

AC IMPEDANCE TECHNIQUE FOR ACCELERATED EVALUATION OF COATED STEEL SUBSTRATE

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الملخص العربي:

ان الهدف الرئيسي من هذه الدراسة البحثية الأولية لتقديم الكهروكيميائية الممانعة الطيفية كأداة تدريبية جديدة يتم تعريفها للمتدرب من قسم اللحام في معهد الشويخ الصناعية لتقييم وفحص طبقات الطلاء المختلفة على الحديد الصلب. وفي هذا الصدد تم إجراء تدريب وتحقيق بحثي على EIS في مواد البناء والتصنيع CBM / في معهد الكويت للأبحاث العلمية للمهندس عماد مال الله الذي يدرب في قسم اللحام.

يتكون التقرير الفني من الدورات التدريبية والدراسة البحثية التالية:

- مسح بحثي على الأنواع المختلفة من الدهانات وآلية الحماية المتوفرة.
- الكهروكيميائية الممانعة الطيفية EIS؛ النظرية وسبل الممارسة بالمختبر.
- التطبيق التجريبي ل EIS على الأنواع المختلفة من الطلاء من أجل فهم الممانعة والتصدي لنطاق واسع من الترددات 0.01 هرتز إلى 100 كيلو هيرتز.
- يتكون نظام الطلاء المختار الذي تم التحقق منه من مادة البولي يوريثين الدهانات HB, (C1&C2) وفوسفات التمهيدي (S2 & S1)، والزنك الايبوكسي مادة البولي أميد (ZE)؛ وكذلك الحديد الصلب الغير مطلي (BN و BP). وكان الحديد الصلب المطلي مغمور في ماء متكون من 3٪ ملح الطعام لمدة الاختبار التي تتراوح بين 0 ساعة إلى 337 ساعة. وقد أشارت نتائج AC الممانعة التباين في الأداء وتدهور سلوك مختلف نظام الطلاء المستخدمة.
- وأخيراً، تم استخدام البيانات التي تم الحصول عليها من EIS لترتيب أنظمة الطلاء المختارة المختلفة وفقاً لأعلى مستوى من أداء الطلاء في محلول كلوريد الصوديوم و سطح الطلاء الخالي من اي آثار للتآكل أو الصدأ. وقد أشارت النتائج الكلية أن أفضل أداء من حيث الترتيب تم الحصول عليها ل $C < S2 < ZE$

ABSTRACT

The main aim of this preliminary research study was to introduce the Electrochemical Impedance Spectroscopy as a new instrument to be introduced to the Trainer of the Welding Department at Industrial Institute Shuwaikh as a training tool in the laboratory for the evaluation and screening of different coatings on steel substrate. In this respect a training and research investigation has been held on EIS at Construction and Building Materials CBM / KISR for Eng. Emad Malallah who is an Trainer at the Welding Department.

The technical report consists of the following training sessions and research study:

- Literature Survey on different types of paints and protection mechanism
- Electrochemical Impedance Spectroscopy EIS; Theory and Lab Practice
- Experimental application of EIS on different generic type of coatings in order to understand the Impedance and capacitance response over a wide frequency range of 0.01 Hz to 100 KHz.
- The selected Paint system that has been investigated consists of; Clear Polyurethane Paints (C1&C2), HB Phosphate Primer (S1&S2), and Zinc Epoxy Polyamide (ZE); as well as un-painted bare steel substrate (BP&BN). The painted steel substrate was

immersed in 3%NaCl solution for test duration ranging from 0 hrs. to 337 hrs. The AC Impedance results have indicated variation in the performance and deterioration behavior of the various paint system employed.

The values of the paint film capacitance (C_c) and resistance (P_{po}) were recorded experimentally from Nyquist plots. Photographic and SEM photomicrographic examination were obtained for the coated steel substrates.

Finally, the EIS data obtained were used for ranking of the different selected paint systems according to the highest paint performance in Sodium Chloride solution and the paint surface free from the on sit of corrosion products, blisters or rust. The overall results have indicated that the best performance in terms of ranking were obtained for:

$$ZE > S2 > CI$$

1. INTRODUCTION

The relevance of this project pertains to material performance in the Middle East, and particularly in Kuwait, Saudi Arabia, and the other countries in the region, where atmospheric conditions off shore and the adjacent to shore are considered to be the most severe marine environment in the world. Corrosion rates of 100 mils per year (2540 micron) are not uncommon. Prior to the early 1950's, corrosion problems in this difficult marine exposure conditions were mitigated somewhat by conventional paints and coatings that were available at that time which included chlorinated rubber, bitumen's and coal tar mastics as well as ordinary metal primers and paint. Oil companies were required to stocks as may as 200 items and suppliers in order to show progress in corrosion control.

In early 1950's vinyl's were under test evaluation and in the mid 50's workable epoxy ester and epoxies with chemical curing agent were being evaluated. In the late 50's and early 60's other materials were available including the zinc rich coating, coal tar epoxies and there were developments in the so called high performance coating (1).

In the State of Kuwait the severe environment pollution from the burning of oil wells are being added in addition to the severe marine environments already existing. This requires a fresh look at and increased attention to coating performance evaluation for condition of immersion (water and chemical service) as well as splash and fumes superimposed in marine environment.

Paint manufacturer and other organizations engaged in surface protection measures have done and are still doing, a great deal of work in the testing and evaluation of painting materials for steel corrosion protection and developing methods for a variety of exposure conditions.

Painting of steel is one of the most important methods of protecting it, and therefore accounts for a major portion of the corrosion bill (2). Approximately, 4 to 5 billion dollars per year are expended in the United States on the maintenance of paints for buildings and equipment (3). In the U.K the annual cost of corrosion prevention and maintenance by paints is estimated at 600 million pounds sterling.

Electrochemical methods have a continuing impact on corrosion technology and are widely used to monitor corrosion performance, to provide accelerated laboratory test to determine the quality of coatings, either for control of conventional products or development of products, and to investigate the mechanism of corrosion protection.

In this work the deterioration behavior of various paints was measured and evaluated by using one method. (a) electrochemical impedance method. The aims of this test have been to optimize accelerated laboratory test which can evaluate new paint system much more quickly than the conventional atmospheric exposure trials. Application of this technique together for a particular system would help establishing and correlating some aspects of the corrosion behavior of coated steel.

2. LITERATURE SURVEY

2.1 ABOUT PAINTS

Painting is the most common method of the surface protection for the steel corrosion control. Paints are pigment-containing fluid compositions that form first a liquid film on surface when applied which subsequently harden to solid coating. They contain as many as 15 to 20 ingredients, each of which has its own function in the overall performance of the coating.

2.1.1 PAINT CONSTITUENTS

Paints usually consist of (4):

1. Pigment (e.g. metal oxides such as TiO_2 , Pb_3O_4 , Fe_2O_3 , or compounds such as $Zn Cr O_4$; mixed metal powder etc.)
2. Base or vehicle (organic or inorganic dispersion).
3. Dryer (high vapour chemical or polymeriser).
4. Solvent or thinner (low surface tension and high vapour pressure properties).
5. Inhibitor.

The drier may accelerate the oxidation or polymerization stages. The thinner is a volatile liquid that enables adequate coverage and ease of application of the paint and then quickly evaporates. The vehicles may be natural oil, such as linseed, that when exposed to air oxidizes and polarizes to a solid, or a synthetic resin that dries by evaporation of the solvent. Pigments are the solid particles in paint which are added to give colour and opacity, to provide corrosion inhibition or to impart special properties such as tensile strength or water resistance.

Pigmentation is very important for adhesion and corrosion. Most primers are formulated to be very near critical pigment volume content (CPVC). At CPVC, the pigment volume is such that there is just enough vehicles in the dry paint film to provide a layer of polymer adsorbed on the pigment surface and to fill the interstices between the polymer covered pigment particles. Above CPVC, voids are left in the films. Having very few voids can help intercoat adhesion between top coat and prime by permitting interlocking between the layers. If there are too many voids, a porous film will result. This is shown clearly in figure [2.1]

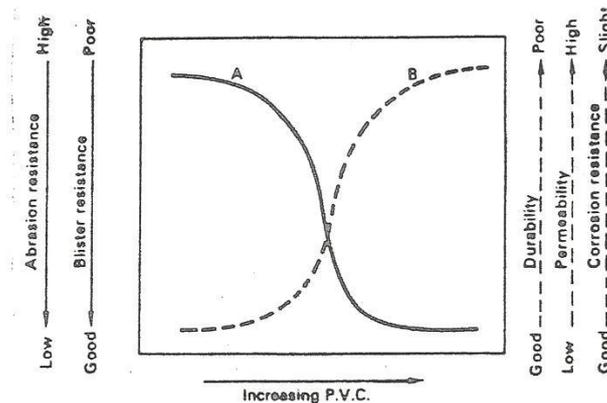


Fig. 2.1 –Influence of pigment volume concentration (P.V.C) on paint performance (ref.5)

2.1.2 GENERAL DESCRIPTION OF SOME COMMON PAINTS

With all the possible variety of paint formulation and treatments, there is much variation in the physical and chemical properties of films and therefore in the corrosion behavior of painted metal parts (4), (5).

The most common paint formulations are summarized below:

- (a) Oil paints
- (b) Alkyd paints
- (c) Emulsion or water-base paints
- (d) Urethane paints
- (e) Chlorinated rubber paints
- (f) Vinyl paints
- (g) Epoxy paints
- (h) Zinc paints
- (i) Stainless steel paints

2.1.3 THE COATING SYSTEM

For sound corrosion protection, paint systems applied to metal surfaces generally include all or some of the following stages; surface Preparation, Surfaces, Pretreatment, Primer Coat, Under Coat (intermediate coat) and one or more Finishing Coats (top coats). The is shown in figure [2.2].

Primers are the key to the adhesion of the total coating and provide corrosion protection by incorporation of an inhibitive pigment. Intermediate coats provide a superior barrier with respect to aggressive chemicals in the environment or when immersed. The top coat is the first line of defense against the environment (5).

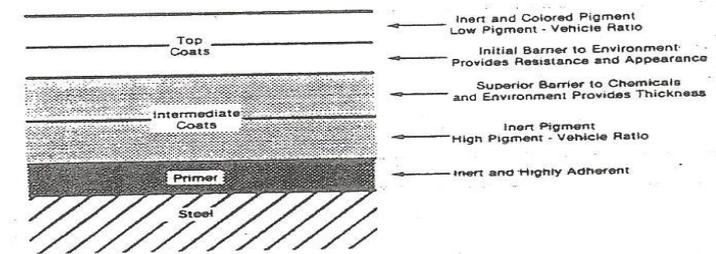


Fig. 2.2 –Five-coat impervious coating system.

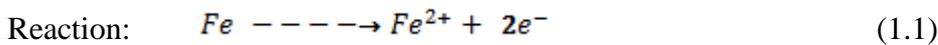
2.2 CORROSION OF BARE STEEL PANEL

Carbon steel will rust only if water or water and oxygen are both present, and the rusting process is greatly accelerated by pollutants in the atmosphere, such as sulphur dioxide from the burning of oil, coal or gas and chlorides from de-icing salts or marine atmospheres-solid pollutants such as soot or fly ash are hygroscopic and act as nuclei to concentrate corrosion causing localised form of corrosion specific points on exposed steel. (6)

2.2.1 MECHANISM OF CORROSION OF BARE STEEL PANEL

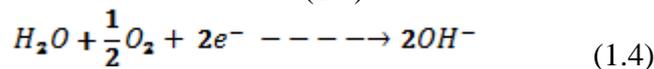
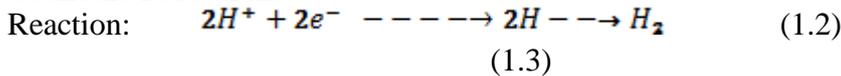
In near neutral and basic environments in the presence of oxygen from the air, water in any form viz. including normal humidity, iron immediately starts the process of oxidation and the iron goes into solution as ferrous ions and the overall corrosion reaction may be written as:

Anodic oxidation

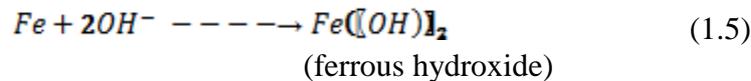


The electrons e, migrate through the steel to the cathode and react there in various ways dependent on the pH value and the availability of oxygen.

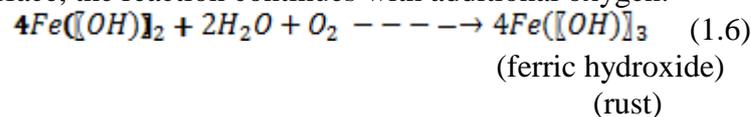
Cathodic reduction



The free hydroxyl ions (OH-) from the cathode together with the ferrous ions from the anode form ferrous hydroxide next to the steel surface. As follows:



At the air to oxide surface, the reaction continues with additional oxygen:



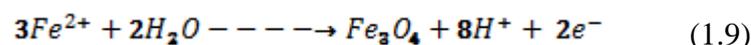
Or may be written as:



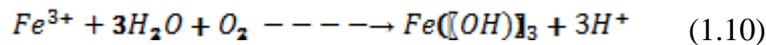
(hydrated ferric oxide)

(rust)

Under conditions of differential aeration and concentration e.g. crevices and pits.

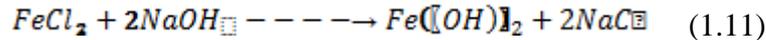


(magnetite)



(ferric hydroxide)

In the presence of sodium chloride, anodic and cathodic reactions are modified, ferrous chloride being formed at the anode and sodium hydroxide at the cathode but overall reaction result in rust formation similar to reaction (1.5) as shown above.



(1.12)

From the above the following points are evident (7):

- (a) The essential component of the corrosion cell in addition to the metal are water, oxygen and a layer of conductive electrolyte with anodic and cathodic sites.
- (b) The pH of the electrolyte at the cathodic sites can increase as a result of cathodic reactions and decrease at the anodic site as a result of anodic reaction. The pH plays an important role in the corrosion reaction.
- (c) If the water contain dissolve salts from sea water or ferrous sulphate from the reaction of sulphur pollution products with steel, then the conductivity is increased, and the extent of corrosion increased because it keeps the corroding surface wet (hygroscopic) for longer periods, and the Cl⁻ ions permeate and destroy any that oxide that formed as a protective oxide film.

2.3 CORROSION PROTECTIVE PROPERTIES OF PAINTS FILMS

It has long been recognized that one of the way paint reduces corrosion is by acting as a mass transport barrier (8). In reality there are no organic coatings which are completely impermeable. Since there always will be cathodic and anodic sites due to oxide heterogeneities, corrosion reaction may proceed under the entire coating surface.

In order to inhibit corrosion it is necessary to stop the flow of current. This can be achieved by suppressing either the cathodic or the anodic reaction or by inserting into the path of the current a high electrolytic resistance which will impede the movement of ions and thereby reduce corrosion current to vanishingly small values.

The purpose of the paint film is therefore to act as a barrier between the environment and the substrate metal and has been described as the combination of a physical barrier, chemical inhibitor and electrical resistor (9).

Electrochemically, the protection of paint film has been described as affording a degree of resistance polarization, due to the high electrical resistance of the film, cathodic polarization due to restricted permeation of oxygen through the film and concentration polarization of the anodic reaction due to the restricted migration of metal ions out through the paint film into bulk solution following corrosion of the substrate.

Therefore, an effective protective coating would be one which (10):

- (1) Permits only a low flux of charge through it
- (2) Has low solution for O₂ and H₂O
- (3) Has low diffusion coefficient for O₂ and H₂O
- (4) Resist the transfer or penetration though the coating of ions or corrosion stimulants which may contract the coating.
- (5) Resist the action of osmosis and electro-endosmosis(e.g. when coating in under cathodic protector)
- (6) Highly adherent to the substrate.

2.4. SURFACE PREPARATION

The success or failure of a coating will often be decided at the surface preparation stage. It is the most important step in painting, to such an extent that a good surface preparation and poor paint is better than bad preparation and good paint.

Degreasing is the first stage in any method of surface preparation to ensure that any oil or grease is removed. Pickling in acid solutions is used to remove residual scale. Acid cleaners

are also used to remove rust, natural air formed oxide and contain wetting agent, inhibitors and this include cathodic and anodic pickling or electrolytic pickling.

After chemical treatments, adequate washing in clean water is essential. Acidic or alkaline residue can be more harmful than his dirt removed.

In flame cleaning an oxyacetylene flame is employed, after a degreasing operation. The scale is heated in order to expand it rapidly so that it will flake off while the underlying metal is kept cool.

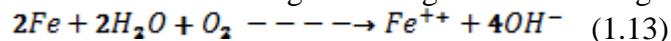
At the end of the cleaning procedure, the surface is given a protective wash, commonly a phosphate bath. This is proven the rusting of the descaled surface and need to be done fairly quickly after removal of the scale. Then it is primed and finally it is painted. (11)

2.5 CORROSION OF PAINTED PANEL

The initiation of corrosion of a metallic substance under paint is known to involve many parameters, such as osmotic pressure, electrolyte concentration, diffusion resistance and adhesion, in all of which the paint film plays a major part. The vulnerability of the substrate itself may be enhanced by a paint-coat on it.

It is also known that the water activity of immersion solution governs the adhesion of organic coatings on metal substrate, and the changes of adhesion values can be linear with the changes of water activity (12). Excellent adhesion does not necessarily mean good corrosion performance, nor does relatively poor adhesion necessarily mean poor performance. The failure of a protective organic coating by corrosion involves some mechanism of coating detachment.

The first indication of insufficient protection by organic coating against corrosion is usually by blister formation. H_2O and O_2 reach the substrate through the paint film, corrosion starts which result in ionic products dissolved in the water at the interface; then an osmotic cell driving the permeation of additional water and formation of hydroxide ions causes saponification, and because ions cannot readily diffuse out, OH^- ions may give rise to adhesion problem and local blistering according to the following equation.



(generated hydroxide ions)

2.7. ELECTROCHEMICAL METHODS OF COATING EVALUATION

Not until the mid-1970's did corrosion specialists begin to discover that electrochemical instruments could be valuable problem solving tools. There has been increasing use of electrochemistry in the study of passivity, inhibitors, organic coatings, corrosion in concrete and many other areas. The latest development being in the study of atmospheric corrosion based upon the use of a Kelvin probe to sense the potential beneath thin electrolyte film. (13).

Electrochemical methods are used in conjunction with accelerated test for organic coatings. Potential, capacitance and resistance measurements, monitor coating changes during accelerated test and are usually correlated with weight loss measurements, visual observation, and long-term performance in service.

Monitoring potential provides a mean to identify the time of film breakdown. Early work by Wormwell and Brasher (14) described the potential time behaviour and weight loss of a painted steel panel exposed to sea water, is shown in fig. [2.3]. From the figure the initial potential decrease corresponds to water and ionic absorption. The potential rise results from blocking of pores by corrosion products and/or from inhibiting action of paint constituents with a corresponding increase in ohmic resistance.

The final potential decrease corresponds to the onset of rusting and paint breakdown as reflected by weight loss.

Mayne (15) used a polarization diagram to explain, the meaning of the potential of a coated electrode. This potential is explained as being a compromise potential between the potentials of anodic and cathodic reactions taking into account the resistance of the coating at the anodic and cathodic areas. The effect of the ohmic resistance or potential drop is shown in fig. [2.4]. Similarly changes of capacitance of paint film as a function of time in sea water has been investigated and is shown in fig. [2.5].

Among the different available electrochemical methods those based on A.C. Impedance measurements have been frequently used to study the behaviour of organic coating on metals immersed in various media.

2.7.1 ELECTROCHEMICAL A.C. IMPEDANCE MEASUREMENTS

Frequently vs. AC impedance scan has been proven to be a powerful tool for the study of coating performance and undercoating metallic corrosion. The technique inherently measures conductivity, and thereby corrosion rates in highly resistive system configuration such as metal-oils, painted surfaces, and reinforcement bars set in concrete to highly complex situation as are found in multiphase alloys, non-aqueous, fused salt, and inhibited systems.

A series of papers dealing with the subject of electrochemical impedance of coated metals were published over a number of years in the Journal of Oil and Colour Chemist's Association. These articles discussed such experimental parameters pertaining to impedance studies of coated metals as:

- (i) Polarization effect
- (ii) Effects of time and potential
- (iii) Film thickness
- (iv) Measurements of constant potential
- (v) Impedance of detached paint film.

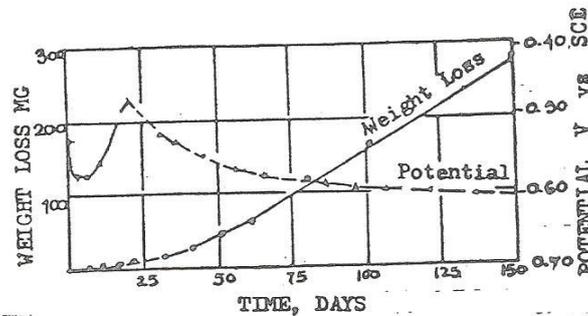


Fig. 2.3 –Potential/current diagram illustrating the polarization of the anodic and cathodic corrosion reactions on a metal specimen immersed in a low resistance medium (ref 7).

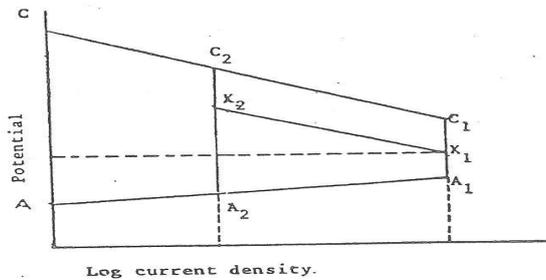


Fig. 2.4 –Schematic polarization diagram of coated steel in NaCl solution. (ref.7)

- Key:
- Anodic polarization curve.
 - Cathodic polarization curve.
 - Anodic ohmic potential drops in dilute and concentrated solutions.
 - The corresponds cathodic ohmic potential drops
 - Corresponds to the corrosion potentials and A1 to the Corrosion currents of the specimen in dilute and concentrated solutions.

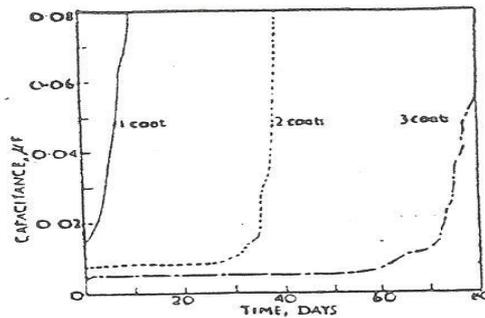


Fig. 2.5 –Capacitance-time curves for three paint systems. A sharp increase in the Capacitance values are an indication of the breakdown of paint film. (ref.7)

AC impedance measurements offer some distinct advantage over D.C. techniques:

- (a) AC. Technique use very small excitation amplitude in the range of 5 to 10 mV peak to peak. This magnitude cause only minimal polarization of the electrochemical test system.
- (b) Since ac. Impedance experiments can provide data on both electrode capacitance and charge transfer kinetics, the technique offers valuable mechanistic information and corrosion rate measurements.
- (c) It does not involve potential scan, measurement can be made in low conductivity solutions where d.c. techniques are subject to serious potential control errors. It can be used to determine the uncompensated resistance of an electrochemical cell (e.g.IR drop).
- (d) Sample deterioration can be detected at an earlier stage than visual observation, and give a clearer quantitative picture, consider being an important advantage of the AC technique.

3.0 EXPERIMENTAL PROCEDURE

The following four assessment methods are used in this study to explain and understand the data obtained:

- (a) AC. Impedance analysis
- (b) DC. Potential time method
- (c) SEM and analytical technique

3.1 AC IMPEDANCE TEST

The electrochemical cell impedance measurements were performed by generating a sinewave voltage with an amplitude of 10mv peak to peak, over a wide frequency range of (0.01 Hz to 100 KHz) using ACM instruments (AC Impedance package) fig[3.1] that has an internal automatic range changing potentiostat, and enables connection directly to an electrochemical cell. DC measurements and Offsetting enables AC test to be performed at either the rest potential or a present DC offset. Access is also available directly to the internal frequency response analyzer (FRA) for test up to 100 KHz. The instrument measurements of the impedance of an electrode over a wide frequency spectrum allow the complex impedance to be separated into individual components allowing a measure of the solution ohmic impedance R_s , the reaction impedance R_p diffusion impedance and other components such as the capacitance. Presentation of data is in the form of Bode and Nyquist diagrams.

The best feature of this instrument is its ability to automatically select the most appropriate range throughout an experiment. This becomes apparent when measuring a thin paint film which has low impedance at high frequencies and very high impedance at low frequencies.

Both FRA and the internal potentiostat were controlled by a program software RS.232 interface using an IBM compatible computer supplied with this instrument.

The impedance test was performed using a three electrode configuration:

- (a) Auxiliary platinum electrode (counter electrode).
- (b) Saturated Calomel electrode as a reference electrode.
- (c) Test specimen (working electrode).



Fig 3.1 – AC. Impedance Instruments (ACM Instruments)

3.2 DESCRIPTION OF AC IMPEDANCE CELL

The AC impedance cell shown in fig.[3.2] was consisted of a block made of Perspex that was rested on the top of each sample, thus holding the electrode at a fixed distance from the paint film, whilst measurement were made.

Four cells were design for this study and the painted steel panel selected for test was mounted horizontally. In order to prevent any leakage of the test solution a gasket was squeezed between the Perspex block and the sample.

The exposed area of the test specimen (working electrode) was equivalent to 23.52 cm². A small portion of the paint film on the upper surface edge was removed to reveal the bright steel substrate to provide electrical contact for the test cell. The panel (test sample) was connected by a wire terminating in a crocodile clip.

The auxiliary electrode and the reference electrode were moved from cell when the measurements were required.

The test solution was of fixed concentration of 3% NaCl for both the tests, viz., ac impedance technique.

Prior to all ac impedance data acquisition, the instrument automatically recorded the E_{corr} value i.e. the steady state potential or the open circuit electrode potential at the time of ac measurements, the time ranging from 0 to 336 hrs. The reference electrode fulfilled this E_{corr} measuring requirements.

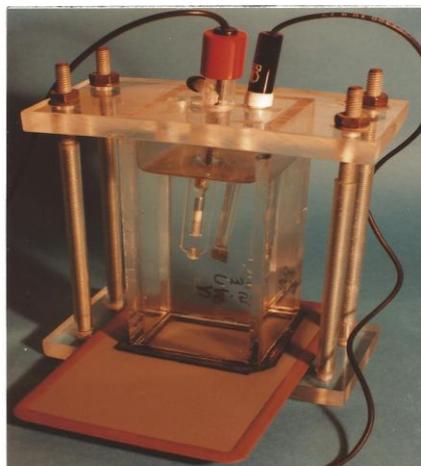


Fig. (3.2) – AC. Impedance test cell

3.3 MATERIAL AND PREPARATION

All samples consisted of steel panel of (150mm x 100mm) area cut out off sheet steel. A total of 16 samples were tested, of these samples 12 were uncoated and polished substrates the remaining 4 were not polished and were tested in the as receiver condition.

The following pre treatments were used to remove the oil and grease from all the steel sample surface:

- (1) Removal of heavy grease with cloth and absorbent paper.
- (2) Vapour degreasing in trichloroethylene for 10 minutes to remove thick grease.
- (3) Wiping with xylene (cleaning agent).
- (4) Wiping with butanone.
- (5) Finally, wiping with acetone.
- (6) Blow drying in stream of hot air.

The clean steel panels were kept in a desiccator until required for painting.

A stainless steel spreader or draw-down bar was used to apply the liquid paint to these panels. The core of the spreader bars are -10 mm diameter stainless steel, and yield a specified paint thickness based on the gauge of the wire oil wound tightly on to them at an inclination. The designation number #8, implies that the spreader will yield a coating of 100 micron thick. The panel with wet paint applied was then dried by curing at 50 degrees Celsius in the oven for 48 hours. The edges and the uncoated face were all masked with thick brown phosphate primer. Surface imperfections were scanned visually and also viewed with a magnifying glass. Experiments on paint evaluation on steel were carried out using the following paint formulation:

C1: clear polyurethane paint: polished steel substrate.

C2: clear polyurethane paint applied over salt sprayed polished substrate.

S2: HB phosphate primer MP 199, brown colour; polished steel substrate.

S1: HB phosphate primer MP 199, brown colour; applied over steel

Substrate without polishing. Two coating thickness was applied:

S1L: large thickness applied with 100 microns bar coater #8.

SIS: small thickness applied with 36 microns bar coater #6.

ZEP: zinc epoxy polyamide coating; on polished steel substrate.

BP: not coated and polished steel substrate

BN: not coated and un-polished steel substrate.

Actual thickness of the coatings of a nominal thickness of 100 microns and 36 microns were measured with an Elcometer (magnetic instrument).

4.0 RESULT AND DISCUSSION

The paint system involved in this study were selected according to the schematic plot shown in Figure [4.1].

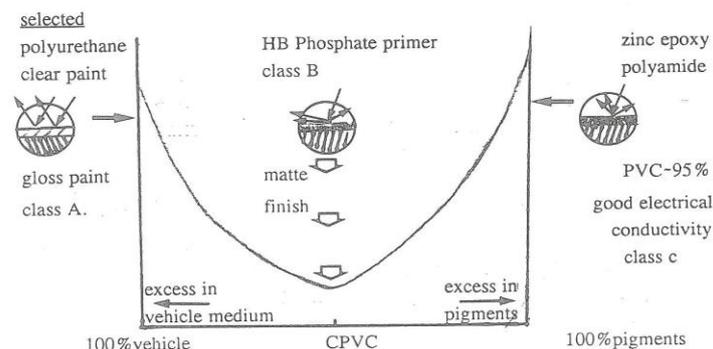


Fig. [4.1] Characteristic pigment volume content (PVC)

The figure above displays the characteristic pigment volume content (PVC) (not the commercially known brand PVC) for each type of paint formulation. The reason for this selection is to study the impedance response with time during immersion in an electrolyte and the behaviour of each system has been reported for immersion in a 3% NaCl solution over a period up to about 337 hours.

Figure 4.1 clearly classified the paint system involved as follows:

A. Polyurethane clear paint has about 85% vehicle and minor additives and pigments or extenders. The clear paint provides the possibility of observing the condition of the underlying steel substrate during exposure to the corroding solutions; and any visual deterioration of the coating material itself is not masked by a filler or pigment. Many commercial coatings are normally formulated from basically the same vehicle. Thus result obtained for one would be expected to be useful for products with different formulator but using polyurethane as the vehicle. Intersect the real axis at low frequencies but follow a straight line of 45 out of phase with the potential excitation), and from an equivalent circuit stand point the diffusion process appear to be midway between a resistor (0 phase shift) and a (90 phase shift), as in t-100 hrs. To t-250 hrs. (19)

Observing all the impedance plots reported, it can be seen that only two systems clear polyurethane and HB phosphate primer – shows a creditable performance after 337 hrs of testing. In step 1, both present an excellent performance with an impedance diagram corresponding to a capacitor, with a very high resistance in parallel. When the diagram reaches step 2 or 3 stage the damage surrounded by the coating gets to be important. Blisters and/or rust on perforated blister may be expected to appear. So, the evolution of the diagram reflects, on the test – time scale, the state (integrity) of the paint coating, anticipating in many cases, visible deterioration.

4.1. AC Impedance Quantitative Measurements;

The equivalent parallel R – C circuit Fig. [4.2] explains quite well the frequency response of the paints systems used in this study.

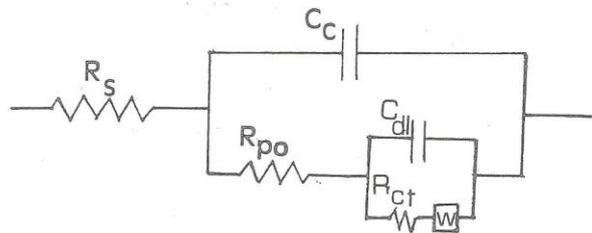


Fig. [4.2] Equivalent circuit model for a coated metal/solution interface under study.

Up to now, the real meaning of C and R for the complex system metal/ paint/ electrolyte is not very well established. In my opinion, at the beginning of the test (C_c) could be related to the capacitance of the paint film, working as a dielectric and to (R_{po}) the ohmic electrical resistance of the paint film, which acts as a barrier to the permeation of substances across it. With time new electrochemical processes would take place and the equivalent circuit would consequently change, involving now the double layer capacitance (C_{dl}) prevalent at the substrate/paint interface and charge-transfer resistance (R_{ct}) besides the diffusion impedance (Z_w).

Thus, the high frequency semicircle is considered to represent paint film information (C_c and R_{po}), whilst the semicircle at lower frequencies is thought to indicate the information of the metal substrate in conjunction (C_{dl} , R_{ct}). The values of R_{po} for the three different paints were obtained from the diameter of the high frequency. The capacitance values C_c were obtained from the frequency f_{max} at the top of Nyquist semi-circle where the reactive component reach maximum values and is given by

$$C_c = \frac{1}{\omega_{max} R_{po}} \quad (4.1)$$

Where: $\omega_{max} = 2\pi f_{max}$

These values are listed in tables [4.2 to 4.7] for the paint system studied.

4. 2. Theoretical Calculation of the Capacitance of Paint Film.

Most polymeric materials have dielectric constant value between 1 and 10. Taking a value in-between, viz., $\epsilon = 5$, and assuming a coating thickness of 100, the capacitance of this coating for an area of 1 cm can be calculated using the following equation.

$$C = \frac{\epsilon \epsilon_0 A}{d} \quad (4.2)$$

Where, C = capacitance (Farads)

ϵ' = dielectric constant of material

ϵ_0 = permittivity of free space 8.854×10^{-12}

A = area (m^2)

d = thickness (m)

Similarly, consider a metal electrode whose area is 1 cm. the actual surface area may be assumed to be one or two orders of magnitude greater, because of the surface roughness affect. The distance between the HELM HOLTZ double layer and the metal electrode is in the order of Angstroms. i.e. 100A, rather than micrometers, and the dielectric constant of the medium can be assumed to be that of water =80 (20).

Table [4.1]. Shows how, by means of the above equation, with a few assumptions regarding the nature and properties of the electrode/electrolyte interface, the capacitance of the electrochemical system can be predicted qualitatively.

Table [4.1]

Capacitance C (F m^{-2})	Effective Area (m^2)	Thickness d in (m)	Dielectric (constant) ϵ	Material
44.27×10^{-12}	10^{-4}	100×10^{-6}	5	Polymer on (Metal)
70.832×10^{-6}	10^{-3}	10^{-8}	80	Metal

Comparison of capacitance value in table [4.1] and [4.2 to 4.7]

Show very good agreement between calculated and experimentally obtained capacitance values.

In general, the HB phosphate primer and polyurethane perform like capacitors at the initial time of testing both systems show a decreasing of R_{po} with time as observed in table [4.2-4.7] and the plots, and R_{po} being the controlling resistance of the process. At the beginning, the resistance corresponds to the paint film resistance, but afterwards charge-transfer resistance is the controlling factor.

The value of the capacitance has been calculated and generally we can observe a continuous increase of capacitance with time. First of all, it shows an average value of 12 n F cm to 40.5 p F cm, which is a characteristic of a paint film in good condition. The capacitance loses its protection efficiency with time.

In this study, to explain the variation of R_{po} data with time. Two phenomena are assumed to occur simultaneously but with variable rates depending on the immersion time:

(1) Increase in the pore density, and (2) the partial sealing of the pores by corrosion products, that become more prominent over long immersion times. Similar discussion was presented by Hepburn and Co-workers (21), who described the depression of the low frequency semi-circle to the presence of two distinct types of corrosion sites: Sites that are initiating and sites that are becoming blocked by corrosion products. The value of C_c is generally considered to provide information on the degree of water penetration through the coatings and in principle its value is expected to increase with time. In this study there is little variation of C_c with

testing time for paint samples S1S, S1L, C1, C2 and may indicate a rapid water uptake in the coating during the initial stage of immersion.

The relatively constant value of C_c with time sample S2. Fig [4.3] suggests that the paint film capacitance values of the small pathways being much less than the parallel capacitance of the remainder of the film which do not contribute significantly to the overall capacitance, even though the pathway control the performance of the paint film (22).

[Table 4.2]: Sample S2; HB Phosphate Primer on polished steel substrate (thickness = 100 μm)

$C_c/\text{F.cm}^{-2} \times 10^{12}$	$f_{\text{max}}/\text{Hz} \times 10^{-3}$	$R_{\text{po}}/\text{cm}^2 \times 10^{-4}$	t_{imm} (hours)
0.305	3.16	1650	0
1	3.16	379	7
9.64	17.7	93.3	24
1	17.7	77.9	30
1	56.2	27.6	100
1	56.2	23.6	150
1	56.2	19.8	200
1	56.2	18.8	250

Key: t_{imm} = immersion time in hours in 3% NaCl.
 R_{po} = paint film resistance or (pore resistance).
 f_{max} = max. frequency at the top of Nyquist semi-circle.
 C_c = capacitance of the paint film $C_c = 1/(2\pi f_{\text{max}} R_{\text{po}})$



Plate.2: C1 after 266hrs of immersion in 3 %NaCl

4.3 Effect of interface contamination by chloride

In order to compare paint performance on well prepared and un-contaminated substrates, pilot experiments were also done on paints applied onto salt contaminated substrates, as well as unpolished substrates (as received condition). NaCl contamination levels applied to a set of steel panels, in order to evaluate the effect produced by C1-contaminant. Figure [4.5] shows the close correlation between the impedance response and visual deterioration of the sample's condition after 337 hrs. of exposure. The chloride causes immediate rusting after 48 hrs even before exposure of the panel to the test solution. Upon immersion, corrosion products form very early on perforated blister with increase in rust spot density beneath the paint film. Whereas in the case of non-chloride contaminated panel (C1) fig. [4.4], the amount of rust was little and scattered and the rust perforation of blister occurred only at the final stages of testing, i.e. towards exposure time > 100 hours. The changing impedance response at the most advanced stage of testing, i.e. smaller diameter of semi-circumference, has been clearly observed at long immersion time.

4.4 Effect of Steel Surface Preparation and Paint Thickness

Figure [4.6 and 4.7] shows the evaluation of the impedance diagram for the HB phosphate primer S1S, S1L system applied to steel surface without polishing. In the same figure photographs of paint film appearance is include after 204 hours of testing. A clear correlation can be found between these different data when the same coating has been applied over

polished steel (S2) in Fig. [4.3], the appearance of the coating is excellent and impedance indicates capacitive behaviour. However, when the paint film is applied over un-polished (S1S) steel, the impedance diagram reaches step 3 quickly, as in Fig. [4.7], which shows the Warburg diffusion control behaviour. Similar findings were observed when comparing two different paint thicknesses (S1S) and (S1L). Callow and Scantlebury (23) showed that a diffusion impedance response is associated with rust spots, occurring on a painted metal surface and due to insoluble corrosion products that build up in the pores of the coating and control the corrosion reactions. In the case of bare polished steel (BP) and un-polished steel (BN), the impedance diagram Fig. [4.8], are characterized by capacitive loops and the size of low frequency loops increase with time and the corrosion process on the bare metal is thought to be due to mixed effect of both charge transfer and mass transport. The resistance is similar to that of the double layer ohmic resistance of the solution and has a very low value when compared with the data on coated steel substrates. The presence of a capacitive loop in Fig. [4.9] may be explained to be due to the lower reactivity of unpolished (BN) panel with respect to the polished samples. R_{po} will be R_{ct} the charge transfer resistance and C_c is equivalent to C_{dL} the double layer capacitance.

[Table 4.3]: Sample C1; Clear Polyurethane Paint on polished steel substrate (thickness = 100 μm)

$C_c/F.\text{cm}^{-2} \times 10^{12}$	$f_{\text{max}}/\text{Hz} \times 10^{-3}$	$r_{po}/\text{cm}^2 \times 10^{-4}$	time (hours)
0.262	3.16	19200	0
0.531	3.16	9480	7
2.99	1.77	3000	24
11.33	5.62	250	30
11.56	5.62	2450	75
3.79	0.999	4200	100
3.32	0.999	4800	170
2.52	3.16	2000	266
503	3.16	10	337

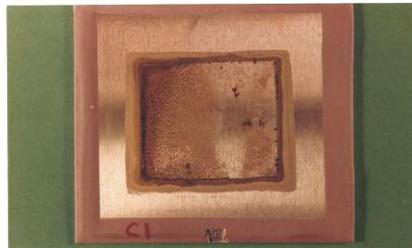


Plate.2: C1 after 266hrs of immersion in 3 %NaCl

[Table 4.4]: Sample C2; Clear Polyurethane Paint on salt sprayed polished steel substrate (thickness = 100 μm)

$C_c/F.\text{cm}^{-2} \times 10^{12}$	$f_{\text{max}}/\text{Hz} \times 10^{-3}$	$r_{po}/\text{cm}^2 \times 10^{-4}$	time (hours)
33.32	0.999	480	0
7.13	17.7	1260	7
14.4	10	1100	24
15.4	10	1030	30
12.8	5.62	2200	75
21.9	3.16	2300	100
7.63	3.16	6600	170
31.48	5.62	900	266
47.2	5.62	600	337

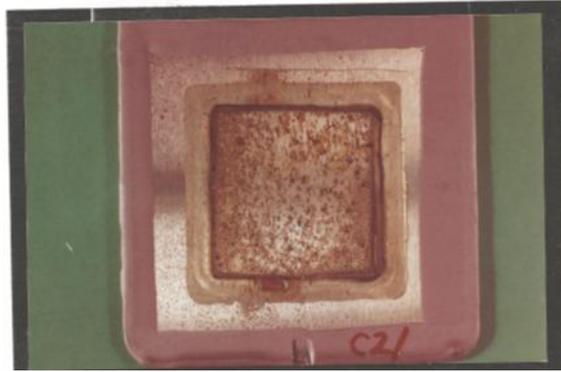


Plate.3: C2 after 266hrs of immersion in 3 %NaCl

[Table 4.5]: Sample S1L; HP phosphate Primer on unpolished steel substrate (thickness = 100 μm)

$Cc/F.cm^{-2} \times 10^{12}$	$f_{max}/Hz \times 10^{-3}$	$rpo/cm^2 \times 10^{-4}$	timm (hours)
0.796	0.999	2000	0
0.2	9.99	609	16
2	1.77	300	40
2	3.16	200	48
1	9.99	80.6	96
2	17.7	40.3	120
2	9.99	56.1	204

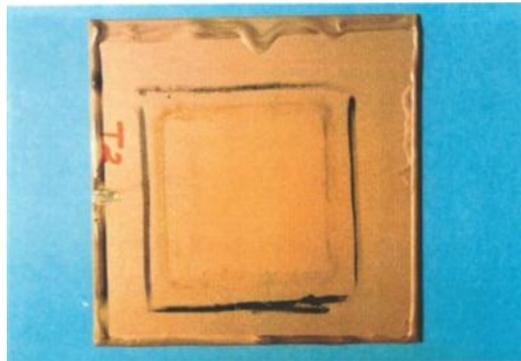


Plate.4: SIL after 204 hrs of immersion in 3 %NaCl

[Table 4.6]: Sample S1S; HP phosphate Primer on unpolished steel substrate (thickness = 36 μm)

$Cc/F.cm^{-2} \times 10^{12}$	$f_{max}/Hz \times 10^{-3}$	$rpo/cm^2 \times 10^{-4}$	timm (hours)
3	3.16	150	0
4	56.2	5.86	16
11	17.7	8.03	40
17	9070	9.07	48
26	6000	6.0	96
76	2090	2.09	120
79	2000	2.0	204

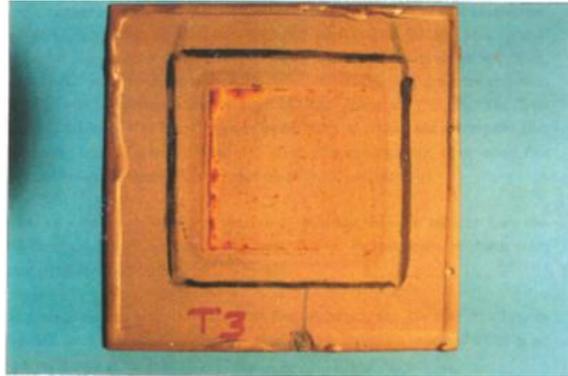


Plate.5 SIS after 204 hrs of immersion in 3 %NaCl

[Table 4.7]: Sample ZE; Zinc Epoxy Polyamide on polished steel substrate (thickness = 100 μm)

Cc/F.cm ⁻² x10 ¹²	fmax/Hz x 10 ⁻³	rpo/cm ² x10 ⁻⁴	tim (hours)
523	1.77	1.72	0
473	1.77	1.9	7
2596	0.99	0.614	24
255	1.77	3.52	30
296	0.99	5.38	75
749	1.77	1.2	100
6107	0.99	0.261	170
276	1.77	3.25	266
596	0.99	2.67	337



Plate.6: ZE sample after 337hrs of immersion in 3 %NaCl

In case of zinc Epoxy Polyamide coated steel substrate fig.[4.10], the impedance response was highly flattened curve at both 24 hrs. and 266 hrs. This is similar to the finding of Periera and co-workers (24). They proposed that this response could be due to changes in bulk properties of the film from one area to another, or could be due to different reactivities of the exposed zinc particle at the surface of the film. The impedance response can be best visualized in conjunction with plate (a) and (b) in fig. [4.10], where no rust spots and/or blister were observed. The rise in resistance and capacitance table [4.7] was thought to be affected by the presence of zinc corrosion products and by the inter-locking of voids in-between the particle. Their basic reaction involved the precipitation of basic zinc salt on cathodic areas as a result of the locally elevated pH that have markedly increased the cathodic polarization and served as a protective layer on zinc pigments surface.

4.5 Potential vs. Time Measurement

Monitoring potential provides a mean to identify the time of film breakdown. Fig. [4.11] and table [4.8] shows corrosion versus time for the paint system involved in this study. It is interesting to notice that the potentials varied with time, for (C1) the final potential rise result from the blocking of pore by corrosion products with a corresponding increase in Rpo values

at 170 hrs. The final potential; decrease in (C2) corresponding to the onset of rusting and gross paint film breakdown, which correlated well with SEM photomicrographic observation that revealed surface perforated blister as in fig. [4.5 (b)] and Plate.(3)

In the case of S2 paint system the rise in potential may be resulted from the inhibition action of the paint constituent; whilst no corrosion products were observed on the paint surface for this system.

The marked rise in potential and paint film resistance for ZE after 337 hrs. in 3%NaCl, were caused by blockage of pore by zinc corrosion products which is an important factor in the protection provided by Zinc Epoxy Polyamide.

4.6 SUMMERY

The marked drop off in R_{po} values with immersion time in 3%NaCl Fig. [4.12] was believed to be indicative of the state of degradation of the paint fil caused by ingress of the solution. The lower R_{po} values for ZE with respect to S2 and C1 was believed to be due to higher electrical conductivity and rapid water up-take of zinc paint through the voids. The higher capacitance values fig. [4.13] over that of (C1 & S2) was attributed to the rapid water uptake at the initial stages of immersion and the cumulative capacitance effect of the interfaces (e.g. substrate/paint/voids/zinc pigments).

Finally, The obtained data were analyzed and used for the ranking of the protective properties of three paint systems selected in this study. The following ranking is in the order of the most highest protective paint substrate performance.

$$ZE > S2 > C1 > C2$$

It is important to notice, that the above paint system when applied in a multi-layer paint structure, are expected to have longer life and higher performance than when it is applied as single layer over steel substrate, for example: HB Phosphate Primer is usually the first layer applied next to the steel substrate with intermediate coats and top coats applied on top of it. Sometimes, the under coats (intermediate) may contain Flake pigments which would reduce the amount of H₂O arriving at the prime layer, and therefore increased the life and performance of this paint.

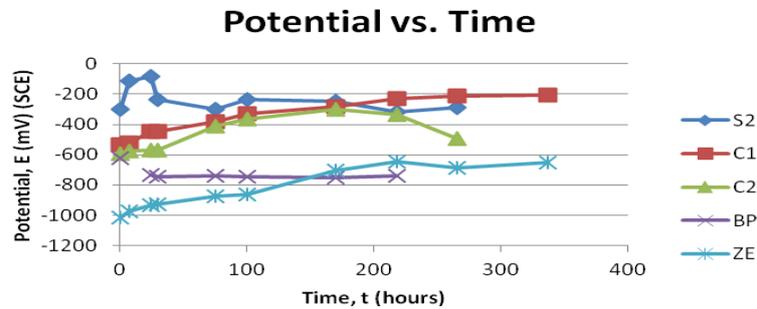
In the case of clear polyurethane paint, adhesion is the rate determining factor for protection. This paint has low adhesion on steel substrate than on polymeric painted substrate; therefore, it is mainly applied as a top coat (finishing coat) to obtain gloss aesthetic appearance and protection with multi-layer paint.

The highest performance of zinc epoxy polyamide is due mainly to sacrificial protection. Depending on the thickness of the paint layer, this paint system sometimes does not require any of the top coat and/or under-coat, and primer.

[Table 4.8]: Potential vs. Time for S2, C1, C2, BP, and ZE during immersion in 3% NaCl for test duration up to 337 hours.

ZE	BP	C2	C1	S2	tim (hours)
-1015	-622	-591	-536	-302	0
-973		-575	-520	-114	7
-932	-734	-567	-449	-83	24
-929	-748	-567	-446	-237	30
-873	-742	-409	-381	-303	75
-861	-743	-363	-332	-239	100
-702	-750	-300	-281	-250	170
-644	-742	-336	-233	-316	218
-685		-496	-211	-286	266
-652			-205		337

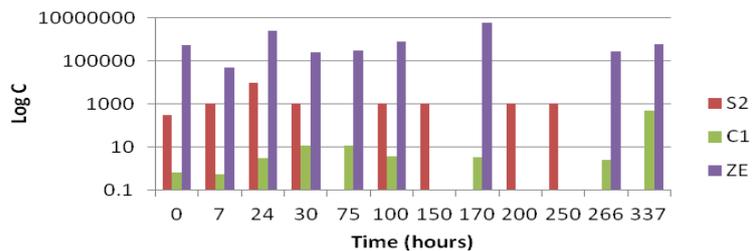
Key: S2 = HB Phosphate Primer (thickness = 100 μm).
 C1 = Clear Polyurethane Paint (thickness = 100 μm).
 C2 = Clear Polyurethane Paint – salt sprayed substrate (thickness = 100 μm).
 BP = Bare polished substrate not painted.



[Table 4.9]: C_c values determined from the high frequency part of Nyquist plots for S2, C1, and ZE paint system.
 C_c (F cm⁻²) x 10¹²

ZE	C1	S2	timm (hours)
532000	0.626	305	0
47300	0.531	1000	7
2596000	2.99	9640	24
255000	11.33	1000	30
296000	11.56		75
749000	3.79	1000	100
		1000	150
6107000	3.32		170
		1000	200
		1000	250
276000	2.52		266
596000	503		337

Capacitance value for S2, C1 and ZE vs. Time (hours)



5. CONCLUSIONS

- Electrical impedance technique seems to be a useful tool in order to follow and anticipate the real pain behavior with respect to the environmental conditions.
- It appears that an immersion time of 7 and 24 hours is necessary to discriminate between the corrosion performance of different category of coatings.
- The magnitude of impedance likely to be registered in an electrochemical system may be as follow:
 - Polymer coated metal/electrolyte system:
 Small capacitance $10^{-9} \rightarrow 10^{-12} \text{ F.cm}^2$
 High resistance $R \gg 10^6 \Omega \text{ cm}^2$

Therefore very high total impedance; high impedance interface required.

- Metal electrode/electrolyte system:
Large capacitance $10^{-2} \rightarrow 10^{-5} \text{ F.cm}^2$
Low charge transfer $R \gg 10^4 \Omega \text{ cm}^2$

Therefore low total impedance; low impedance circuit may be used.

- Impedance measurements carried out less than 100 mv peak-to-peak allow significant decrease of testing time and is dominated by the diffusion phenomenon which occurs at the same time as charge transfer, and is known as the Warburg impedance response on the Nyquist plot. Whereas, the 10 mv peak-to-peak has a negligible effect on the polarization of the sample and consequently on the testing time. Therefore, the testing is more pronounced at 10 mv than 100 mv.
- It should be cautioned, however, that correlating results from coating which are based on different types of vehicles borders and systems can result in gross errors in the evaluation of a new coating. For example, if a new coating is to be evaluated, its test results should be compared with an established coating based on a similar vehicle system.
- The decrease in paint film resistance with time suggests that solution ingress permanently damages the paint film locally at discrete pathways, increases with time. The highest paint performance was observed for ZE and has been ranked as follows:

$$ZE > S2 > C1$$

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