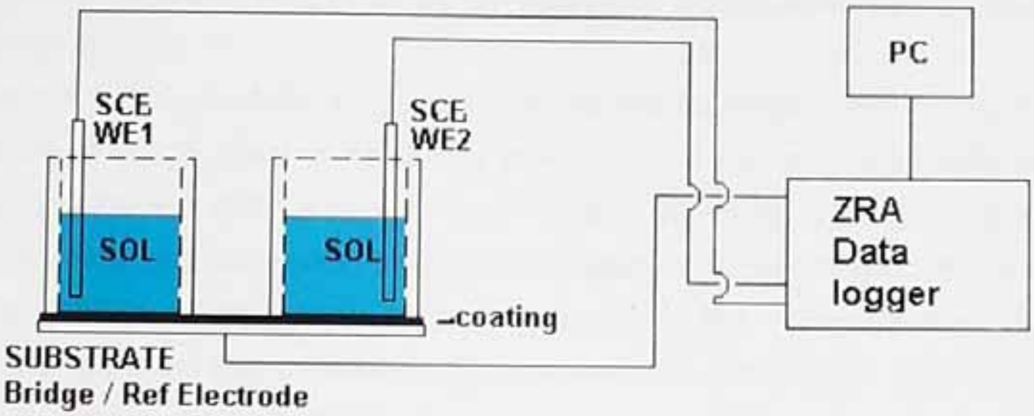


Figure 17 Schematic diagram showing the configuration of the Single Substrate technique developed and employed by Mabbutt *et al.*, 1998

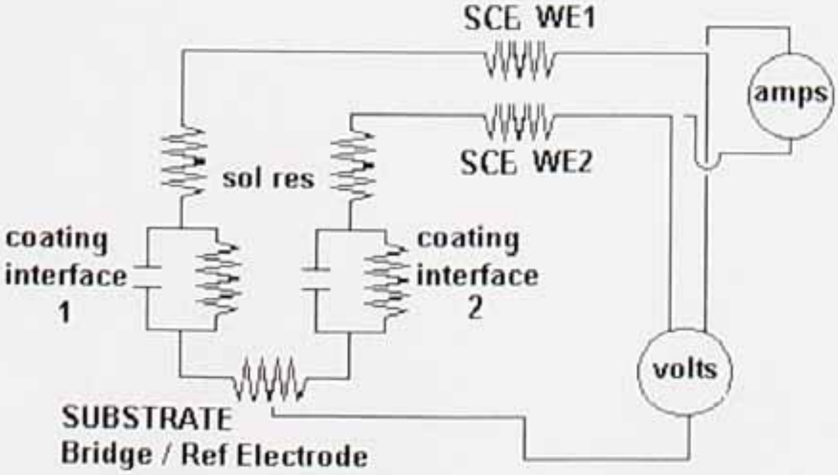


Figure 18. Schematic equivalent circuit for Single Substrate technique (reproduced from Mabbutt & Mills, 1998)

5.3 No Connection to Substrate (NOCS)

The NO Connection to Substrate (NOCS) arrangement was 'invented' by the author after discussion with Dr. Mills following a paper given by Malgarzohe Shroder at an Advances in Electrochemical Techniques for Organic Coatings (AETOC) conference in Sintra, November 2003 (Mills 2003, Private communication). The paper discussed the difficultly which had been experienced in making a connection to a coated substrate by people trying to make electrochemical measurements. It was considered that a re-configuration where a reference electrode was on the far side of coated substrate might be as capable of giving an accurate R_n value as the 'Standard' bridge or Single Substrate configurations.

The title NOCS has been given to the configuration of the ENM arrangement described in this chapter. As can be seen from the arrangement configuration (fig. 19) there is ***NO C***onnection to ***S***ubstrate, hence the acronym NOCS. Similar methods have been investigated theoretically and practically by Bertocci *et al.* (1997a, 1997b) where he investigated different 'measurement schemes', considered to be the equivalent of 'arrangements' described in this work, using either three or four electrodes. It was concluded that R_{sn} (f), taken from data transformation in the frequency domain, is equal to the impedance modulus (Z) based on two noisy electrodes and a 'noiseless' RE. Arrangements based on three and four electrodes may be simpler to implement where it is difficult to employ a 'noiseless' RE. The R_n was shown to be equal to the zero frequency limit of the impedance, but only if certain conditions are satisfied.

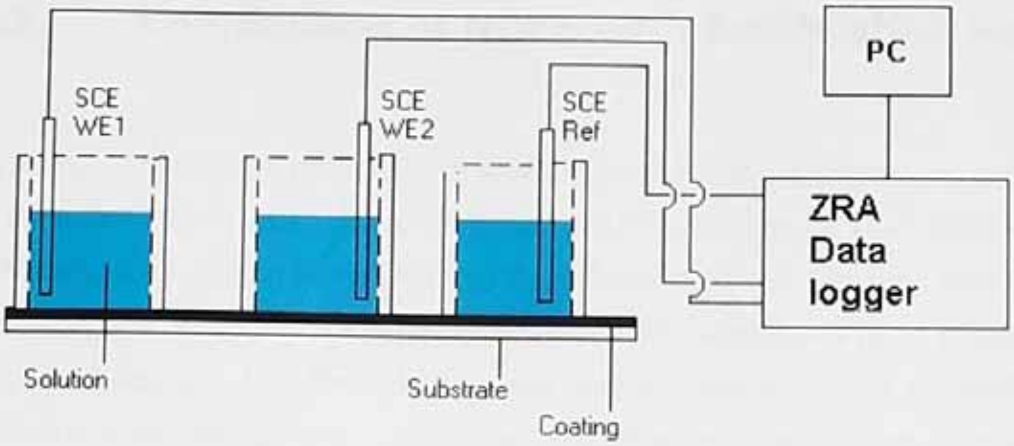


Figure 19. Electrochemical Noise arrangement – NO Connection to Substrate (NOCS)

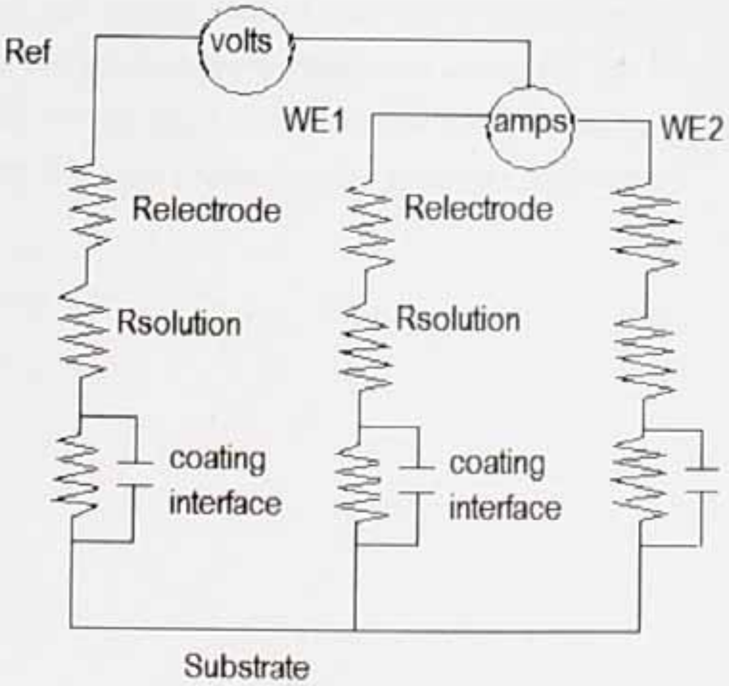


Figure 20. Schematic equivalent circuit for NO Connection to Substrate arrangement

To justify this 'new' method, work on comparison with the standard test methods was needed. The following section gives some results obtained using this NOCS configuration in comparison with DC resistance and the ENM techniques; conventional 'bridge' and single substrate.

5.3.1 Comparison of NOCS with Established Methods

The general protocol for this piece of work involved using triplicate groups of samples with high (> 1E7), medium (around 1E6) and low (< than 1E6) DC resistance values. These were selected from among all the samples that had been put through the testing in the earlier work reported in chapter four. Because samples had been on test for a reasonably lengthy period of time (in excess of 700hrs) the resistances were fairly stable and thus were unlikely to change between experiments as various ENM test configurations were tried (NOCS, Single Substrate, Bridge). At the end of testing the DC resistance was again measured and was noted to be relatively unchanged in all cases.

Note that the NOCS method takes results from three samples. Therefore comparison has to be made with pairs (in the case of Single Substrate and Bridge) and single samples in the case of DC resistance.

It was also considered of interest to investigate what would happen if not all three resistances were identical i.e. to find out which would dominate the NOCS result. Hence high, medium and low resistance samples were rearranged and results are also presented for these experiments.

5.3.1.1 Results

The results of various experiments involving the NOCS experimental arrangement are shown in Figures 20-23.

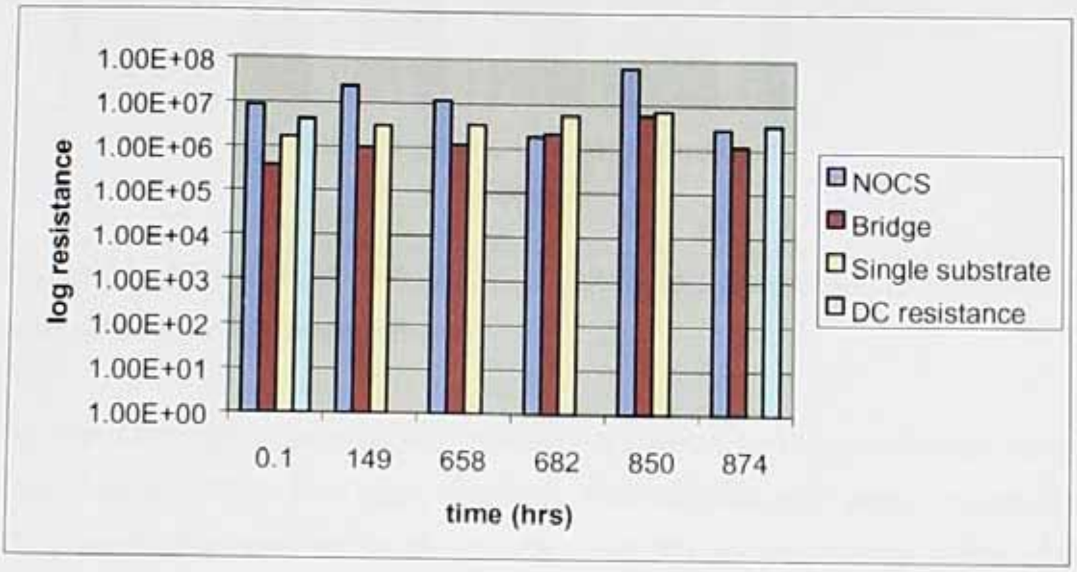


Figure 20. NOCS compared with other methods made on medium resistance samples measured at different times

Figure 20 shows results obtained from one set of medium (DC) resistance samples over a long period of time. At each time period NOCS has been measured and been compared with Bridge and/or SS methods. DC Resistance values are also given.

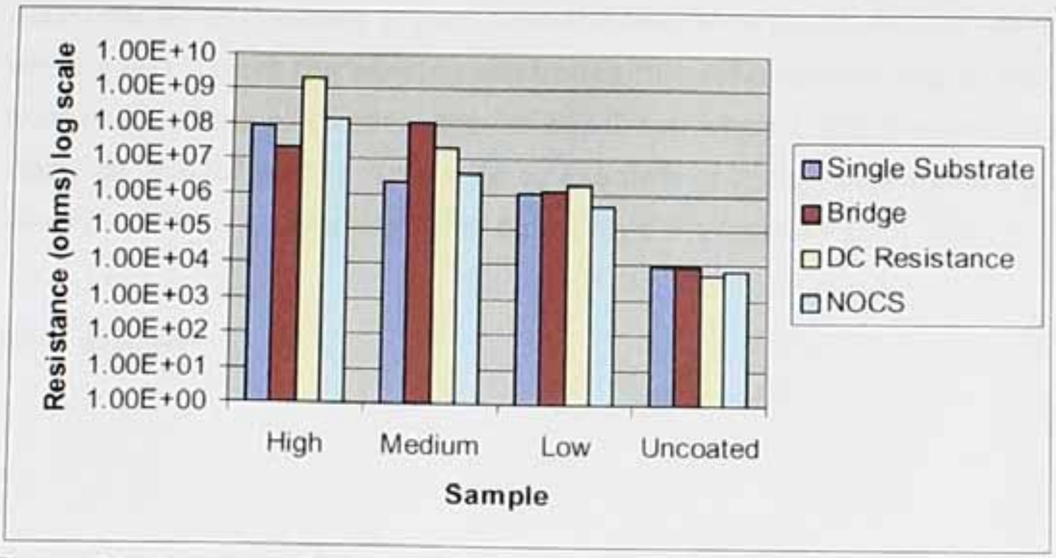


Figure 21. Assessment using various ENM and DC methods of sets of samples with differing resistance values

To generate the results shown in Figure 21 three similar resistance samples were tested which either had high, medium, low resistance or were not coated at all. They were all examined by three different ENM arrangements. Additionally DC resistance was used as a comparison after testing. The value on the histogram was the geometric mean of the three samples.

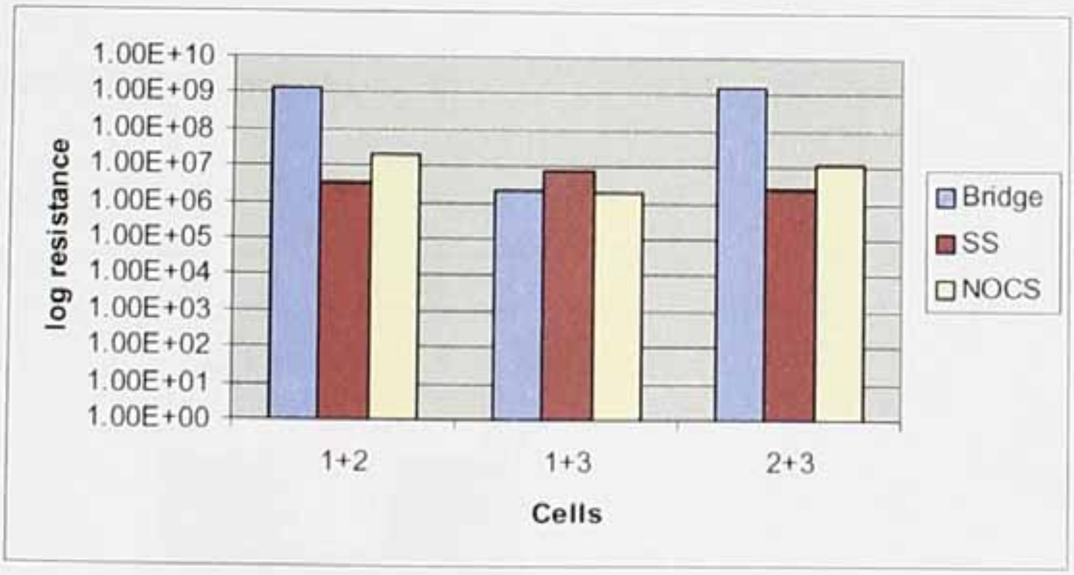
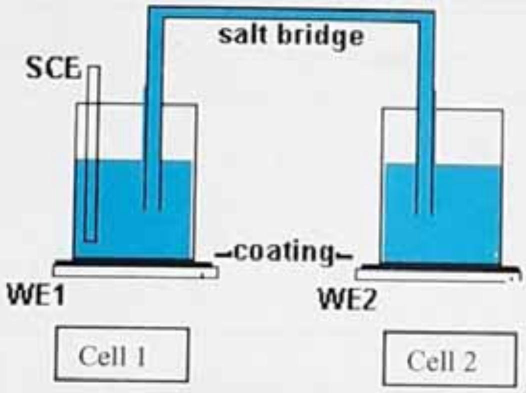


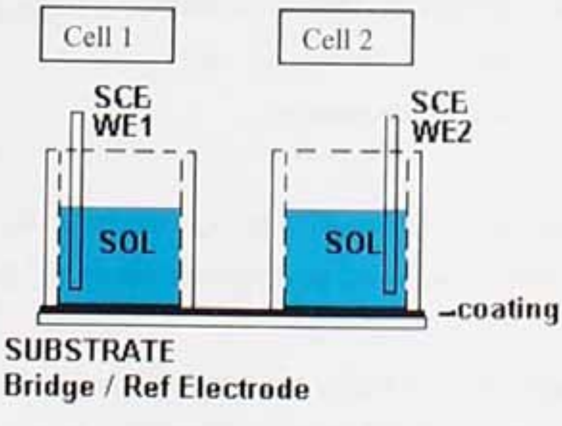
Figure 22. Comparison of NOCS with other ENM arrangements for different combinations (pairs) of samples

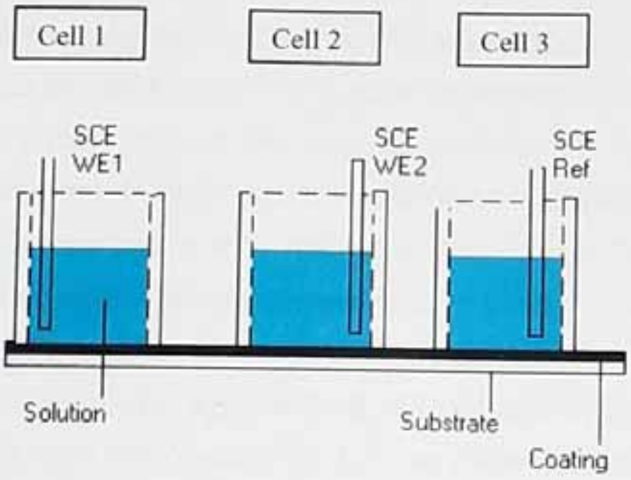
Figure 22 shows results from measurements made on different combinations of three samples 1, 2 and 3 (Each had a medium DC resistance value). For SS and Bridge type measurements pairs were used e.g. 1 and 2, 1 and 3 and 2 and 3. To obtain NOCS values all three cells/electrodes were used for all three measurements. However in each case the reference electrode was varied (i.e. when 1 and 2 were the working electrodes, the ref electrode was 3, when 1 and 3 were the working electrodes, the ref was 2 and when 2 and 3 were the working electrode the ref was 1). To clarify an example of the arrangements used is shown in the schematic diagrams below for Cells labelled 1+2:

ENM Bridge



ENM Single Substrate





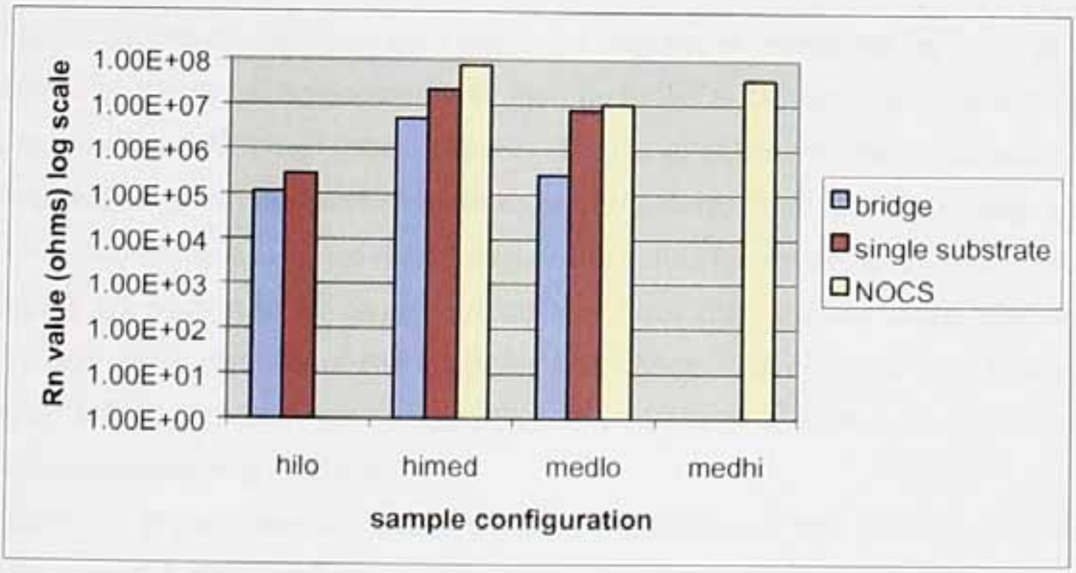


Figure 23. Comparison of different ENM methods when the resistance of the two samples (or three samples in the cases of NOCS) were NOT the same

Figure 23 shows the results when the resistance values of the three samples were not the same. The reference of the labelling i.e. hilo – the hi part – when reporting for NOCS measurements indicates the two working electrodes are measuring from high resistance samples and the lo part is measuring from a low resistance sample which the reference is measuring (the labelling is as follows: hi: high; med: medium and lo: low resistance). In the case of single substrate and bridge values the measurement was taken between the working electrodes.

5.3.1.2 Discussion

Examining Figure 20 it can be seen that over the time of the test the resistance of the samples remained virtually constant as is shown by the DC resistance. This is not surprising as the samples used for the testing had been exposed to 0.5% ammonium sulphate for a period of ten weeks and were therefore assumed to have stabilised with respect to resistance. The figure also shows that there is a good relationship between the resistance values for all techniques used. The NOCS method shows a trend to generate values slightly higher than other test methods which indicates it may be driven by the higher resistance area and/or areas of the coating i.e. I areas (Mills & Mabbutt, 2000). However, it can also be seen that after 874 hrs on test the resistance measured by the NOCS method and by DC generate an almost identical value which indicates the NOCS method agrees with the Bacon, Smith and Rugg (1948) criteria of ranking protective coatings.

Figure 21 shows coatings with varying resistances measured by several different ENM experimental arrangements. Also included is DC resistance which again is used as a 'confirming' measurement. In this experiment the NOCS method appears to give values of resistance slightly lower than DC, excluding the uncoated samples. However all resistances obtained with single substrate and NOCS are shown to be clearly separated. They also show a close relationship with DC and allow ranking of the coatings resistance. The conventional bridge method also ranked the coatings successfully apart from the value obtained from the highest resistance coating.

Figure 22 shows that variation in the configuration of the tested cells has little effect on the resistance value generated for single substrate and NOCS arrangements. However, values using alternative testing configurations are lower than the values obtained by the conventional bridge method in two cases out of three. This suggests that the Cell 2 has a higher resistance than Cells 1 and 3. This again may be as a result of the high integrity areas of the coating giving high resistance. This dominates the Bridge result but is 'evened out' by the other configurations.

Figure 23 shows how varying the configuration of the test cells with known resistances can still generate results which can be used to rank the coatings tested and afford information which is useful in the prediction of the coating's performance in service. It can be seen in Figure 23 that the working electrodes and not the reference drive the NOCS method giving similar values in two cases out of three to the conventional bridge method.

The conclusion from this piece of work is that all electrochemical measuring techniques show good correlation in their ranking of the coatings tested. It is also evident that the NOCS method has successfully ranked coatings by their resistance, indicating their corrosion protection. This new ENM configuration has benefits in the form of increased mobility for site testing and/or monitoring. The NOCS test configuration is essentially simulating connection through one large piece of metal and not through an external solution via reference electrodes and so avoiding the need for any connection to the test substrate.

5.3.2 Consideration of alternative electrodes in the NOCS configuration

When the above work was presented at Advances in Corrosion Protection of Organic Coatings (ACPOC), Cambridge (2004) a question was raised about whether the use of calomel electrodes was influencing results. Work was therefore conducted using two other different types of electrodes, silver/silver chloride (AgAgCl) and platinum (Pt) and comparing them with the saturated calomel electrodes. Results are given in figures 24 and 26.

5.3.2.1 Results

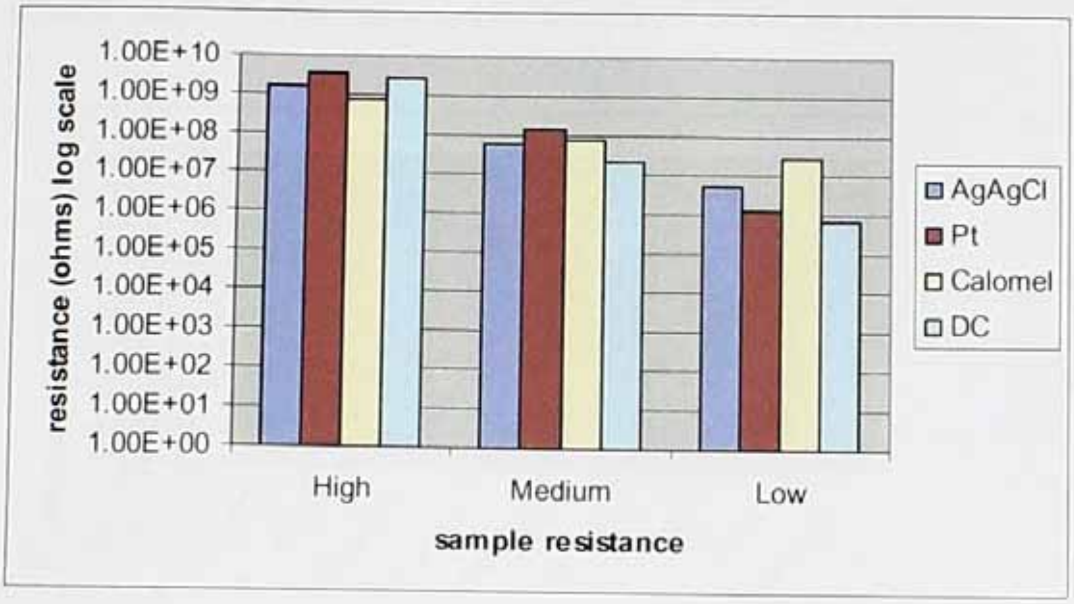


Figure 24. Comparison of alternative electrodes used for NOCS measurements

This work was done using samples from coating systems which gave resistances within the Bacon, Smith and Rugg ranges, hence the x axis showing samples with high, medium or low resistance values. Figure 24 shows there was no visible ranking between the electrode type, and although there is the usual scatter within the data, the trend through the coating resistance ranges is clear.

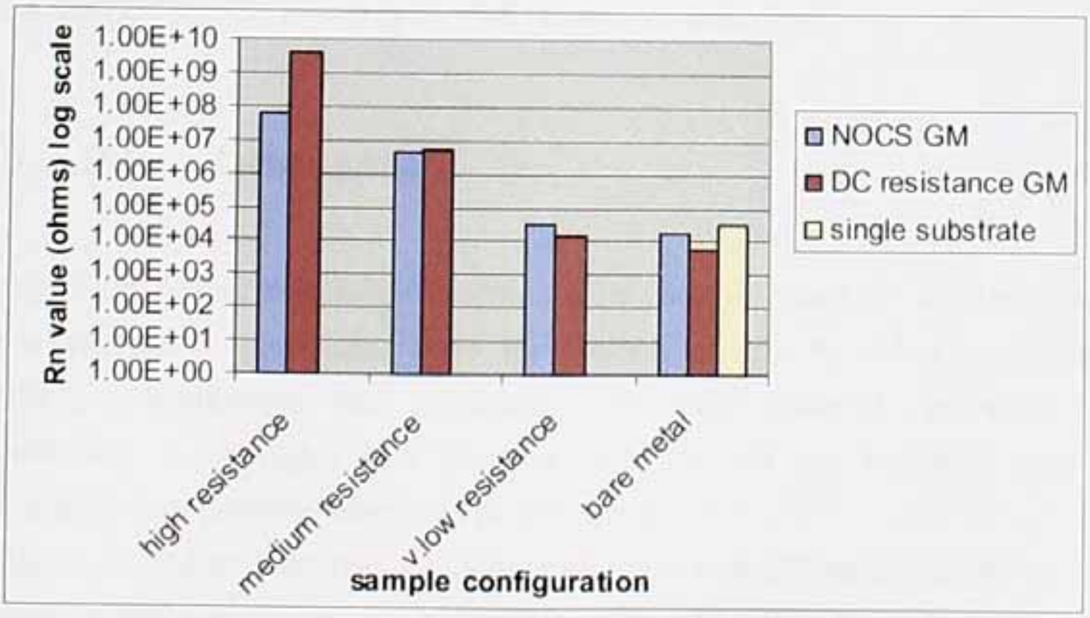


Figure 25. NOCS used on coatings with varying resistance in comparison with other electrochemical techniques

Both ENM arrangements and DC resistance techniques have been used to evaluate samples with known resistances. It can be seen from the results that the

NOCS ENM arrangement and DC resistance values are effective methods for assess the anti-corrosive properties of coatings, according the Bacon *et al.* (1948) criteria, and useful for ranking their associated predicted performance.

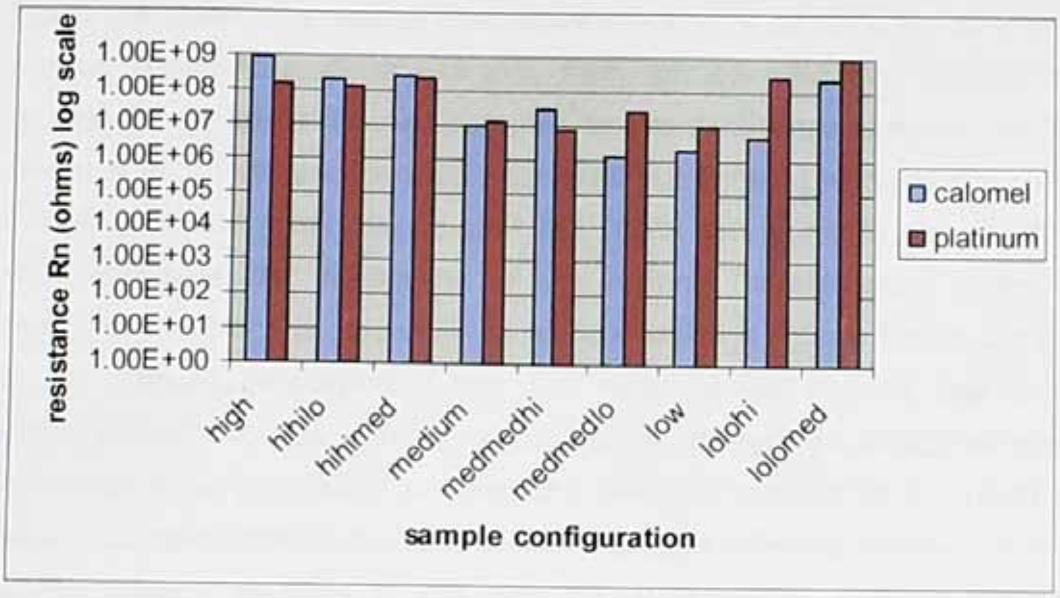


Figure 26. NOCS investigating alternative configurations of coatings with varying levels of resistance with alternative electrodes

Varying the combination of test samples with differing resistances shows that effective ranking of the samples can be achieved using the NOCS ENM arrangement. Alternative electrodes do not give contradicting results and give no visible ranking for medium to high resistance samples.

5.3.2.2 Discussion

Figure 24 shows that when coatings with varying levels of resistance are tested, the alternative electrodes have little effect on the R_n value generated for the NOCS arrangement. This evidence lends itself towards validating the NOCS technique as a viable test method which is not too sensitive and does not measure any possible electrical interference.

Figure 25 shows both the NOCS arrangement and DC resistance to be effective in ranking the resistance of the coatings. The alternative techniques also give very correlation to one another with the exception of the high resistance samples. Samples investigated had been on long term exposure prior to this investigation hence the resistance values obtained were assumed to be stable. Firstly, DC resistance measurements were taken before NOCS measurements. The lower resistance value obtained from NOCS evaluation may be a result of the high voltage imposed upon the coating during DC resistance measurements and subsequently physically damaging the coating and disrupting the dynamics of the corrosion cell.

Figure 26 shows the use of alternative electrodes on differing configurations of coating resistances. On the x-axis from left to right the coating resistances change from high resistance samples to low resistance samples (according the Bacon *et al.*, 1948, anti-corrosive performance criteria) with varying combinations in-between. The graph shows that the NOCS arrangement can identify a trend with regard to the resistance of the coating (combination) under test. The reference electrode is placed in the sample which is referred to in the third listing in the sample configuration title i.e. hihilo would have a test configuration comprising of the two working electrodes being high resistance samples and the reference a low resistance sample. The results indicate that the resistance value where the reference electrode is placed does not influence the results and ranking of the coating systems is still possible. Results also indicate that the NOCS arrangement is more effective at ranking coatings with a medium to high R_n value where little difference is seen between the calomel and platinum electrode used. Differences between values are evident were alternative electrodes are used with low resistance samples.

5.4 Further practical considerations

The experimental work reported here indicates that the Electrochemical Noise Method when used with the NOCS configuration looks like it may well be applicable to use in the field for monitoring organically coated substrates and indicating the current state of protection being afforded by the coatings. Note if measurements are made at two different times some element of prediction may be possible. An example where this would be useful is in planning maintenance. However there are a number of practical aspects which need to be taken into consideration. Signal interference is more likely in the field than in the laboratory e.g. there are other sources of noise about and ways of filtering those out or compensating for them would need to be developed (signal processing). Also some check on the data that it is "good data" and giving a correct value will be needed (confidence factor). There are other practical considerations too in terms of development of suitable dismountable electrode that are built into little cells (e.g. pads) that would enable solution to be in contact with the sample while the measurement is being made. However this is a further development area and even more challenging is the possibility of building in a continuous monitoring device (perhaps with an electrode system in-build under the coating) which will wirelessly inform the user of the state of the coating system in real time. These are all exciting future possibilities requiring more research.

5.5 Conclusions

In conclusion, it would appear that ENM (both conventional and new arrangements) and DC resistance can all be used to assess coatings in the laboratory and hence assist in development of new coatings. However, when it comes to monitoring over a period of time ENM has many benefits. This is particularly so if the NOCS test configuration is used which simulates connection through one large piece of metal and not through an external solution via reference electrodes and so avoids the need for any connection to the test substrate. The work reported here has shown that the NOCS method is giving similar results to the SS and standard 'Bridge' method and hence there can be some confidence in its use. The work shows that the R_n value obtained via the NOCS configuration is not affected by the choice of electrode used in this experiment, with no significant difference between calomel, silver/silver chloride and platinum electrodes.

However, further work is needed to fully "harden up" the method before it can be used with full confidence to monitor the coatings on real structures.

Chapter Six – Comparison of Electrochemical Noise Measurement (ENM) and Electrochemical Impedance Spectroscopy (EIS)

6.1 Introduction

Both of the above mentioned electrochemical measurement techniques have been discussed in variable amounts of detail in the previous chapters. It is the objective of this chapter to compare the techniques and hence discover whether use of either technique is equally valid when assessing the performance of anti-corrosive coatings.

6.1.1 Electrochemical Methods

The Bacon, Smith and Rugg (1948) performance criteria subsequent expectation of behaviour are still largely in use today but the methods for measurement has changed. In 1979 AC Impedance was beginning to be applied to coatings (Scantlebury & Ho, 1979). A large amount of work has been done since using EIS and as discussed in chapter two, the standard ISO 16773 is being developed. In the late 80's / early 1990's the Electrochemical Noise Method (ENM) was first applied to coatings by Skerry (1987). This was followed by further work by Bierwagen *et al.* (1994, 1995) and subsequently by Mills and co-workers; Steve Mabbutt (1997, 1998, 2001) and the current author.

Because EIS (AC impedance) is the most common method used in well equipped laboratories with trained personnel, hence the development of the ISO 16773 standard, it was considered to be a good idea to specifically compare ENM with EIS. This was facilitated by the fact that the Gill AC instrument that was available can be used in either 'mode' and switched from one to the other relatively easily although a different configuration of the test cells is required in order to do this.

6.1.1.1 AC Impedance (EIS)

In this method a small alternating current is imposed on the system and the phase shift analysed Generally the data is presented as Nyquist (linear) and Bode (log) plots.

The claim is made that the corrosion system can be modelled as an equivalent circuit and under ideal conditions EIS plots can provide separate values of Polarisation resistance (R_p), Coating resistance and Solution resistance. Mechanistic information can also be obtained from Nyquist plots. This makes EIS particularly useful for investigating protection at scribes. Often though in intact paints work where very high resistances are being measured the paint resistance dominates. Hence people resort to taking just one number e.g the R_p where the semi-circle in the Nyquist plot intersects the x axis. They may also work out the Capacitance because this relates to water uptake but the resistance has been shown many times to be a more effective predictor of anti-corrosive ability than capacitance.

6.1.1.2 Electrochemical Noise Method ENM

The easiest method for small paint companies to get to grips with is the Electrochemical Noise Method. The company which the author worked with recently now has this as its standard electrochemical method for assessing and monitoring its anti-corrosive coatings. The Electrochemical Noise Method always needs 3 electrodes – two WE and one Ref. However the actual configuration of these can be varied e.g. one method doesn't involve connection to the substrate (NOCS) as discussed in chapter five. In the standard bridge method the voltage (between WE and ref) and the current (between the two WE) data is measured over a period of say 5mins at 0.5 sec intervals. Thus a ZRA and a computer are needed. Commercially available equipment is available from ACM, Gamry, and CML. This equipment can be battery operated and taken out on-site.

The biggest advantage of the method is that it is electrically non-intrusive i.e. measurement does not disturb the sample being examined. Hence one can continuously monitor if one wishes so to do. Normally a comparison is done with DC resistance at the end as a 'confirming' exercise. This was typical throughout this investigation.

6.2 *Experimental*

Both EIS and ENM measurements were taken using the methods previously described (Fedrezzi *et al.*, 2003; Mabbutt & Mills, 1998 respectively). Samples which had been on test previously were separated to give samples of low, medium and high resistances, i.e. they would be expected to give high, medium and low level anti-corrosive performance. The groups were then used to compare EIS and ENM techniques. Samples were tested over the range of resistances and separately compared as a function of time. After a period of time the AC impedance measurement was made and immediately after an ENM (bridge) measurement was taken. This was repeated at subsequent times. The samples for this work were provided by Liquid Plastics Ltd. and varied in chemical composition as shown in Table 2. The coatings were applied at recommended coverage rates as described in chapter four.

6.2.1 Parameters of the coatings assessed

Paint	**Type of paint/description**	**Number of coats**	**Dry film thickness (μm)**
A	One-pack waterbased styrene acrylic primer	One	40
B	One-pack waterbased styrene butadiene co-polymer	One	400
C	One-pack moisture curing polyurethane topcoat direct to metal without anti-corrosive pigement	One	700
LPL1	Two-pack polyurea topcoat direct to metal without anti-corrosive pigment	One	470-702
LPL2	Two-pack epoxy primer with anti-corrosive pigment and two-pack polyurea topcoat without anti-corrosive pigment	Two	714-1128
LPL3	Two-pack epoxy primer with anti-corrosive pigment	One	81-108

Table 2 Description of coating system and film thickness

6.3 Results

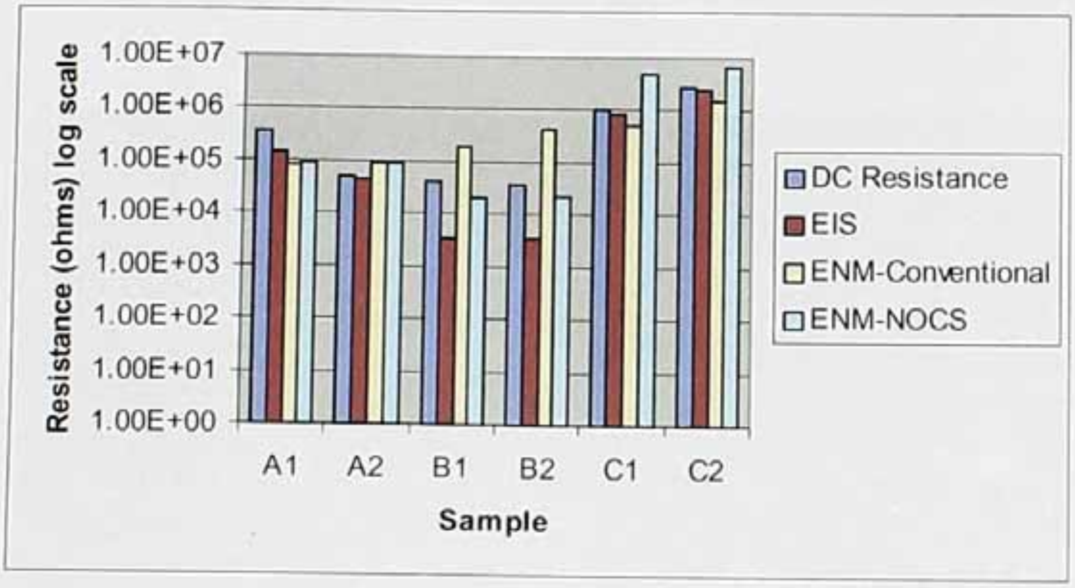


Figure 27. Results obtained using varying electrochemical techniques upon initial exposure

Figure 27 shows initial results from samples with varying resistance values evaluated using three different electrochemical techniques. Samples A and C show good correlation between techniques whilst sample C shows a degree of scatter. These results show that DC resistance, EIS and NOCS are effective at ranking the coatings with regard to anti-corrosive properties.

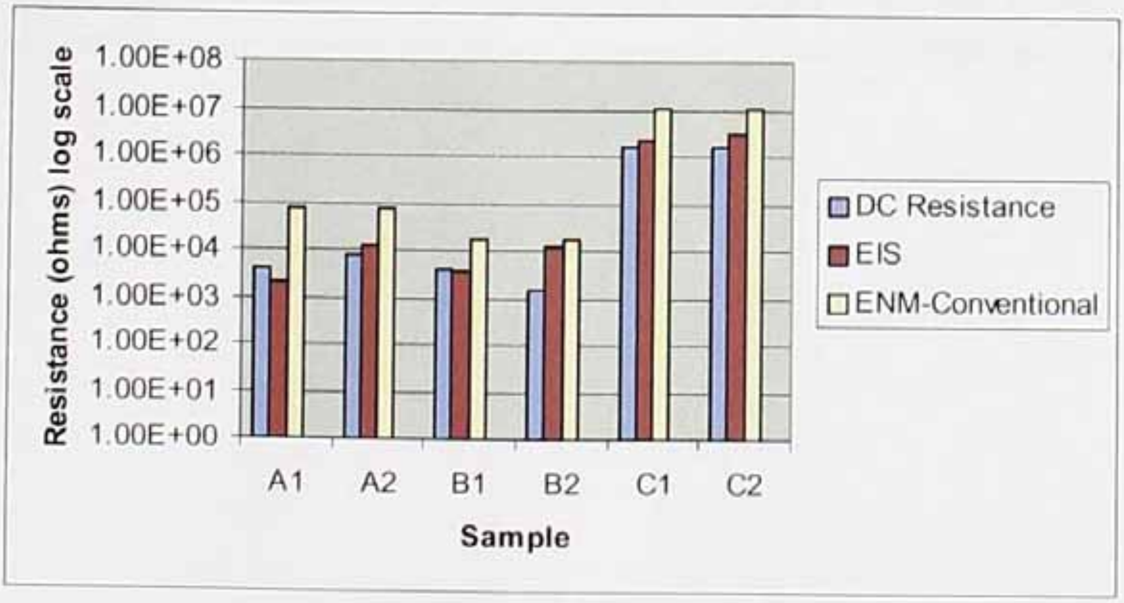


Figure 28. Results obtained using varying electrochemical techniques upon initial exposure

Figure 28 shows results for coatings A, B and C after an exposure period of 816hrs. Samples with varying resistance values were evaluated using three different electrochemical techniques. Results show that all techniques are effective at ranking the coatings with regard to anti-corrosive properties.

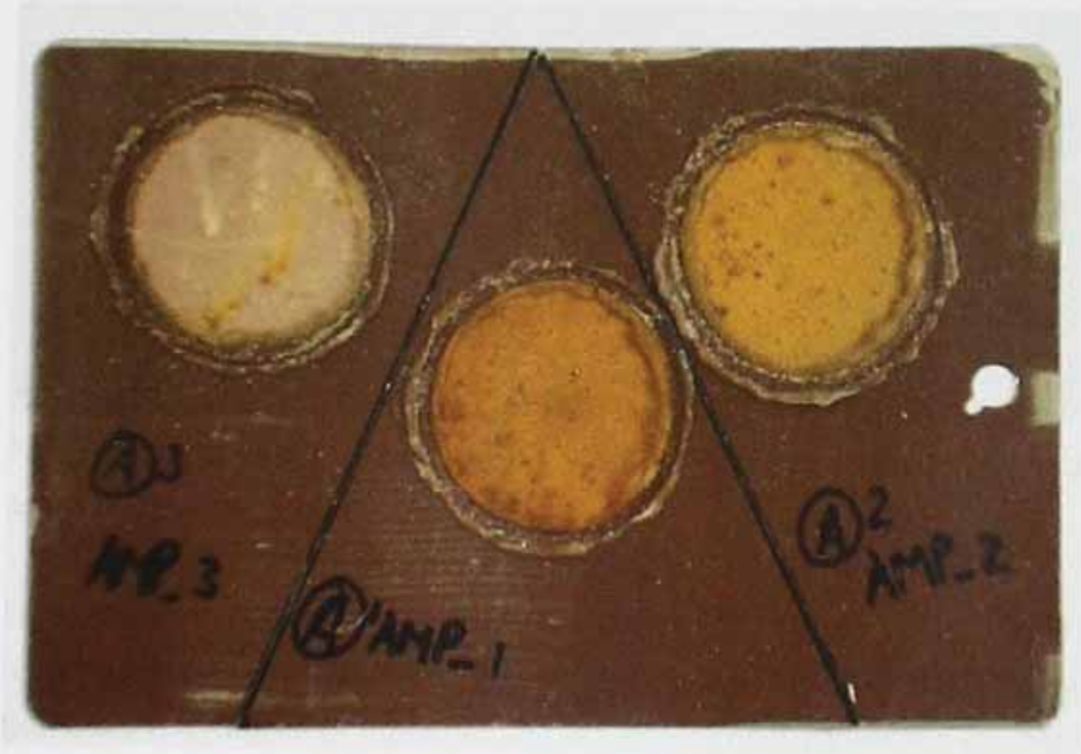


Figure 29 Paint A after 816hrs immersion in 0.35% ammonium sulphate 0.05% sodium chloride

Figure 29 is a photograph taken of Paint A at the end of the test. It shows that Paint A has suffered extensive rusting after an 816hr immersion period. Blisters can be seen with varying frequency between the three individual samples.

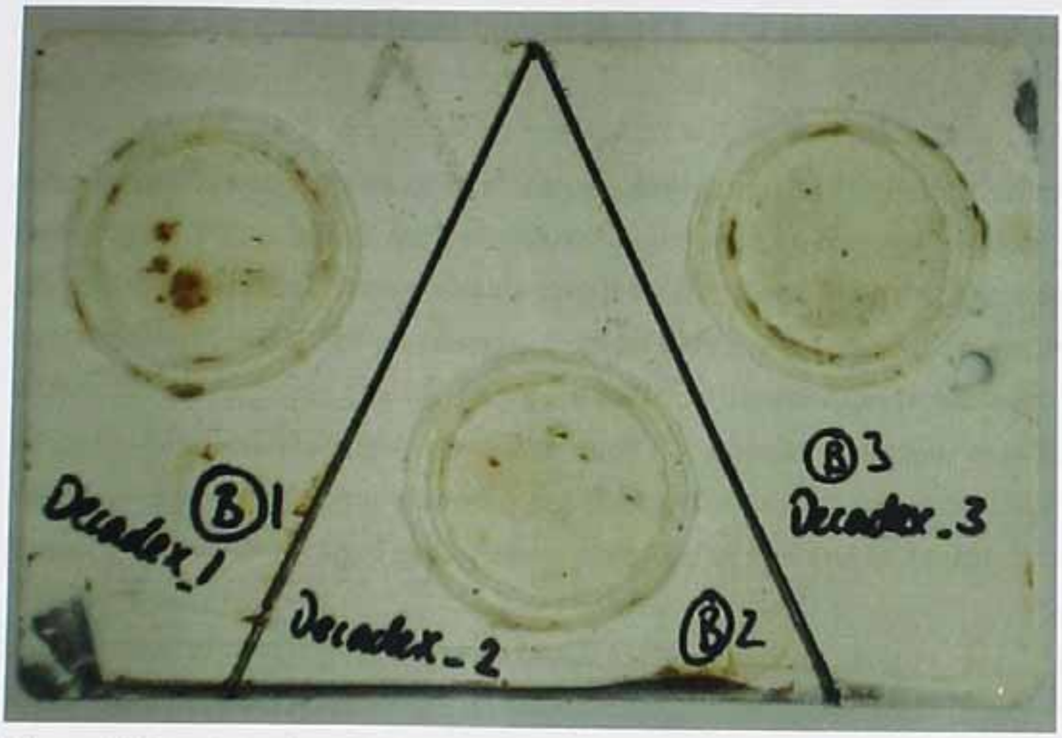


Figure 30 Paint B after 816hrs immersion in 0.35% ammonium sulphate 0.05% sodium chloride

Figure 30 is a photograph of Paint B at the end of the test. The sample highlighted as B1 in figure 30 shows the most rust staining of all the samples, however, the degree of blistering occurs with similar frequency to that of the other samples.

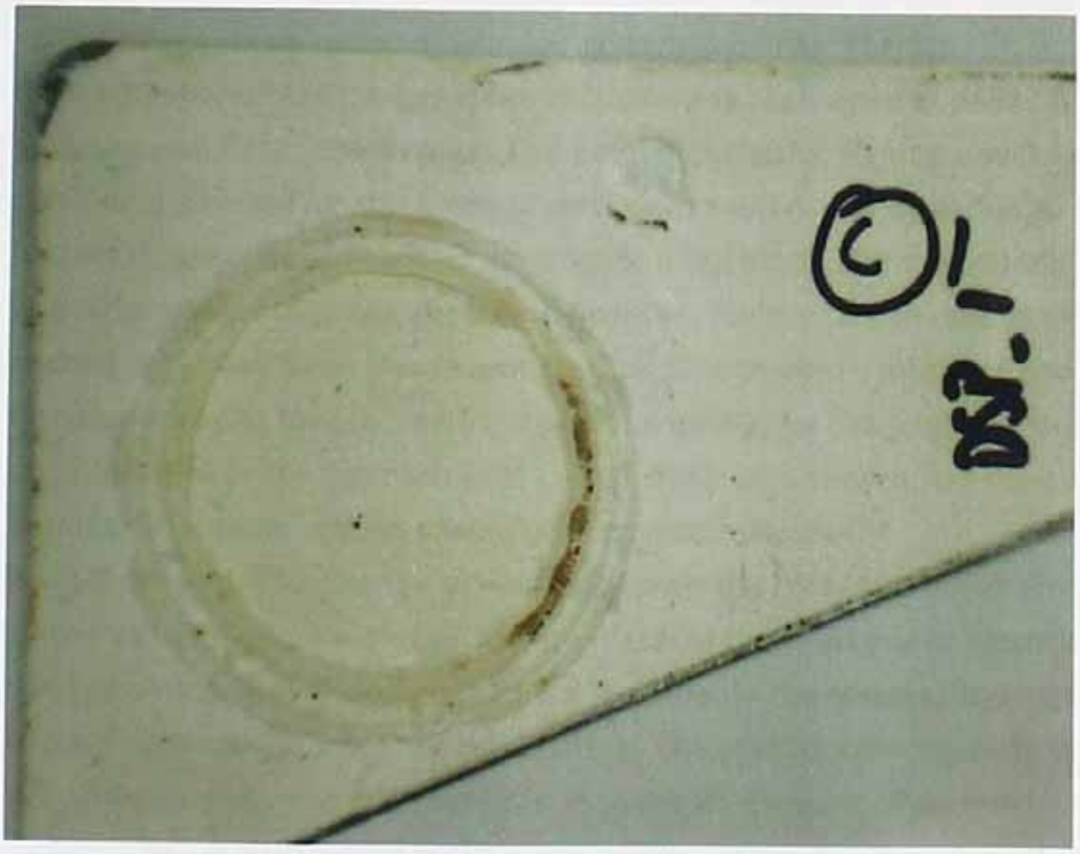


Figure 31 Paint C after 816hrs immersion in 0.35% ammonium sulphate 0.05% sodium chloride

Figure 31 is a photograph of one of three sample areas for Paint C after 816hrs immersion. The exposed area shows little evidence of corrosion which corresponds with resistance values taken by the three different electrochemical techniques after 816hrs immersion. Typical values for the coating are in the order of 5×10^7 ohms using the ENM 'bridge' method. In addition to showing little sign of corrosion products the coating film does not appear blistered, again indicating sound protection of the underlying substrate. The visual appearance of the samples is representative of the other samples at the end of testing.

6.4 Discussion

Results given in figures 27 and 28 show various electrochemical techniques being utilised to monitor the anti-corrosive properties of organic coatings. Figure 27 shows that all techniques display a trend with respect to the performance of the coatings allowing for their ranking. The techniques are generally in good agreement with one another, allowing for the usual scatter within the data, perhaps with the exception of the standard ENM 'bridge' method which has given values above those recorded from other techniques for Paint B.

Figure 28 shows that the general trend is for the resistance of paints A and B to go down with time. The samples had been exposed for 816hrs under immersion conditions allowing for the onset of corrosion. Paint A was designed as a primer for metal substrates. After this investigation the protection the coating may give to a substrate would raise question. However, the dry film thickness of the coating may have been insufficient to afford the desired protection and it would be recommended that this be increased. Secondly, by the nature of the coating, it is designed to prime substrates for combination with subsequent topcoats and together the whole system should protect more effectively.

Paint B showed little change in resistance over the course of the immersion test as the values given are similar to bare metal in the presence of electrolyte. This level of protection is inadequate and it is probably the result of the high water vapour permeability value for this coating. The coating was originally designed for the protection of walls and therefore requires an element of permeability to allow moisture to be released from the substrate to reduce the risk of blistering and subsequent adhesion failings.

Figures 27 and 28 show Paint C to display good anti-corrosive properties from the initial exposure to the completion of immersion. The resistance of Paint C remains relatively high throughout the period of exposure. This performance is evident from the resistance values taken from all electrochemical methods. Note that the NOCS configuration was used successfully in the identification of this trend after initial exposure (figure 27), (however the technique was not used again at the completion of immersion testing). The high resistance of the coating throughout the investigation may be attributed to the dry film thickness which would be considered high. Whilst Paint C does not contain any active anti-corrosive pigment, the barrier properties afforded by the coating would be expected to be sufficient to eliminate or delay the transmission of oxygen and/or water through the polymer matrix to the coating/substrate interface.

6.5 Increase in solution concentration

6.5.1 Experimental

Samples were prepared as described previously in chapter four. Samples were exposed to 0.5% ammonium sulphate and tested periodically using three different electrochemical techniques; ENM, EIS and DC resistance. The ENM readings were taken before EIS measurements so not to effect the R_n values obtained as a result of changes in coating structures due to the relatively high voltage applied during EIS.

After an original exposure period of 1176hrs to 0.5% ammonium sulphate the test solution was changed to a more concentrated solution - 3% sodium chloride, and the coating resistance monitored using ENM and EIS.

The samples for this work were provided by Liquid Plastics Ltd. and varied in chemical composition as shown in Table 2. Measurements were taken over the period of April to June 2006

6.5.2 Results

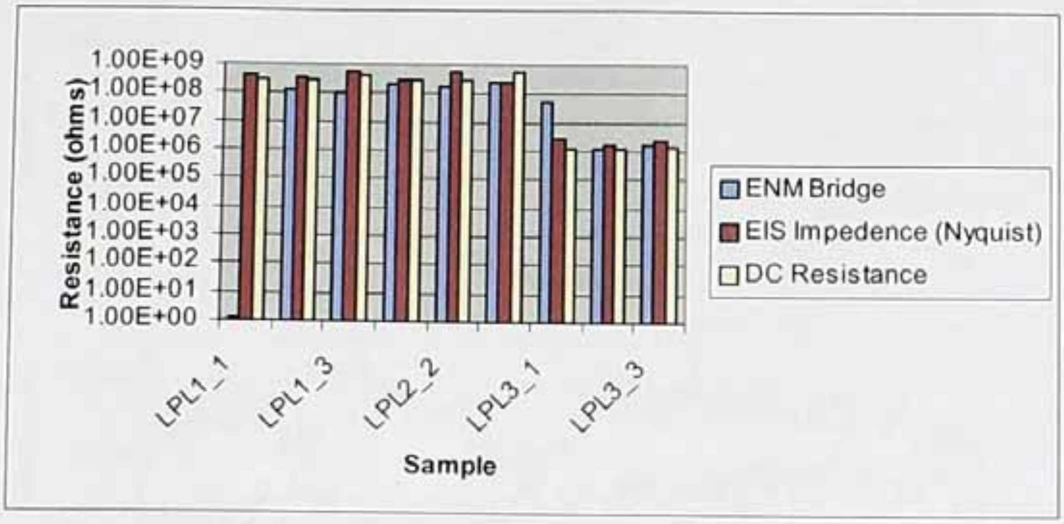


Figure 32. Initial resistance results for Paints LPL1, LPL2 and LPL3 for comparison of EIS and ENM and DC to assess the anti-corrosive properties of coatings

Test Period	Time (hrs)	Test Solution
1	0.1	0.5% NH_4SO_4
2	816	0.5% NH_4SO_4
3	984	0.5% NH_4SO_4
4	1176	3% NaCl
5	1992	3% NaCl
6	2544	3% NaCl

Table 3 Exposure time with corresponding test period for figures 33 - 35

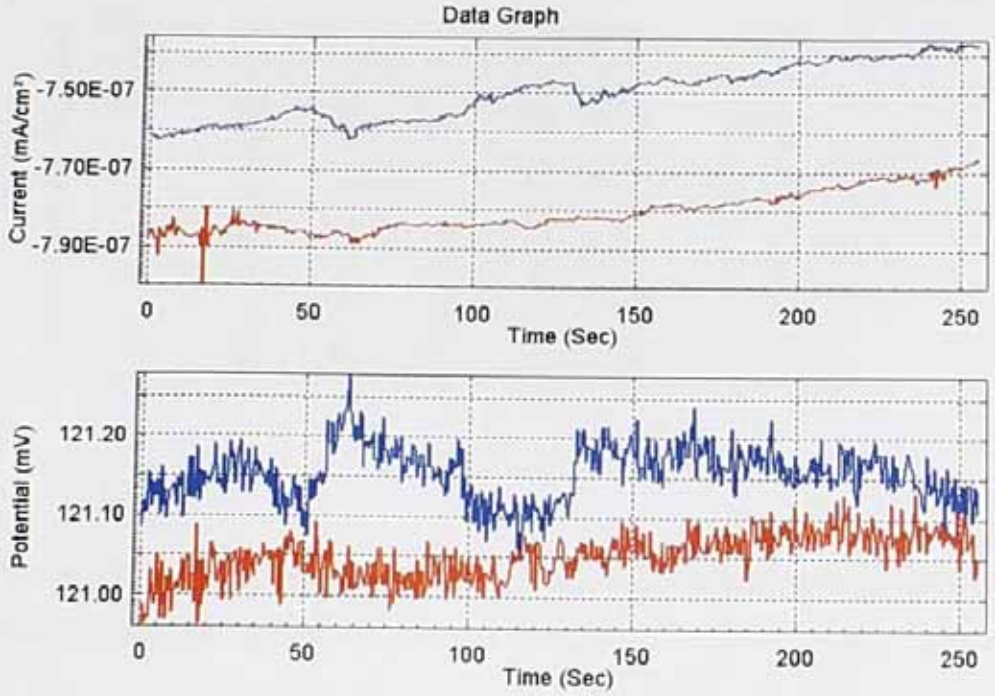


Figure 33. Two consecutive ENM data sets for LPL1. The red plot is the first data set and the blue plot the second, from which the R_n is taken.

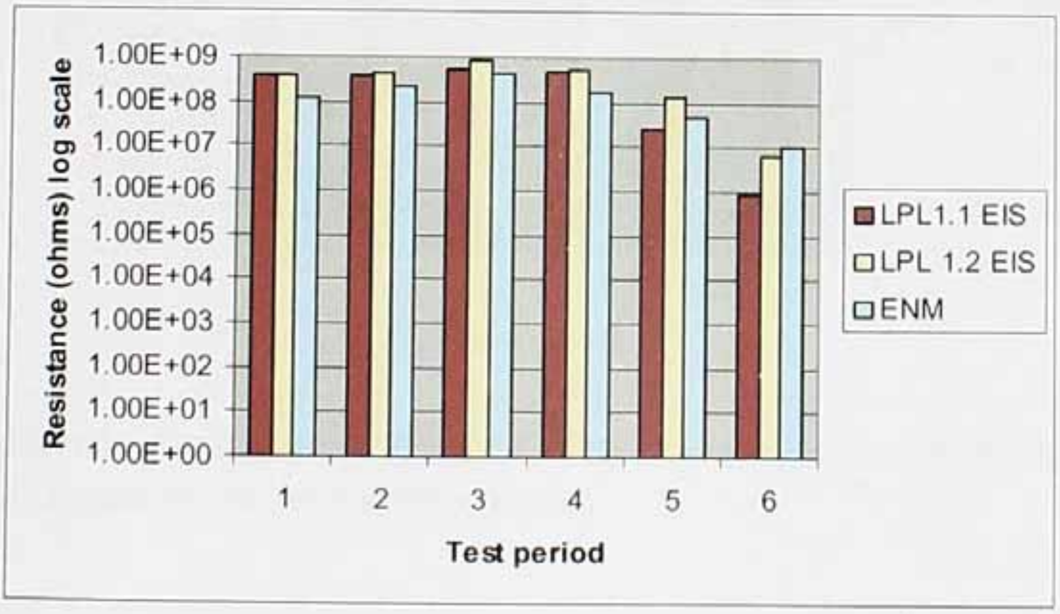


Figure 34. Comparison of EIS and ENM to assess the anti-corrosive properties of LPL1 (solution changed at test period 4)

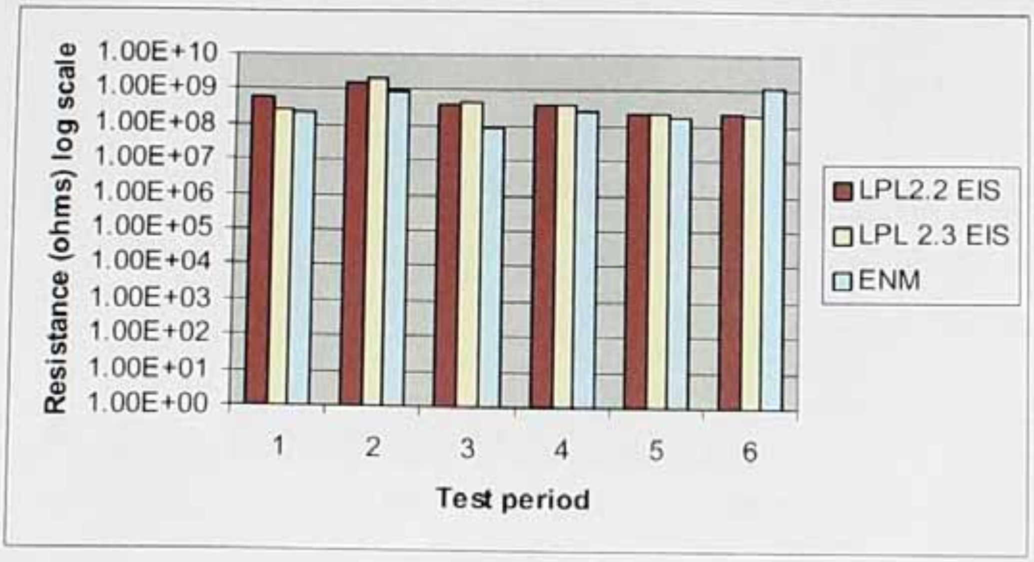


Figure 35. Comparison of EIS and ENM to assess the anti-corrosive properties of LPL2 (solution changed at test period 4)

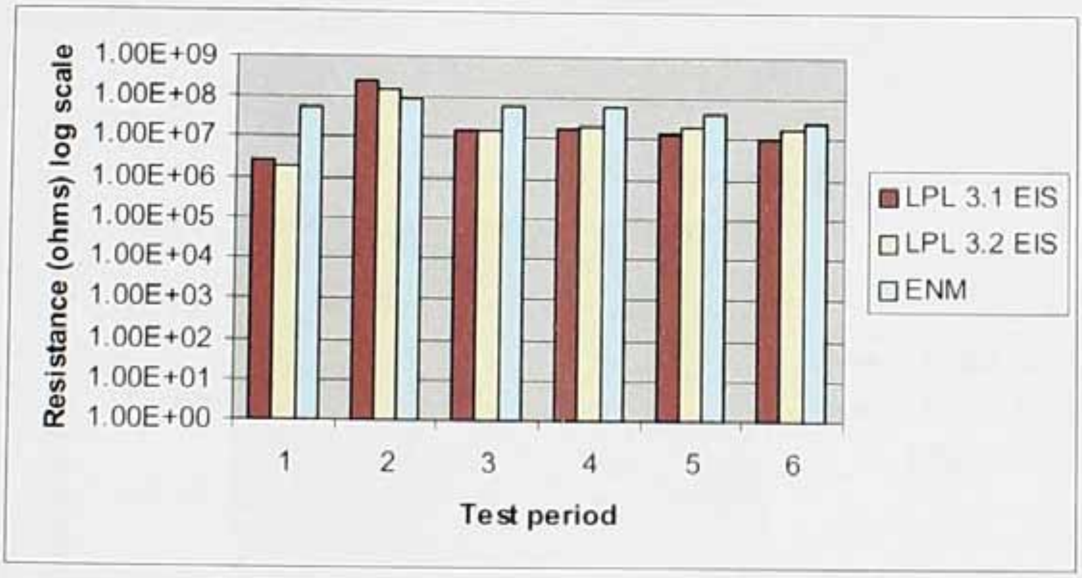


Figure 36. Comparison of EIS and ENM to assess the anti-corrosive properties of LPL3 (solution changed at test period 4)

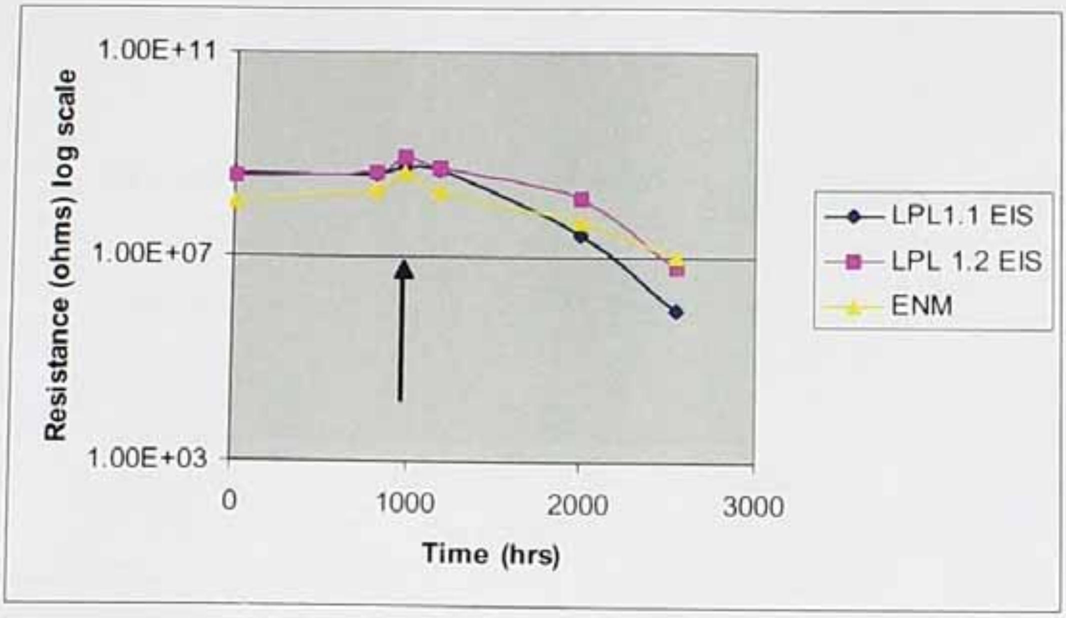


Figure 37. Comparison of EIS and ENM to assess the anti-corrosive properties of LPL1 coatings over 2500hrs exposure. The arrow indicates an increase in the electrolyte concentration.

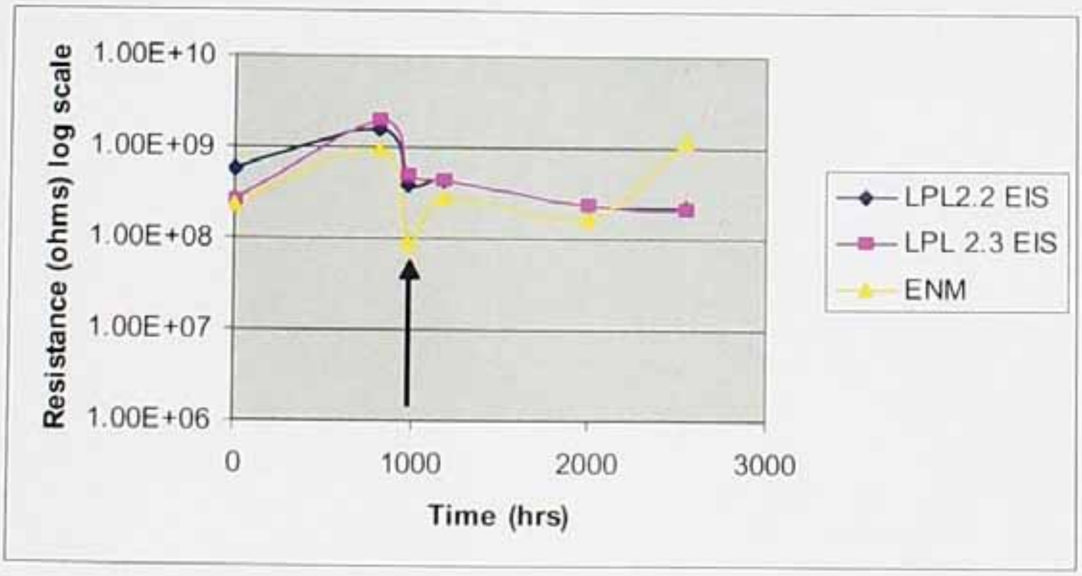


Figure 38. Comparison of EIS and ENM to assess the anti-corrosive properties of LPL2 coatings over 2500hrs exposure. The arrow indicates an increase in the electrolyte concentration.

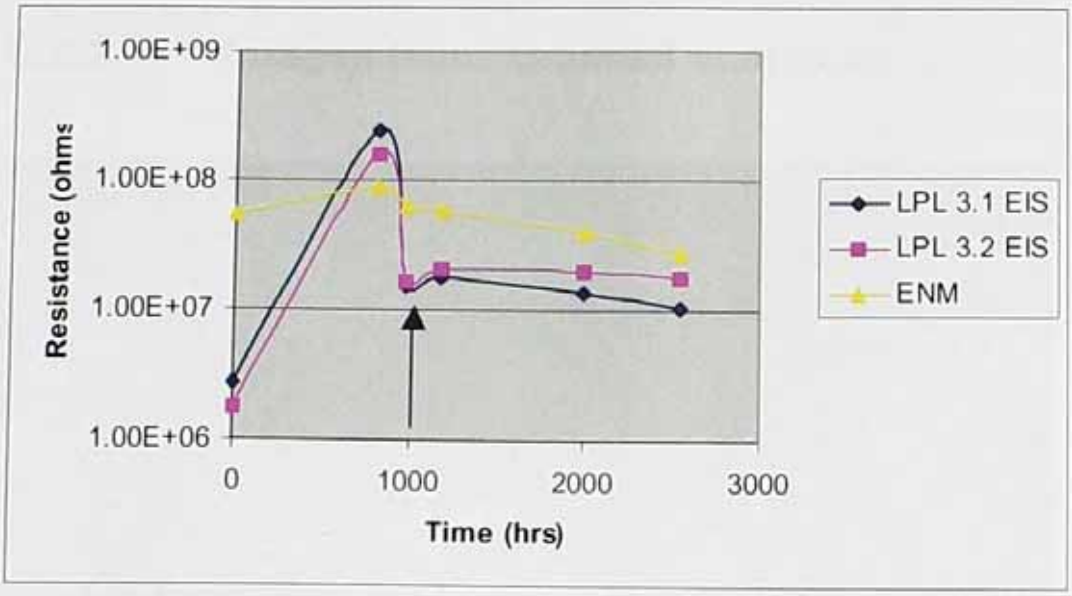


Figure 39. Comparison of EIS and ENM to assess the anti-corrosive properties of coatings for LPL3 over 2500hrs

6.5.3 Images from exposed samples

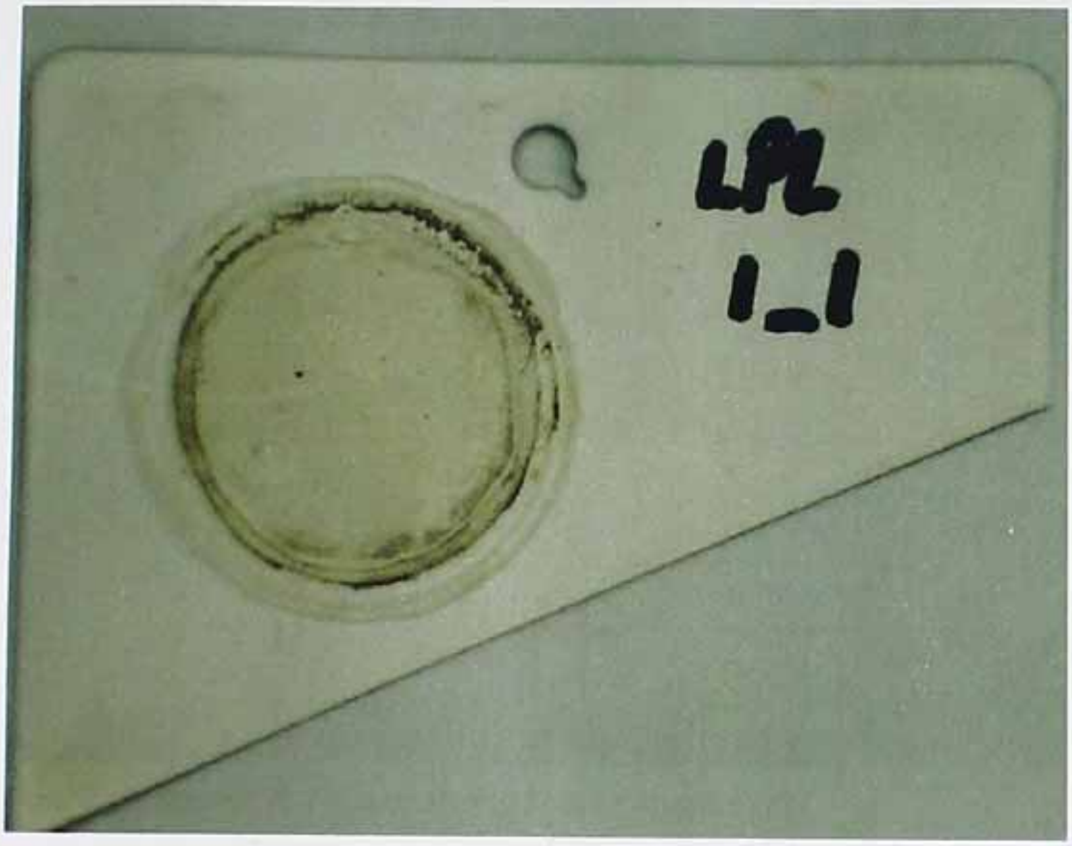


Figure 40. Paint LPL1 intact after 2500hrs immersion

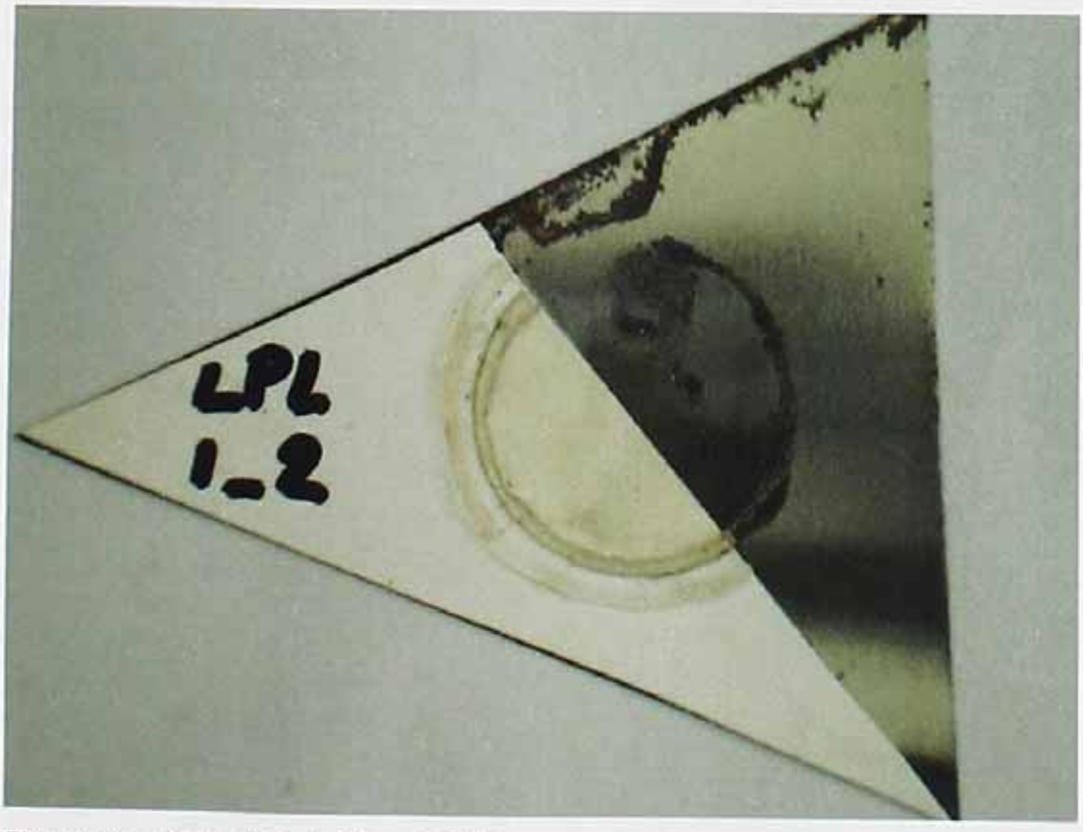


Figure 41. Paint LPL1 after 2500hrs immersion – coating removed to expose underlying substrate

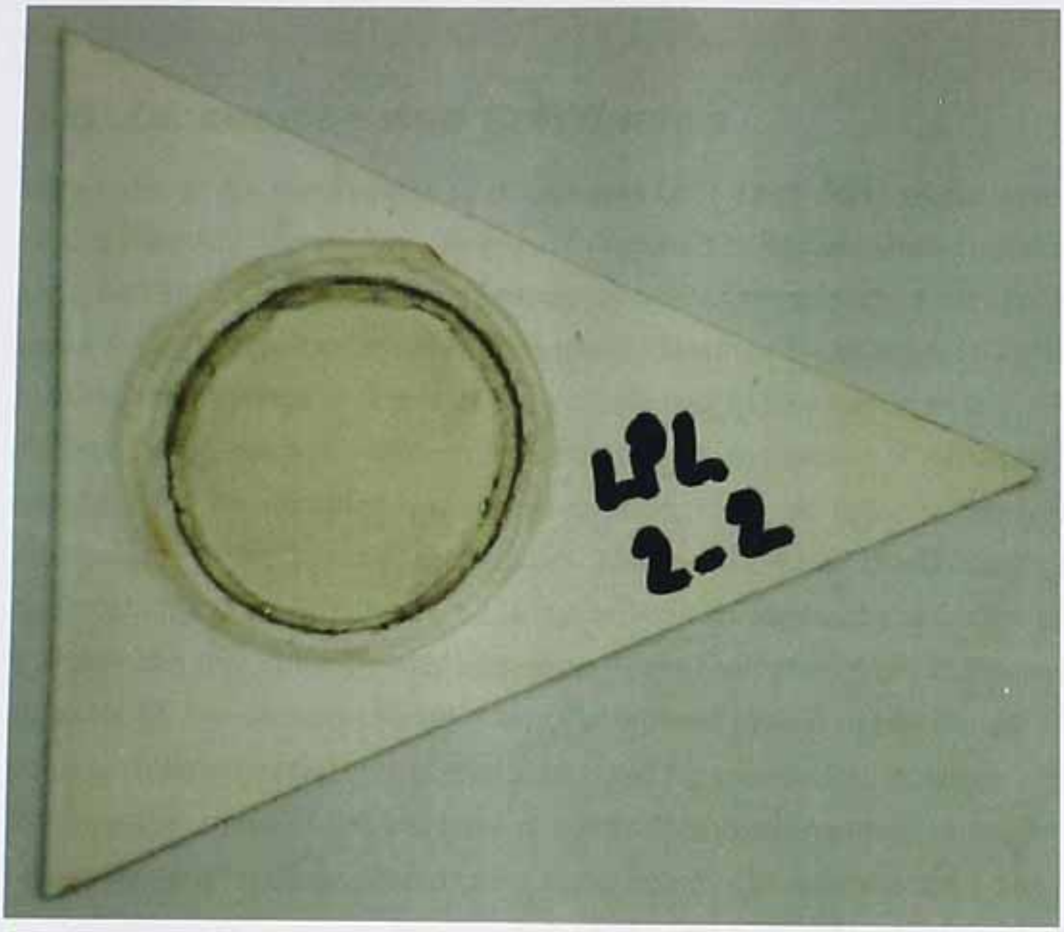


Figure 42. Paint LPL2 intact after 2500hrs immersion

Figure 43. Paint LPL3 after 2500hrs immersion – coating partially removed to show a small area of the underlying substrate

6.6 Discussion and Conclusion

Initial results for the evaluation of samples LPL1-LPL3 using alternative electrochemical techniques are given in figure 32. Results show that coatings LPL1 and LPL2 have high initial resistance values using all techniques, whilst LPL3 has a medium resistance value. The trend identified by all techniques is useful for ranking the coatings in terms of the criteria laid out by Bacon *et al.*, 1948.
Figures 34-36 show the individual coatings over the period of exposure. The resistance of the samples was recorded periodically, as listed in table 3, using the alternative electrochemical techniques. The results for all three coatings show the electrochemical techniques to be in agreement throughout the investigation. After 1176hrs the test solution was increased in concentration from 0.5% ammonium sulphate to 3% sodium chloride. The histograms shown in figures 34-36 show good correlation between the methods used for evaluation, however, figures 37-39 show the effect of the increase in electrolyte concentration upon resistance values more effectively. The arrows in figures 37-39 indicate the point at which the solution concentration was increased. At this point the resistance values of all three coatings can be seen to decrease. Both ENM and EIS show the same trend when the test solution concentration was increased.
In conclusion, this work shows ENM and EIS to be in good agreement, with both techniques identifying the trend with regard to resistance over time and identifying changes in resistance were increases in solution concentration had taken place. This conclusion has been noted in other studies (Le Thu *et al.*, 2001).

Chapter Seven – General Discussion and Conclusions

7.1 Reflection

The development of protective coatings will continue for the foreseeable future, as legislation dictates. Throughout this development various technologies will become less used, in some cases disappear, due to market demands to environmental pressures and improved Health & Safety practice.
As legislation increases with respect to strict VOC requirements for coatings (PG6/23 and many others) and raw material legislation (REACH) certain technologies are increasingly at risk of being phased out.
In addressing these issues the development of current and new technologies is required. With the development of current technologies previous knowledge can be drawn from experience with regard to anticipated performance under various exposure conditions. However, new technologies do not have the associated performance experience and, therefore, complete test programmes are required to predict the performance of a coating with exposure to various environments. This shift of emphasis onto laboratory testing requires the acceleration of predictive testing whilst retaining a high level of correlation with natural weathering.

Upon application and exposure, a coating system is immediately under attack from the various external stresses forced upon it by the surrounding environment. In the case of extreme conditions such as those experience upon offshore exposure, a combination of stresses can be expected, including, high concentrations of aggressive ionic species typical of a marine environment in combination with possible temperature fluctuations, UV exposure and varying levels of water permeability contributing towards ion transfer. When combined with the internal stresses of various coatings comprising the system then a severe environment is created in which the coating is expected to perform. Throughout exposure these stresses can take their toll on the coating system and make it more prone to failure, in the form of cracking and/or blistering, and subsequent corrosion onset. Differing technologies will resist this better than others and thus extend the performance period of the coating.
Field performance testing in relevant environments can reproduce these conditions and any subsequent mode of failure over a period of years rather than months. This can be site specific. In terms of laboratory performance testing, it is

these conditions that need to be reproduced in an accelerated manner to provide correlation with any mode of failure experienced in weeks or months rather than years.

This requirement for a reduction in the timeframe of testing has seen electrochemical testing come to fruition. Various techniques can be used under difference exposure conditions to predict the anti-corrosive performance of a coating.

Although samples are continuously immersed in a corrosive environment, certain testing procedures cannot be correctly defined as an accelerated test as the time required to assess the long-term behaviour is too long. Furthermore, samples which are not exposed to UV radiation and subsequent deformation do not represent the actual working conditions that a coating is likely to encounter throughout its working life.

Hence, in this work in order to speed up the degradation of the coating protective properties, samples were subjected to a high temperature thermal cycle when immersed in the aggressive electrolyte.

7.2 Discussion

The majority of the coatings under investigation have been formulated to reduce volatile organic compounds. This route of formulating typically requires an increase in the 'solids' component of the coating. Therefore, a combination of two methods can be considered, which are an increase in the polymer content and/or an increase in the pigment content. As part of this investigation was to produce low VOC/high solids coatings, detail regarding the formulating of the products is available upon request. To develop coatings with the desired technical properties both of the above mentioned methods of formulating were employed. In some cases the pigment volume concentration (PVC) maybe taken above the critical point at which the amount of binder available to bind the pigment within the formulation is exceeded. This is known as the critical pigment volume concentration (CPVC), and was discussed in chapter one. When the PVC exceeds the CPVC, stresses within the coating may be greatly exaggerated resulting in the formation of voids. These voids severely reduce the coatings durability by providing a route for water, pollutants and other harmful chemicals, which may react with the coating and cause the onset of degradation (Bierwagen, 1975, 1982, 1987)

The resultant failure of the coating with regard to anti-corrosive properties can be attributed to the ingress of water and aggressive ionic species through the coatings polymer matrix to the coating/substrate interface. Where water can penetrate to the metal substrate surface the onset of metallic corrosion occurs, causing the coating to delaminate resulting in the loss of integrity. The delamination and resulting loss of adhesion between the coating and substrate results when metallic corrosion occurs in the anodic areas of the corrosion cell, the cathodic reaction ($O_2 + H_2O = 4OH^-$) occurs in the cathodic areas concurrently. Subsequently, pH may rise in the cathodic areas resulting in a alkaline environment. The high pH can allow for a variety of plausible mechanisms to destroy the bond between the polymer and the substrate metal (Castle, 1997).

7.2.1 NO Connection to Substrate (NOCS) configuration

The NOCS configuration for ENM investigation shows that R_n values can be obtained which give indication as to the performance of the coating with respect to anti-corrosive properties. The results obtained also showed a good correlation between this method and other, more established, electrochemical techniques. The NOCS configuration has also been shown to be insensitive to the electrode type selected for testing further supporting the possible versatility of the techniques for on-site testing. Investigation of the results obtained via the NOCS configuration has been studied by Mabbutt *et al*. (2006) and shows that when NOCS is being used the distribution and contribution of the noise data is independent of the type of electrode.

The main advantage of the NOCS configuration over other electrochemical techniques, in particular, alternative ENM configurations, is its ability to make measurements without the requirement of making an electrical connection to the substrate.

This work has introduced the technique to ENM testing and monitoring and has made some ground towards validating its use as an alternative electrochemical test method. However, further investigation is required to fully validate the NOCS configuration to give greater confidence in its application. Further work to incorporate the method in combination testing is recommended later in this chapter.

7.2.2 ENM Vs EIS

Both ENM and EIS are useful electrochemical techniques for the assessment of anti-corrosive properties of protective coatings. The results from this investigation show that either method can be used successfully to identify the performance of coatings and rank them accordingly when tested for comparative purposes. Although EIS is currently one of the most commonly used electrochemical methods for evaluating the anti-corrosive properties of coatings it can be difficult to use for an inexperienced operator. ENM is less commonly used but is an easier method than EIS to apply and to use. Indeed, this technique does not perturb the electrochemical system as the measurement made at the free corrosion potential is of the spontaneous voltage and current fluctuations between two nominally identical electrodes. The electrochemical parameters available from ENM allows the ranking of organic coating systems performance, even if relationships between ENM parameters and EIS classical parameters are true only under certain circumstances (Le Thu *et al.*, 2001).

7.2.3 Blistering

Yang *et al.*, (2001) proposed a mechanism for blister formation where coatings which are degraded under the combined function of UV radiation, water and oxygen, soluble degradation products become concentrated in the coating. As a result, additional water is adsorbed into the coating which in turn forms osmotic cells under the coating surface layer. With the cycling of water adsorption and desorption, the osmotic cell continues to develop and the formation of blisters occurs on the coating surface. A number of samples exposed to continuous immersion conditions displayed evidence of blistering throughout this investigation. The formation of the blisters was coating/system dependant and also appeared to be influenced by the dry film thickness.

Blisters formed under an osmotic pressure in a wet/dry alternating environment where salt and soluble degradation products accumulate in the coating can signal the initial stages for the degradation of the coating. Yang *et al.* (2002) also showed that one condition for blister formation is a wet/dry alternating environment as undertaken in Prohesion testing. The formation of blistering is a common phenomenon in coating degradation, which represents the initial physical change upon exposure to cyclic testing. The blisters seen which are formed under Prohesion exposure are the result of osmotic cells caused by salt exposure during the salt fog period which penetrates into the coating and promotes the formation of osmotic cells in the coating (Yang *et al.*, 2002).

7.2.4 Coating Erosion

Another contributing factor towards the degradation of the coating and subsequent tailing off of anti-corrosive protection could be attributed to the erosion of the coating as a result of test cycles. This factor has not been quantified here but evidence has been given by Yang *et al.*, (2003) to support this hypothesis where a decrease in coating thickness, probably corresponding with the erosion of the pigment component, correlates with a decrease in protection. Fedrizzi *et al.* (2006) also states that the barrier properties of an organic coating can diminish by the generation of internal defects in the polymeric matrix and by decreasing the coating thickness. UV light has also been shown to diminish ionic barrier properties of outer layers of organic coatings (Donoghue & Mills, 2007).

7.2.5 Application techniques

Application methods can contribute to coating inhomogeneity. Spraying would be the preferred method as it is used in practice and once 'set-up' correctly is capable of delivering a reasonably uniform film. Spreader/application bars should, in theory at least, give the most uniform coating thickness though in some cases result in a significant reduction in dry film thickness, but they are only applicable in the laboratory environment. Powder coatings and electrostatic coatings are the best 'practical' methods, although robotic spraying is reasonably good.

7.2.6 Coating profile

The coating profile or inhomogeneity of a coating has been raised as a cause of reduction in coating performance by several workers (Mayne, 1952; Mills & Mayne, 1981; Kinsella & Mayne, 1969; Scantlebury). This inhomogeneity may significantly affect the properties of organic coatings, in particular their corrosion protection ability. Common findings indicate that the rust on a coated metal surface normally initiates at the localised weaker areas of the coating, where coated samples have a lower DC resistance than those which do not display as much rust (Mayne, 1952; Mills & Mayne, 1981). Subsequently, coating inhomogeneity therefore has the potential to greatly influence the reproducibility of electrochemical and accelerated weathering evaluation of organic coatings. Detailed information regarding the inhomogeneity of the coating has proven to be useful when identifying the more protective or non-protective areas of organic coatings in combination with the influence of the coating's thickness and coating system composition (Wu *et al.*, 1995). Pores and fissures are obvious coating defects that can cause coating inhomogeneity. This kind of profile of the coating can simply be visually or microscopically identified. However, in most cases, coating inhomogeneities cannot be identified by these means. Mayne and co-workers (Mills, 1973; Kinsella, 1967; Scantlebury, 1969) found that most inhomogeneity of coatings is not due to pores or fissures but instead due to the inhomogeneous bonding within the polymer film which may have various rates of reactivity. The rates of polymer reactions are dependant upon its chemical composition and curing mechanism, resulting in random polymerisation. This level of inhomogeneity cannot be observed by using an electron microscope but can be detected using electric resistance measurements. They found that there is a significant difference in electric resistance between different areas of an organic coating. This was done by cutting a large coating sample into smaller pieces (1cm x 1cm) and measuring the DC resistance of each individual sample (Mills, 1975; Mills & Mayne, 1981). Some pieces of the coating sample gave a very low DC resistance whilst others displayed a much higher resistance. They named the areas of high resistance type films 'I' (indirect) areas and the low resistance type films 'D' (direct) areas. Normally the film resistance for an I-type film in around 10^{10} - 10^{12} ohms cm^2 and for a D-type film is around 10^6 - 10^8 ohms cm^2. They assumed that the D-type areas are about 75 - 250µm in diameter and are randomly distributed across the coating surface according to Poisson's law. They also found that the metal surface under D-type film is very sensitive to corrosion (Mills, 1975; Mills & Mayne, 1981; Mayne, 1952).

7.2.7 Thermal cycling/High temperature exposure

An interesting method of accelerating weathering cycles experienced externally is the thermal cycle which was first allegedly developed by Bierwagen and co-workers (Li *et al.*, 1998; Beirwagen *et al.*, 2000). However, Cherry and Mayne had incorporated a similar cycle as long ago as 1963.

Samples in contact with the electrolyte are stressed by a cyclic exposure to temperatures well above the room temperatures which the samples had been exposed to during the initial stages of exposure. The increase in temperature is designed to enhance the water uptake usually occurring during the service life and to speed up the loss in adhesion between the coating/substrate interface and the subsequent onset of delamination. The successful use of high temperature incursions has been shown separate anti-corrosive coatings on a performance basis in this work.

The effects of cycling will be to put the coating through exposure to water as well as temperature cycling. The ingress of water could be associated with the increase in temperature. This has been shown to be the case in other studies (Bierwagen *et al.*, 2000; Valentinelli *et al.*, 2002; Fedrizzi, 2003). If water plasticizes the coating, the effects would be auto-accelerating, in that, the lowering of the Tg by water allows faster ingress up to the saturation concentration.

During thermal cycles, temperature variation may cause a rearrangement of the polymeric chains which would favour water uptake. Furthermore, the pressure generated by polymer shrinkage during the cooling stage, can favour water accumulation inside the coating at the pigment/polymer matrix interface or the coating/substrate interface (Valentinelli *et al.*, 2002).

If there is irreversible damage done shown by a change in R_n measured after the film is cooled the damage can be considered to be similar to extended room temperature immersion of the film. These changes in R_n were observed in this work and are similar to observations made by Bierwagen *et al.*, 2000. The 'damage' done to the coating would appear to be largely due to physical ageing, rearrangement of polymer molecules due to thermal mobility, with a small amount of chemical damage done with some covalent bond breakage due to hydrolysis or local oxidation.

Coatings with higher resistance to coating degradation in hygrothermal ageing will maintain good adhesion which will lead to little water penetrating the interface between the coating and substrate.

True reversibility with regard to a drop-off in resistance and subsequent increase is a good indication of the performance of a coated metal system after thermal cycling. This reversibility indicates the systems ability to resist water uptake whilst retaining a high level of adhesion between the coating and the metal (Bierwagen *et al.*, 2000).

The reduction in the R_n value after the high temperature thermal exposure could be a consequence of the high temperature reached in the cycle that has accelerated the diffusion of the electrolyte inside the polymer matrix to fill pores in the matrix or voids that can be present at the substrate/coating or pigment/polymer interfaces. This R_n reduction could be due to new defects and pores created by the thermal cycle itself. These defects can be a consequence of chemical ageing due to the high temperature reached in the cycle, or can be generated by the redistribution of macromolecules that is caused by the ingress and egress of water in the structure during the heating and cooling stages. Furthermore, existing voids and pores can be filled by water and enlarged when the polymer structure shrinks during cooling.

The degradation of the coatings polymer matrix is not as evident before thermal ageing, however during thermal cycles defects can be created in the coating which can propagate due to the stresses generated by the water uptake and by water over saturation.

7.2.8 External weathering

Results from external weathering panels exposed for two years correlated with ENM results giving an equivalent ranking of the coatings.

Exposure to ultraviolet (UV) radiation is considered a useful way to reproduce the photo-degradation of a coating which is subjected to solar radiation (Skerry *et al.*, 1988; Simpson *et al.*, 1991; Bierwagen and co-workers). It is also considered to be a useful tool in accelerating the degradation of the coating to a level considered suitable with regard to reproducibility whilst displaying good correlation with naturally exposed external panels (Beirwagen and co-workers), though this is dependant on wavelength. The effect of UV and oxygen on the aesthetic and anti-corrosive properties of an organic coating is strictly dependant on the groups and chemical bonds of the polymer, on the impurities that are always present in the film and on the type and concentration of pigments and additives, such as UV stabilisers and/or absorbers, used. UV radiation combined with oxygen in the atmosphere can result in the lowering of the molecular weight of the binding polymer and in the formation of reaction products, such as free-radicals. This can affect the superficial aspect of the polymer and increase the permeability of the matrix. Photo-oxidation also induces the formation of some groups, including ketones, alcohols, hydroperoxides, and carboxylic acids, which increase the solubility of water inside the polymer and finally favour the hydrolytic degradation (Fedrizzi *et al.*, 2006).

Titanium dioxide (TiO_2), a common pigment found in most commercial coatings is also susceptible to breakdown upon UV exposure when not surface treated. This breakdown results in the formation of homologous acids which contribute towards polymer degradation (Worsley, 2007).

UV exposure and photo-oxidation can affect the polymer structure resulting in a more stiff, cross-linked coating and the associated altering of some chemical bonds.

7.3 SEM

When examining the coating bulk with SEM cross-section, it was found that after Prohesion exposure the coating was still intact and there was no obvious degradation observed. However, at the point of the scribe there was evidence of deposits which had built up through the period of exposure. Results from this part of the investigation are in Appendix 4.

7.4 Future Work

Although the correlation between Electrochemical Noise Measurement (ENM), Prohesion and Electrochemical Impedance Spectroscopy (EIS) testing appears to be in agreement in this investigation, test conditions differ between the three methods resulting in differing test environments. Both ENM and EIS subscribes to conditions of continues immersion, whereas Prohesion adopts cyclic exposure conditions, relying on subjective interpretation of results. Whilst a controlled test environment is essential for reproducibility, the tests, in their own right, are restricting with regard to testing conditions and do not consider the severe exposure environment a coating is likely to encounter. If an attempt is to be made to combine the various internal and external stresses a coating is expected to be subjected to throughout its 'working life', the results from testing are required to be more realistic with respect to predicting the performance of coatings in-service.

To do this, combination testing would be required which would involve the inclusion of various exposure cycles to best replicate the anticipated exposed environment. Whilst this is not a new concept and it is not uncommon to test coatings in this manor, various combinations have not been considered to the knowledge of the author. One of the most common stresses a coating is exposed to has not been considered in this investigation – that is ultraviolet (UV) radiation exposure. This method of accelerating the degradation of the coating has been common practice within academia and industry for many years and has dedicated standards (ASTM G85-53) for evaluating and reporting coating performance. UV exposure accelerates the breakdown of coatings using UV-B radiation which is a lower and more damaging wavelength (313nm) than that experienced by the sun after filtration (~340nm). The subsequent degradation of the coating under exposure results from the breakdown of hydrogen bonds within the 'cured' coating releasing free-radicals which are further damaging to the integrity of the coating through further destruction of bonds. However, although this is commonly thought to be the mechanism of degradation within the coating, UV exposure at higher wavelengths, which are less damaging, may offer advantages to the protection afforded by a coating. Recent work by Donoghue & Mills (2007) has shown that after exposure to UV radiation the resistance (R_n) of coatings is typically increased after ENM evaluation. In addition to the increase in resistance the hardness of the coating also increases. The increase in hardness may be the result in further cross linking of the coating as a result of UV exposure, this in turn increases the barrier properties of the coating resulting in a reduction in the diffusion of ions through the coating to the coating/substrate interface. This piece of work can be developed further to include the cyclic test proposed by Simpson *et al.* (1991) whereby UV exposure and Prohesion testing are undertaken alternately for 200hr exposure periods for a total of 2000hrs. The work by Simpson *et al.* (1991) relied on subjective interpretation of the results in accordance with various ASTM standards, giving qualitative results. It is proposed by the author that this cycle of testing is undertaken with the inclusion of ENM testing, most interestingly with the inclusion of the NOCS configuration for evaluation and comparison, at the end of each cycle to quantify the performance of the coating with respect to anti-corrosive protection. This method of quantifying results allows for subsequent testing to be more comparative in combination with using an exposure cycle which is more akin to that which an anti-corrosive coating is likely to encounter.

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Appendix 1 Data for chapter four graphs

Time (hrs)	Sample 1_4	Sample 2_5	Sample 3_6
0.1	2.33E+05	1.50E+06	2.65E+05
24	1.45E+05	2.25E+06	8.98E+04
48	2.24E+04	6.63E+04	9.11E+04
144	8.91E+03	2.91E+05	1.21E+05

Table 4.1 Data for Figure 5

Time (hrs)	Sample 1_4	Sample 2_5	Sample 3_6
0.1	7.05E+05	6.64E+05	4.92E+05
24	2.56E+04	2.64E+05	1.46E+05
48	1.83E+04	1.37E+05	4.91E+03
144	6.42E+04	4.20E+04	9.91E+04

Table 4.2 Data for Figure 6

Time (hrs)	Sample 1_4	Sample 2_5	Sample 3_6
0.1	7.93E+05	3.87E+05	1.48E+04
24	2.31E+04	3.00E+04	1.35E+04
48	9.33E+03	1.39E+05	5.78E+04
144	3.17E+04	1.15E+04	1.47E+04
168	5.00E+03	2.41E+03	4.62E+04
480	2.49E+03	2.10E+04	1.00E+04
504	3.01E+03	8.52E+03	1.54E+04
648	6.85E+03	1.10E+04	2.19E+04

Table 4.3 Data for Figure 7

Time (hrs)	Sample 1_4	Sample 2_5	Sample 3_6
0.1	9.61E+06	4.45E+06	8.04E+06
192	5.98E+07	8.95E+06	2.51E+07
240	4.88E+07		2.26E+06
312	1.90E+08		8.16E+06
336	1.97E+07	1.73E+07	9.80E+06
408	5.50E+07	1.35E+07	6.13E+06
528	1.73E+07	3.64E+06	1.08E+07
648	1.75E+06	1.02E+07	1.74E+07

Table 4.4 Data for Figure 8

Time (hrs)	Paint D	Paint E	Paint F	Paint G
0.1	3.98E+05	4.99E+06	7.36E+06	6.70E+06
24	2.22E+04	9.86E+06		
48	6.87E+04	7.13E+07		
144	1.93E+04	1.32E+05		
168	1.78E+04	6.71E+05		
192			3.12E+07	8.88E+06
240			2.55E+07	1.27E+07
312			9.90E+07	2.95E+07
336			1.56E+07	1.73E+07
408			4.32E+07	7.89E+06
480	1.11E+04	3.42E+10		
504	8.97E+03			
528			1.05E+07	3.58E+07
648	1.32E+04		9.78E+06	5.16E+07
672		1.48E+09		

Table 4.5 Data for Figure 9

Time (hrs)	Paint D	Paint E	Paint F	Paint G
0.1	6.66E+05	5.84E+05	6.20E+05	2.64E+05
24	8.28E+05	2.13E+05	1.45E+05	5.70E+04
48	5.99E+04	1.64E+04	5.34E+04	9.18E+03
144	1.40E+05	1.94E+05	6.84E+04	4.78E+04

Table 4.6 Data for Figure 10

Time (hrs)	Sample 1_4	Sample 2_5	Sample 3_6
0.1	3.74E+07	4.72E+07	1.27E+08
3	4.89E+06	3.58E+07	5.66E+07
5	6.36E+06	6.16E+06	8.54E+07
20	1.07E+07	2.65E+06	4.47E+07
24	7.82E+06	1.10E+06	4.66E+07
36	4.15E+07	2.56E+06	4.76E+07
48			2.70E+07
72			
96	9.25E+06	5.00E+06	1.26E+07
120			
144	5.42E+08	2.00E+07	1.93E+08
172	3.08E+08	5.33E+06	
192	1.58E+07		9.38E+06
216		7.83E+06	1.17E+07
240	7.26E+07	9.31E+06	8.90E+06
264	2.84E+07	2.19E+06	1.15E+07
288	6.06E+06	1.86E+06	
312			1.04E+07
336	9.25E+06	3.94E+08	
360	9.92E+06	5.90E+06	2.01E+08
384	7.53E+07	1.40E+06	4.27E+06
408	9.53E+06	6.83E+05	3.23E+06
432	3.08E+07	5.92E+05	

Table 4.7 Data for Figure 11

Time (hrs)	Paint D	Paint E	Paint F	Paint G
0.1		70533333		
3		32430000		
5		32640000		
20	3.51E+05	19350000	1.34E+07	3.01E+07
24	1.38E+06	18506667	1.50E+08	2.08E+08
36	3.71E+05	30553333	1.30E+08	1.68E+08
48		9000000		1.21E+07
72	1.34E+04	0	1.65E+07	
96		8950000		
120	2.96E+04	0	3.77E+06	1.48E+07
144	1.78E+06	2.52E+08	6.10E+07	2.53E+08
172		1.04E+08		
192	9.40E+06	8393333	1.40E+08	4.68E+05
216	1.31E+07	6510000	3.59E+07	1.00E+06
240	1.28E+07	30270000	3.65E+07	1.22E+06
264		14030000		
288	1.72E+07	2640000	7.27E+07	1.53E+06
312	6.50E+06	3466667	7.23E+07	1.22E+06
336		1.34E+08		
360	1.74E+07	72273333	1.60E+06	8.73E+06
384		26990000		7.53E+04
408	2.44E+07	4481000	2.54E+07	
432	1.37E+07	10464000	1.79E+07	1.76E+05

Table 4.8 Data for Figure 12

Time (Hrs)	Paint D	Paint E	Paint F	Paint G
0.1	7.76E+04	2.44E+05	2.78E+05	8.41E+04
6	1.81E+05	5.59E+05	1.93E+05	1.31E+05
24	2.50E+05	1.96E+05	1.19E+05	2.20E+06
48	4.13E+05	3.70E+06	5.06E+05	2.32E+05
50	2.87E+05	2.32E+05	1.52E+05	1.59E+05
54	2.27E+04	2.56E+04	2.03E+04	4.23E+04
120	6.59E+04	8.32E+04	4.33E+04	5.34E+04
144	5.00E+04	9.81E+04	5.61E+04	1.25E+05

Table 4.9 Data for Figure 13

Sample	Sample 1 (av)	Sample 2 (av)	Sample 3 (av)
D	4.35	5.72	5.06
E	4.84	4.16	4.56
F	7.88	5.1	6.9
G	7.24	6.4	6.92

Table 4.10 Data for Figure 14

Time (hrs)	Paint F	Paint H	Paint H2	Paint J	Paint S
0.1	7.36E+06		8.45E+08		4.08E+08
2			5.42E+08		
5			4.87E+08		
10			4.2E+08		
12					3.82E+06
13					4.90E+07
15					8.53E+07
16			4.2E+08		8.23E+07
17			1.34E+09		
24			2.42E+08		
36			1.54E+08		
36.6					
37					
48		9.26E+08		9.30E+08	4.40E+07
52		9.67E+08		8.90E+08	
65					
67					
72		1.00E+09		9.88E+08	2.67E+07
89					
96					1.89E+07
161					
168		1.49E+08	49276252	1.79E+08	2.10E+07
185					
192	3.12E+07				2.87E+07
209					
233					
240	2.55E+07	3.50E+09		9.79E+08	4.35E+07
257					
268					7.17E+07
312	9.90E+07				
336	1.56E+07		1.4E+08		
408	4.32E+07	3.87E+09		2.00E+09	1.33E+07
436					2.95E+06
480					1.33E+07
504				3.47E+08	2.65E+07

528	1.05E+07		36206112	
545			22856661	
576		7.01E+08	9413101	5.49E+08
593			24117703	5.14E+08
648	9.78E+06		9584884	
744		9.69E+08		8.90E+08
1008		6.08E+09		7.80E+08

Table 4.11 Data for Figure 15

Time (hrs)	Paint D	Paint N	Paint P
0.01	165608.2	21954002	8920400
0.5	0	1094829	1772775
3	0	1743560	2551568
10	0	5028081	7139646
17	0	806678.4	1350427
24	21071.19	2806065	3884740
36	0	1081167	2175817
36.6	0	1066001	535219.8
37	42163.96	359047.4	872741.3
65	0	3684442	8946900
89	0	6379226	398601.3
161	17499.47	581507.3	234276.1
185	8226.397	3941052	183504.1
209	0	574605.8	185644.4
233	0	129487.3	193765.1
257	8056.373	222018.9	182679.2
545	7336.838	172199.8	162546.9
593	11817.05	301903.8	167991.9

Table 4.12 Data for Figure 16

Appendix 2 Data for chapter five graphs

	NOCS	Bridge	Single substrate	DC resistance
0.1	8.59E+06	3.76E+05	1.61E+06	4.20E+06
149	2.47E+07	1.00E+06	3.13E+06	
658	1.18E+07	1.20E+06	3.42E+06	
682	1.91E+06	2.20E+06	5.73E+06	
850	6.97E+07	5.90E+06	7.09E+06	
874	2.84E+06	1.15E+06		3.50E+06

Table 5.1 Data for Figure 20

	Single Substrate	Conventional	DC Resistance	NOCS
High	7.88E+07	1.99E+07	2.00E+09	1.56E+08
Medium	2.29E+06	1.10E+08	2.00E+07	3.66E+06
Low	1.02E+06	1.19E+06	2.00E+06	4.81E+05
Uncoated	8.88E+03	9.48E+03	5.50E+03	7.14E+03

Table 5.2 Data for Figure 21

	Bridge	SS	NOCS
8+9	1.32E+09	3.42E+06	1.94E+07
8+10	2.20E+06	7.76E+06	1.91E+06
9+10	1.59E+09	2.68E+06	1.18E+07

Table 5.3 Data for Figure 22

	conventional	single substrate	NOCS
high	1.04E+08	1.05E+08	
medium	9.01E+06	2.21E+07	
hilo	1.11E+05	2.93E+05	
himed	4.95E+06	2.15E+07	7.67E+07
medlo	2.62E+05	7.59E+06	1.02E+07
medhi			3.70E+07

Table 5.4 Data for Figure 23

	AgAgCl	Pt	Calomel	DC
High	1.69E+09	3.48E+09	7.66E+08	2620741394
Medium	6.25E+07	1.40E+08	7.85E+07	21544346.9
Low	5.12E+06	1.29E+06	2.84E+07	669432.95

Table 5.5 Data for Figure 24

	NOCS GM	DC resistance GM	single substrate
high resistance	65871859	3779763150	
medium resistance	4616562	5192494.1	
v.low resistance	33580.51	14422.4957	
bare metal	18022.34	5500	3.29E+04

Table 5.6 Data for Figure 25

	calomel	platinum
high	8.91E+08	1.43E+08
hihilo	1.97E+08	1.40E+08
hihimed	2.61E+08	2.20E+08
medium	9.32E+06	1.35E+07
medmedhi	3.22E+07	7.46E+06
medmedlo	1.34E+06	2.87E+07
low	1.96E+06	9.59E+06
lolohi	4.75E+06	2.74E+08
lolomed	2.46E+08	9.46E+08

Table 5.7 Data for Figure 26

Appendix 3 Data for chapter six graphs

	DC Resistance	EIS	ENM-Conventional	ENM-NOCS
A1	3.50E+05	1.50E+05	8.41E+04	9.34E+04
A2	5.00E+04	4.50E+04	9.23E+04	9.37E+04
B1	4.10E+04	3.50E+03	1.91E+05	2.09E+04
B2	3.70E+04	3.50E+03	4.43E+05	2.35E+04
C1	1.00E+06	9.00E+05	5.30E+05	4.99E+06
C2	2.90E+06	2.50E+06	1.49E+06	6.49E+06

Table 6.1 Data for Figure 27

Time 0.1hr

	DC Resistance	EIS	ENM-Conventional
A1	3.50E+05	1.50E+05	8.41E+04
A2	5.00E+04	4.50E+04	9.23E+04
B1	4.10E+04	3.50E+03	1.91E+05
B2	3.70E+04	3.50E+03	4.43E+05
C1	1.00E+06	9.00E+05	5.30E+05
C2	2.90E+06	2.50E+06	1.49E+06

Table 6.2 Data for Figure 28

	ENM Bridge	EIS Impedence (Nyquist)	DC Resistance
LPL1_1	1.23E+00	3.88E+08	3.00E+08
LPL1_2	1.17E+08	3.73E+08	3.20E+08
LPL1_3	1.12E+08	5.56E+08	3.90E+08
LPL2_1	2.15E+08	2.81E+08	3.20E+08
LPL2_2	1.72E+08	5.80E+08	3.20E+08
LPL2_3	2.31E+08	2.64E+08	6.40E+08
LPL3_1	5.46E+07	2.69E+06	1.10E+06
LPL3_2	1.29E+06	1.80E+06	1.15E+06
LPL3_3	1.63E+06	2.48E+06	1.50E+06

Table 6.3 Data for Figure 32

LPL 1

	Time	LPL1.1	LPL 1.2	
Code	(hrs)	EIS	EIS	ENM
t1(5-4-06)	0.1	3.88E+08	3.73E+08	1.17E+08
t6	816	4.10E+08	4.41E+08	2.06E+08
t7	984	5.29E+08	9.00E+08	4.45E+08
t13%NaCl	1176	4.82E+08	5.40E+08	1.77E+08
t23%NaCl	1992	2.75E+07	1.34E+08	4.66E+07
t33%NaCl	2544	8.90E+05	6.30E+06	1.01E+07

Table 6.4 Data for Figure 33

LPL 2

	Time	LPL2.2	LPL 2.3	
Code	(hrs)	EIS	EIS	ENM
t1(5-4-06)	0	5.80E+08	2.64E+08	2.31E+08
t6	816	1.53E+09	2.00E+09	9.41E+08
t7	984	3.75E+08	4.83E+08	8.87E+07
t13%NaCl	1176	4.20E+08	4.24E+08	2.75E+08
t23%NaCl	1992	2.31E+08	2.32E+08	1.62E+08
t33%NaCl	2544	2.25E+08	2.05E+08	1.21E+09

Table 6.5 Data for Figure 34

LPL 3

	Time	LPL 3.1	LPL 3.2	
Code	(hrs)	EIS	EIS	ENM
t1	0	2.69E+06	1.80E+06	5.46E+07
t6	816	2.40E+08	1.60E+08	8.86E+07
t7	984	1.50E+07	1.62E+07	6.20E+07
t13%NaCl	1176	1.76E+07	2.11E+07	5.84E+07
t23%NaCl	1992	1.35E+07	1.97E+07	4.00E+07
t33%NaCl	2544	1.05E+07	1.79E+07	2.70E+07

Table 6.6 Data for Figure 35

LPL 1

Code	Time (hrs)	LPL1.1 EIS	LPL 1.2 EIS	ENM
t1(5-4-06)	0.1	3.88E+08	3.73E+08	1.17E+08
t6	816	4.10E+08	4.41E+08	2.06E+08
t7	984	5.29E+08	9.00E+08	4.45E+08
t13%NaCl	1176	4.82E+08	5.40E+08	1.77E+08
t23%NaCl	1992	2.75E+07	1.34E+08	4.66E+07
t33%NaCl	2544	8.90E+05	6.30E+06	1.01E+07

Table 6.7 Data for Figure 36

LPL 2

Code	Time (hrs)	LPL2.2 EIS	LPL 2.3 EIS	ENM
t1(5-4-06)	0	5.80E+08	2.64E+08	2.31E+08
t6	816	1.53E+09	2.00E+09	9.41E+08
t7	984	3.75E+08	4.83E+08	8.87E+07
t13%NaCl	1176	4.20E+08	4.24E+08	2.75E+08
t23%NaCl	1992	2.31E+08	2.32E+08	1.62E+08
t33%NaCl	2544	2.25E+08	2.05E+08	1.21E+09

Table 6.8 Data for Figure 37

LPL 3

Code	Time (hrs)	LPL 3.1 EIS	LPL 3.2 EIS	ENM
t1	0	2.69E+06	1.80E+06	5.46E+07
t6	816	2.40E+08	1.60E+08	8.86E+07
t7	984	1.50E+07	1.62E+07	6.20E+07
t13%NaCl	1176	1.76E+07	2.11E+07	5.84E+07
t23%NaCl	1992	1.35E+07	1.97E+07	4.00E+07
t33%NaCl	2544	1.05E+07	1.79E+07	2.70E+07

Table 6.9 Data for Figure 38

Appendix 4 Scanning Electron Microscope images

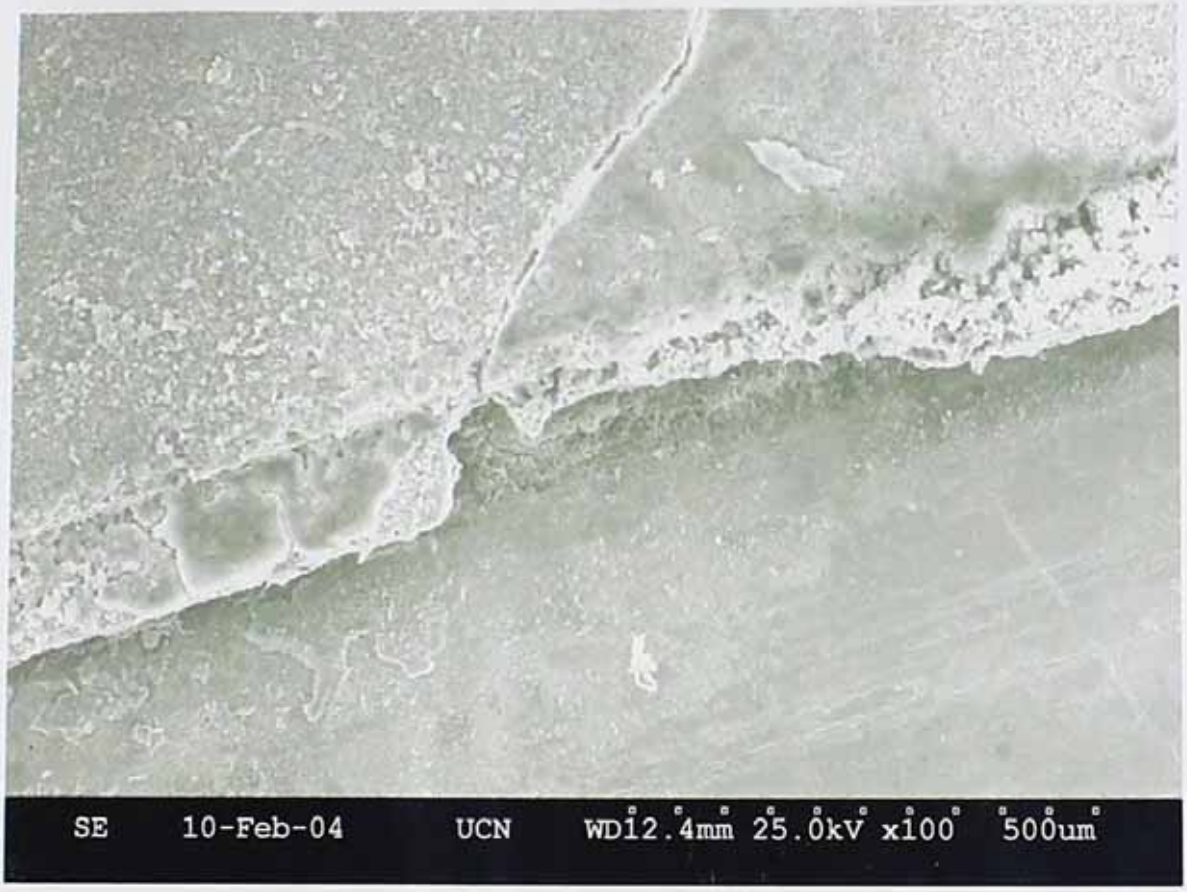

Figure 7.1 SEM image x100 magnification of Paint D, scribed

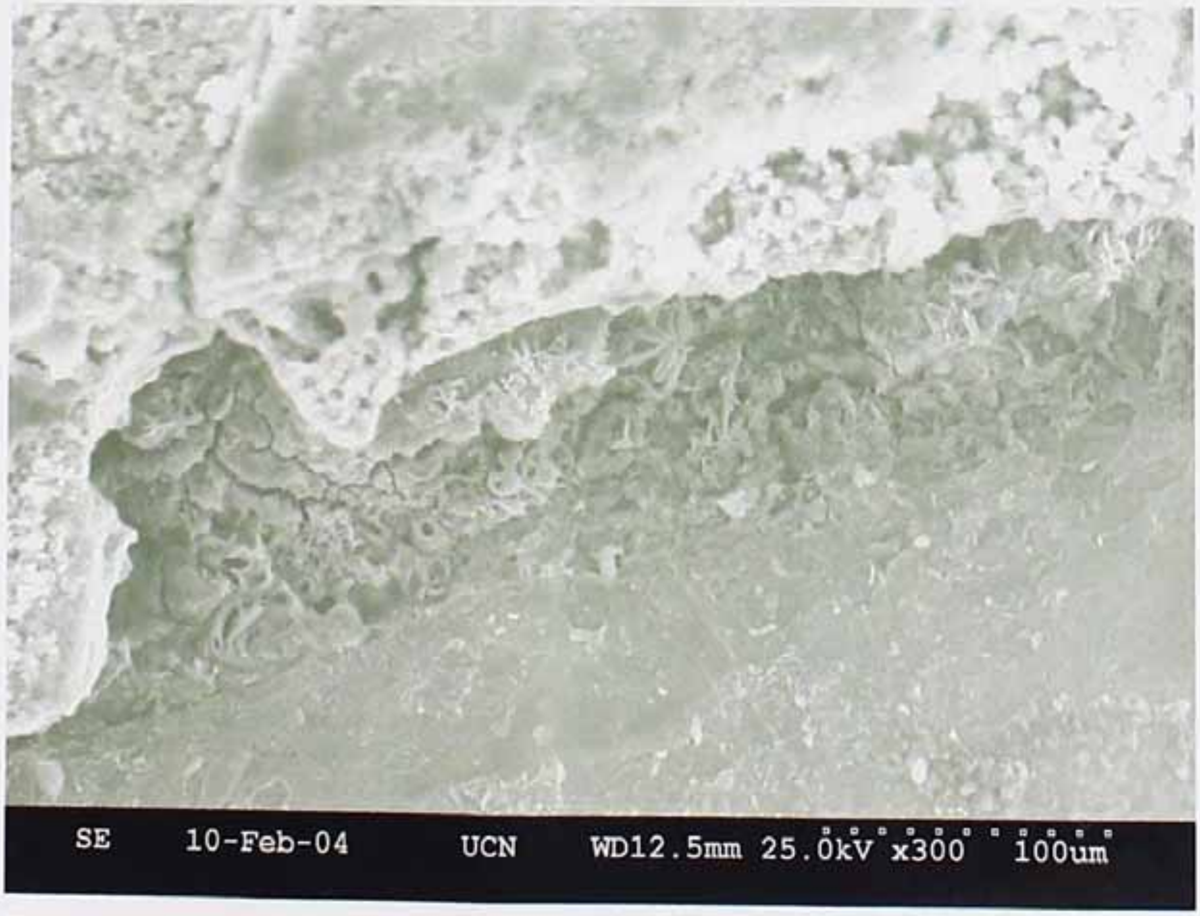

Figure 7.2 SEM image x300 magnification of Paint D, scribed

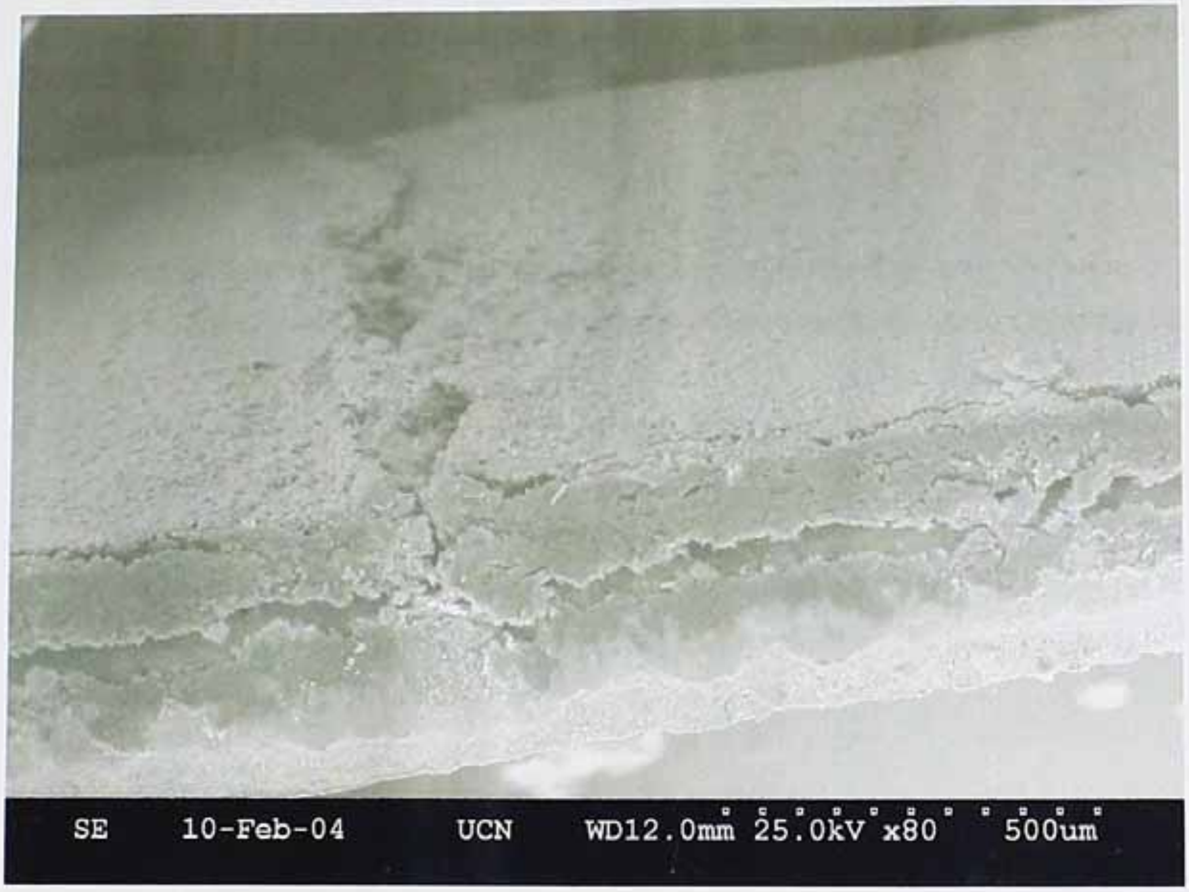

Figure 7.3 SEM image x80 magnification cross-section of Paint D, scribed

Figure 7.4 SEM image x1000 magnification of Paint D, scribed

Appendix 5 List of co-author publications and presentations 2002 – 2004

Refereed Journals

1. Use of electrochemical noise method to investigate the anti-corrosive properties of a set of compliant coatings Progress in Organic Coatings 52 pp 257-262 (2005)
2. Using Novel Electrochemical Test Methods to aid in the Development of low Volatile Organic Compound (VOC) Coatings The Journal of Corrosion Science and Engineering, submitted 2004
3. Developments of the electrochemical noise method (ENM) for more practical assessment of anti-corrosive coatings Progress in Organic Coatings (2006) In press

Refereed Conference Proceedings

1. EUROCORR 2003, September 2003, Budapest, Hungary
2. Advances in Electrochemical Techniques for Organic Coatings (AETOC) 2003, November 2003, Sintra
3. Advances in Corrosion Protection of Organic Coatings (ACPOC) 2004, September 2004, Cambridge, UK
4. Advances in Electrochemical Techniques for Organic Coatings (AETOC) 2005, April 2005, Villard de Lans, France

Presentations

1. 43rd Corrosion Science Symposium, Cardiff, UK, 2002
2. 44th Corrosion Science Symposium, Southampton, UK, 2003
3. 45th Corrosion Science Symposium, Sheffield, UK, 2004