Chapter 2

EXPERIMENTAL

CHAPTER 2 : EXPERIMENTAL TECHNIQUES

This chapter deals with the methods of preparation of epoxy-silicone, silicone-titanate and rhodorsil silicone resins and its paints (primer & top coat). The test methods employed to study heat resistance, corrosion, physical and mechanical properties of the paints are also highlighted.

2.1 PREPARATION OF RESINS AND PAINTS

Preparation of epoxy-silicone resin
(heat-resistant anti-corrosive resin)

The following chemicals were used for the preparation :

a) Epoxy resin (epoxide value : 180-210)
b) Silicone resin
c) Hardener, Polyamide (Amine value : 340-400mg)
d) Xylene
e) Methyl Iso Butyl Ketone (MIBK)
f) Butyl cellosolve

The epoxy resin was supplied by the CIBA Geigy Ltd., Bombay, India. The hardener polyamide was supplied by Synpol Pvt. Ltd., Ohdav, Ahmedabad, India. The silicone resin was supplied by the Rhone- Poulnec (Malaysia) Sdn. Bhd., Malaysia. The solvent used for this preparation is commercial grade.

A 50 percent epoxy resin was prepared by using a 1:1:1 (v/v) mixture of xylene, butyl cellosolve and methyl iso butyl ketone (MIBK) solvents. The above resin and the solvents were added to a round bottom flask and refluxed to dissolve the resin.

A 50 percent rhodorsil silicone resin was prepared by dissolving with xylene solvent .

Then, the 50 percent rhodorsil silicone resin was stirred with the 50 percent epoxy resin solution and diluted with xylene in the ratio of 1 : 10.

A 50 percent of polyamide hardener was prepared by dissolving in 1:1:1 (v/v) mixture of xylene, butyl cellosolve and MIBK solvents.

This coating system is two pack and so the resin and hardener are mixed at the time of application. The mixing ratio of the resin and hardener is 6:1.

Preparation of epoxy-silicone primer

The heat resistant anti corrosive primer was prepared by dispersing pigments such as titanium di-oxide(TiO_2), red iron oxide, talc, mica, silica in epoxy-silicone resin using a ball mill. The mixture of pigments and resin are ground in the ball mill with the help of porcelain or iron balls. The iron balls are added for the ingredients are ground and mixed well in the ball mill for 30 minutes to get the Hegman Gauge value of seven.

Paint formulations of epoxy-silicone primer

(1) First pack

Epoxy-Silicone resin (50 percent solution)	-	185	gms
Titanium di-oxide	-	100	gms
Red iron oxide	-	125	gms
Talc	-	37	gms
Mica	-	37	gms
Silica	-	37	gms

(2) Second pack

Hardener, polyamide (50 percent solution)	-	26.5	gms

Pigment volume concentration(**PVC**) = 30

Preparation of epoxy-silicone top coat

The heat resistant anti corrosive top coat was also prepared by using the same resin and pigments used for the preparation of the primer. Here the pigment volume concentration (PVC) was considerably less than that of the primer formulation.

Paint formulations of epoxy-silicone top coat

(1) First pack

Epoxy-Silicone resin - 300 gms
(50 percent solution)
Titanium di-oxide - 80 gms
Red iron oxide - 65 gms
Talc - 25 gms
Mica - 25 gms
Silica - 5 gms

(2) Second pack

Hardener, polyamide - 100 gms
(50 percent solution)

Pigment volume concentration(**PVC**) = 18

Preparation of butyl titanate resin

The following chemicals are used for the preparation :

a) Butyl titanate monomer (L. R. grade)
b) Triethanolamine (A. R. grade)
c) Tricresyl phosphate (A. R. grade)
d) Chlorinated paraffin (L. R. grade)
e) Xylene
f) Butyl cellosolve
g) Toluene

Method of preparation

85 grams of butyl titanate monomer, 20 grams of triethanolamine and 50 grams of xylene have been taken together in a round bottom flask and refluxed for two hours. After cooling the solution the butanol formed during the reaction and the solvent are removed by distillation. 100 grams of titanate complex thus obtained is mixed with 10 grams of tricresyl phosphate and 5 grams of chlorinated paraffin used as plasticizers and dissolved in 100 grams of 1 : 2 mixture of butyl cellosolve and toluene. The solvent used are commercial grade.

Preparation of silicone resins

The following chemicals are used for the preparation :

a) Silicone resin
b) Rhodorsil silicone resin
c) Xylene
d) Butanol
e) Silicone oil

The silicone resin and silicone oil are supplied by the Metroark Ltd., Calcutta, India. The Rhodorsil silicone resin is supplied by Rhone-Poulnec (Malaysia) Sdn. Bhd., Malaysia. The solvent used for this preparation is commercial grade.

Methods of resins preparation

Two types of heat resistant resins are prepared for studying the heat and corrosion resistant properties.

Silicone-Titanate resin

Silicone resin was diluted with xylene to improve the flexibility of the coating. A small quantity of silicone oil was added as a flexibilizer. This resin solution was heated with 10 percent of polymerized butyl titanate resin for 30 minutes. After cooling the resin mixture, a 50 percent silicone-titanate heat resistant resin was prepared using a 1 : 1 mixture of butanol and xylene.

Rhodorsil silicone resin

A 50 grams of rhodorsil silicone resin is added to a round bottom flask containing 50 grams of xylene solvent to dissolve the resin. Thus, the 50 percent of rhodorsil silicone resin solution prepared for heat resistant paint preparations.

Preparation of heat-resistant paints

Three different types of heat resistant primer and top coats are prepared by using the above resins.

Preparation of heat-resistant paint (I)

[silicone-titanate]

The primer was prepared by dispersing pigments such as titanium di-oxide, mica and silica into the silicone titanate resin using an attritor for 20 minutes. The mixtures of pigments and the resin were ground in attritor with the help of porcelain or iron balls. The primer was tested for fineness of grinding using Hegman's Gauge to get a value of eight.

Composition of primer (I)

Silicone - Titanate resin	-	180	gms
Titanium di-oxide	-	120	gms
Silica	-	30	gms
Mica	-	30	gms

Pigment volume concentration (PVC) = 35

The top coat of the system was also prepared by using the same resin and the pigments used for the preparation of the silicone-titanate resin based heat resistant primer, but with a low pigment volume concentration(PVC).

Composition of top coat (I)

Silicone - Titanate resin	-	150	gms
Titanium di-oxide	-	40	gms
Silica	-	15	gms
Mica	-	15	gms

Pigment volume concentration (PVC) = 25

Preparation of heat-resistant Paints (II & III)
[with ceramic pigments]

The primers **(II & III)** were prepared by dispersing pigments such as titanium di-oxide, mica and ceramic pigments such as zirconium oxide, quartz into the silicone-titanate and rhodrosil silicone resins respectively. The ingredients were mixed using an attritor for 20 minutes to get a Hegman's value of eight.

Paint formulation of primer **II**

Silicone - Titanate resin - 360 gms
Titanium di-oxide - 240 gms
Mica - 60 gms
Zirconium oxide - 30 gms
Quartz - 30 gms
Pigment volume concentration(PVC) = 35

Paint formulation of primer **III**

Rhodorsil Silicone resin - 360 gms
Titanium di-oxide - 240 gms
Mica - 60 gms
Zirconium oxide - 30 gms
Quartz - 30 gms
Pigment volume concentration(PVC) = 35

The top coats of the system was also prepared by using the same resin and pigments used for the preparation of the primers, but with a low pigment volume concentration(PVC).

Paint formulation of top coat **II**

Silicone - Titanate resin	300	gms
Titanium di-oxide	80	gms
Mica	30	gms
Zirconium oxide	15	gms
Quartz	15	gms

Pigment volume concentration(PVC) = 20

Paint formulation of top coat **III**

Rhodorsil Silicone resin	300	gms
Titanium di-oxide	80	gms
Mica	30	gms
Zirconium oxide	15	gms
Quartz	15	gms

Pigment volume concentration(PVC) = 20

2.2 PREPARATION OF PAINTED SPECIMENS

Cold rolled mild steel (**MS**) specimens (Q-panel) were used in order to ensure uniform substrate surfaces for testing purposes. All test panels of various sizes (5cm x 7.5 cm, 10cm x 20cm and 10cm x 10cm) have been degreased with trichloroethylene and then sand blasted to SA 21/2 [71] (pressure 0.7 MN/m^2 sand size : passed through a 300 μm opening and retained on a 150 μm opening), to remove rust and mill scale from the surface of the iron.

The primers were applied over mild steel specimens by brush. After allowing the primer to dry for one day, the top coats were applied over the primer coated specimens by brush, in such a manner to build up the total dry film thickness [DFT] of the primer and top coat from 3 mil to 5 mils. M. L Staples [61] studies indicate that the heat resistant paints with not exceeding the DFT 5 mil offered best heat resistance protection to mild steel substrates. The painted specimens were allowed to cure under ambient air conditions for one week prior to testing.

Paint dry film thickness were determined by using Positest meter and the thickness were maintained within the range 3 to 5 mils.

2.3 TESTING OF LIQUID PAINTS

The liquid paint is standardized by the following tests: specific gravity, viscosity, fineness of grind and dry film thickness.

Specific gravity

The specific gravity of the liquid paint is determined by means of weight per gallon cup [72]. The cup has a known volume. The difference in weight of the cup filled with paint and the empty cup gives the weight of the known volume of paint. The ratio of the weight of the known volume of the paint to that of the known volume of water is the specific gravity of the paint.

Viscosity

Viscosity measures the fluidity of the paint. Tests for viscosity are quantitative but the method of measurement must be chosen according to the properties of the paint.

The test instrument consists of a cup with an orifice at the bottom. Both cup and orifice are of controlled volume, diameter and length. The cup is filled at a standard temperature and the time required for the paint to flow completely through the orifice is measured. The ford cup is widely used for viscosity determination [73]. The ford cup No. B4 is used in the present study.

Fineness of grind

The test is based on the use of Hegman Gage [74]. It is employed as a manufacturing control test to ascertain whether the pigment is dispersed properly and uniformly into the resin or not. The paint paste is placed into the grooves in a carefully machined steel block and a scraper is drawn over the block in the direction of grooves. The grooves are graduated uniformly in depth from zero at one end to 10 μm at the other end. The reading is taken at the point at which the specks (large particle) in the film appeared to predominate.

Dry film thickness

Many methods are used for dry film thickness [DFT] measurements. In the present work [75], instrument based on magnetic function is used. magnetic thickness gauges are based on the principle that attractive force between a permanent magnet and a magnetic material is inversely proportional to the distance between them. Posittest is based on the above principle and it is used for measuring the thickness of the coating.

2.4 DETERMINATION OF THE PHYSICAL PROPERTIES OF THE COATED METAL

Abrasion test (Taber Abraser)

In this test [76], the coated specimens of 10x10 cm square is mounted on a turn table that rotates at 100 rpm. Under a pair of weighed abrading wheels of closely controlled composition in such a manner as to cause side slip between the abrading wheels and surface of the test specimen. Abrasion resistance of coatings is generally expressed in terms of weight loss per 1000 revolution under a 1000 gms load. abrasion resistance of the primer coated panels were determined.

Conical mandrel test

This method gives an idea of adhesion and extensibility of coatings when applied to flat sheet metal of uniform surface texture [77]. In this test, the primer is coated on thin (30 - 32 gauge) cold rolled carbon steel strip of the dimensions of 10 cms width, with a maximum length of 19 cm. The test specimen is kept up right on its length wise position between the mandrel and draw bar (with the finish side towards the draw bar). It is then tightly clamped in position in such a way that end of the coated specimens adjacent to the narrow end part of the conical mandrel is almost touching the side of the draw bar level frame. The lever is moved through about 180 degree at uniform velocity to bend the specimen approximately in about 15 seconds. The bend surface of the specimen is examined for any damage to the film. The percentage of elongation is calculated by using the formula, $(t / 2r + t) \times 100$, where 't' is the thickness of the panel and 'r' is the radius of the mandrel at which the coating passes the test.

Impact resistance test

This was measured by falling weight method [78]. In this test, a tub of weight 2 pound is allowed to fall over the painted specimen from a known height. The specimen is then examined for any damage to the film.

Adhesion test (Cross-Hatch tester)

In this method the assessment of adhesion is made by the area of film detached from the substrate [79]. A coated film is cut through its thickness to the substrate by means of close parallel cuts and then another set of parallel cuts made at right angles to the former. An adhesive tape is pressed on to the surface of the cut film and sharply pulled off. The number of squares of film detached is counted and used as a comparative measure of the adhesion.

Water absorption

The coated weighed glass plates are immersed in a water bath. After 24 hours, it is taken out and the excess water is removed by filter paper and then weighed. This procedure is repeated till the identical values are obtained. From the amount of water absorbed the percentage of water uptake is calculated.

2.5 HEAT RESISTANCE TEST

The heat resistance test methods give the evaluation of the heat resistant properties of coatings designed to protect steel surface exposed to elevated temperatures during their service life.

The heat resistance capability of the painted panels were assessed in two ways.

In terms of

(1) The highest temperature sustained by the paint and

(2) The number of hours of exposure to a selected temperature endured by the paint.

The painted panels were placed in a muffle furnace maintained at different temperatures according to ASTM specification D 2485 [80]. Thus, the painted panels (Paints I, II & III) are exposed to a muffle furnace maintained at 478 K (205^0 C) for 8 hour, then increase the temperature to 533 K (260^0 C) for 16 hour. By then increase the temperature 55 K (55^0 C) increments, alternating the time periods indicated, to the final temperature maximum the coating gets visual cracking. Thus the schedule would be

478 K (205^0 C) for 8 hours
533 K (260^0 C) for 16 hours
588 K (315^0 C) for 8 hours
643 K (370^0 C) for 16 hours
698 K (425^0 C) for 8 hours
753 K (480^0 C) for 16 hours
808 K (525^0 C) for 8 hours

The epoxy silicone coated panels are exposed to a muffle furnace maintained at the test temperature for 24 hours. Thus the schedule would be

423 K (150^0 C)
473 K (200^0 C)

498 K (225^0 C)

523 K (250^0 C)

A visual inspection of the heated panels were made at the end of the each temperature. The failure of the coating was assessed for chalking, blistering, cracking and colour change. Good adhesion and absence of cracking or chalking indicate heat resistance and high thermal stability.

2.6 ACCELERATED TEST

Chemical resistance properties of the coated panels

Immersion tests

Painted panels are immersed in the following solution for a period of three months in beakers; distilled water, 5% sodium hydroxide solution, 5% sodium chloride solution and 5 percent hydrochloric acid. The plates are taken out and washed in running water, dried and the performance of the coated panels are examined as per ASTM standards. The paint was removed from the surface with knife and surface condition was examined.

Salt Spray Test [81]

Salt spray chamber has been used to simulate atmospheric marine exposure. The coated specimens are suspended in the salt spray (fog) test chamber from horizontal rods parallel to the flow of the fog and the interface between specimens and the direct impingement is avoided. The solution used is 5 percent sodium chloride. Clean compressed air is used for atomization. The atomized solution is continuously supplied to the test chamber and the temperature of the chamber is maintained at 30 - 35^0 C. Periodic examination of the specimens were made. The painted panels in triplicate are exposed in the salt spray chamber with and without scratch. After 720 hours of this test, the specimens are taken out and the corrosion spots are counted with the help of a magnifying lens. This test was conducted as per the ASTM specification B 117 for 720 hours.

Solvent resistance

The painted panels are immersed in common solvents like xylene, acetone, toluene and trichloroethylene and kept for 24 hours, and they are taken out, dried and examined for discoloration, chalking or detachment of the film.

2.7 ELECTROCHEMICAL METHODS OF EVALUATION

Several experimental techniques are used to study the performance of organic coating/metal systems [82-86] to understand the process of the corrosion. In the present study, we have used potential - time measurements and electrochemical impedance spectroscopy method to understand the above said techniques. The basic principle of these techniques will be discussed below:

2.7.1 Potential - Time measurements [87]

The simplest of all the electrochemical test is the measurements of the electrode potential of the coated metal as a function of immersion time. The coated specimen was immersed in 3 percent sodium chloride solution at 35 ± 2^0 C and the potential of the coated metal was followed by means of electrometer with time using Saturated Calomel Electrode (SCE) for six months duration. This method is shown in figure 2.1.

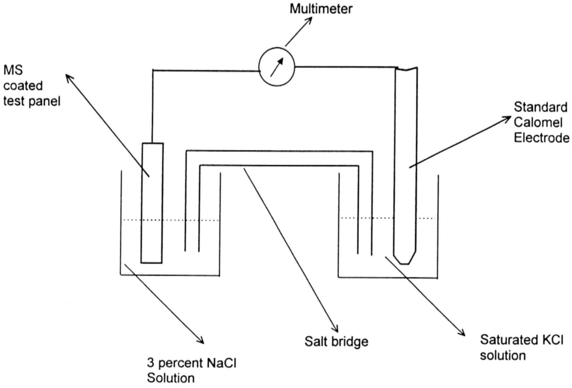
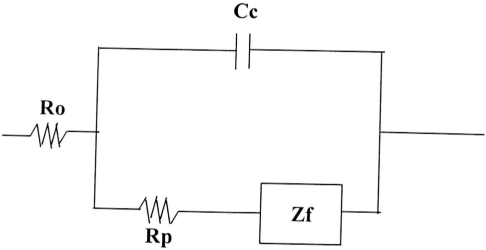


Figure 2.1 : The experimental set up for Potential - Time measurement

2.7.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is widely used to obtain good results for the electrochemical characterization of protective organic coating on metals [88-92]. The important purpose of the EIS characterization is to obtain information about the properties of the organic coating such as presence of defects, reactivity of the interface, adhesion, barrier properties and etc. Knowledge of these parameters is very useful for predicting anti-corrosive behavior of paints.

The aim of this work is to introduce the new approach of electrochemical impedance data interpretation for studying the heat resistance properties on coated metals.

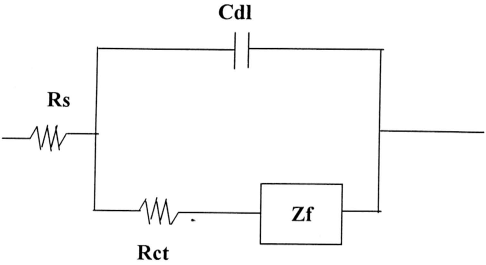


Ro = Electrolyte resistance
Rp = Pore resistance
Cc = Coating capacitance
Zf = Faradaic Impedence

Figure 2.2 : General equivalent electrical circuit for organic coated metals

The pioneering work on EIS characterization of organic coatings was done by Mansfeld et al. [93] and it is also suggested a general model of an equivalent electrical circuit from which a large number of other models can be derived (Figure 2.2). This circuit is composed of the electrolyte resistance, followed by a capacitance (coating capacitance C_C) in parallel with a resistance (the coating, pore resistance R_P) and an finally an element Z which represents the electrochemical process at the metal interface. It is the definition of Z which mainly distinguishes the circuit proposed in the literature. However, the model in figure 2.2 contains an important assumption: the ion flow and the corrosion process are localized under the coating and they are not homogeneous on the surface. This is because the corrosion process is presumed to be at the base of the defects in the coating, and not involving all the testing area (in this case the Faradic reaction would be in series with the coating capacitance).

The works of Mansfeld et al. [93,94] proposed a different circuit modeling for the corrosion reaction shown in figure 2.3. The circuit is composed of a capacitance (the double layer capacitance C_{dl}) in parallel with a resistance (the charge transfer resistance R_t) which describes the electrochemical reaction under activation control. This model of the interface is very popular and it is quite simple and suitable for many different systems, including those where there are macro-defects in the coating [95,96].



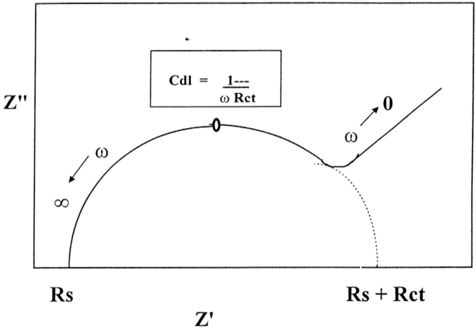
Rs = Solution resistance
Rct = Charge transfer resistance
Cdl = Double layer capacitance
Zf = Faradaic Impedence

Figure 2.3 : Equivalent electronic circuit of painted metal/solution interface

The main advantage of using the EIS technique over more traditional DC electrochemical techniques are the ability to study corrosion in low conductivity media, the use of small signals which do not disturb the system to be measured and the elimination of the errors due to a potential drop across a high-resistance organic coating. EIS seems able to detect early signs of coating degradation and also provide information on the mechanisms of corrosion of a coated metal. The EIS data for coating degradation studies are plotted either in complex (Nyquist) or bode representation.

The Nyquist Plot

In this format the imaginary component Z" is plotted against the real impedance component Z' at each excitation frequency. Figure 2.4 illustrates the response of a corroding system which has both anodic and cathodic activation controlled reaction presented.



where Z' = Real part Z" = Imaginary part

Figure 2.4 : Nyquist plot for a simple electrochemical system

This format is also known as a Cole - Cole plot or a complex impedance plane diagram. Note that at high frequencies only the uncompensated resistance contributes to the real portion of impedance, while at very low frequencies the polarization resistance also contributes to this measurement. Once the excitation waveform becomes much faster than the charge-transfer rate, the electrochemical impedance (Rct) becomes transparent to the technique. A solution resistance (Rs) on the other hand, will represent a constant impedance at all frequencies. This is consistent with the fact that Rct can also be measured by the dc technique while Rs cannot. The polarization resistance can be used, for example, to calculate the corrosion rate of an electrode materiel in a given electrolyte [97].

From this impedance plot, the values of Rs, Rct and C_{dl} can be measured as below:

$$\text{Rct} = (\text{Rs} + \text{Rct}) - \text{Rs} \quad \text{and}$$

$$C_{dl} = 1 / \text{Rct}\ \omega_{max} \text{ where } \omega_{max} = 2\pi f_{max}$$

The Bode plot

Figure 2.5 illustrates the Bode plot response of a corroding system of the coated specimens. The Bode plot is a useful alternative to Nyquist plot. The Bode plot examines the absolute impedance, as calculated by the equation $|Z|$ $(= \sqrt{Z'^2 + Z''^2})$ and the phase shift, θ, of the impedance, each as a function of frequency. Since the frequency appears as one of the axes, it is easy to understand from the plot how the impedance depends on the frequency. The plot uses the logarithm of frequency to allow a very wide frequency range to be plotted on one graph, but with each decade given equal weight. The bode plot also shows the magnitude ($|Z|$) on a log axis so that you can easily plot wide impedance ranges on the same set of axes.

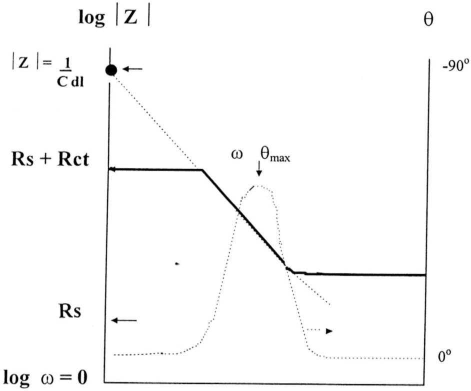


Figure 2.5 : Bode plot for a simple electrochemical system

The log | Z | Vs log ω curve can yield values of Rct and Rs. At the highest frequencies, the solution resistance dominates the impedance and log Rs can be measured from the high frequency horizontal plateau. At the lowest frequencies, charge transfer resistance contributes and log (Rct + Rs) can be measured from the low frequency horizontal plateau. At intermediate frequencies, this curve should be a straight line with a slope of -1. Extrapolating this line to the log | Z | axis at which ω =1 can yield the value of C_{dl} from the relationship:

$$|Z| = 1 / C_{dl}$$

2.8 EIS STUDIES FOR COATING EVALUATION

EIS measurements were made using a system based on *Solartron 1250 Frequency Response Analyzer* (FRA), which consists of a generator, correlator and a display. The generator supplies a sine wave voltage of low amplitude to a potentiostate (Solartron 1286) wired as a Galvanostat where it is converted to a sine wave current and then passes to a polarization cell. This cell consists of three electrode configuration, the coated metal as a working electrode, a high surface area platinum mesh and saturated calomel electrode were used as counter and reference electrodes, respectively. The impedance measurements in all cases were carried out over a frequency range of 100 kHz to 0.1 Hz using a 10 mV peak to peak sinusoidal voltage. A computerized semicircle or bode plot fitting routine was used to analyze the experimental data. The schematic diagram of electrochemical three-electrode testing cell is shown in the figure 2.6 below.

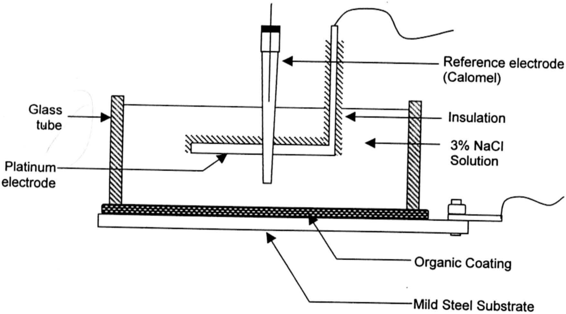


Figure 2.6 : Electrochemical three-electrode testing cell

The electrochemical tests were carried out in a quiescent aerated 3 percent sodium chloride (saline) solution. The surface area of the coated specimens exposed to the electrolyte was 1 cm^2. A three-electrode electrochemical cell was formed by sticking a glass tube onto the coated panels and previously heated painted panels and filling it with the solution of the corrosive electrolyte (3 percent saline solution).

The charge transfer resistance (Rct) is obtained from the Nyquist or Bode plots. The values of Rct + Rs correspond to the point where the plot cuts Z' axis at low frequency and Rs (solution resistance) corresponds to the point where the plot cuts the Z' axis at high frequency. The difference gives the Rct value. The capacitance (C_{dl}), values are obtained from the Nyquist plots from the following relation,

$$C_{dl} = 1 / 2\pi f_{max} Rct$$

Where f_{max} is the maximum frequency at which the imaginary part is maximum, Rct is the charge transfer resistance of the coating.

Also, the complex impedance data were used to determine the relative permitivity (ε_r) of the coating using the relation

$$C_{dl} = \varepsilon_0 \varepsilon_r A / d$$

Where C_{dl} - double layer capacitance

ε_0 - absolute permitivity of free space (8.85×10^{-12} F/m)

ε_r - relative permitivity of the coating

A - area of the coating and

d - thickness of the coating.

2.9 NON-ELECTROCHEMICAL TESTS

Scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX)

SEM was carried out with the Philips 515 scanning electron microscope. Since its invention in the early sixties, SEM has been utilized in many surface science studies[98].

Scanning electron microscope consists of 4 main parts, they are the electron source/gun, a deflection system, a detection system and a vacuum system as shown in figure 2.7. Electron gun produces a source of electrons and accelerates these electrons to an energy in the range 1 - 40 keV. Electron lenses are used to reduce the diameter of this source of electrons (spot size, less than 10 nm) and to place a small, focused electron beam on the specimen.

A deflection system consist of two pairs of electromagnetic deflection coils (scan coils) are used to control the raster of beam in order to produce contrast in an image. The interaction of the electron beam with the specimen causes the generation of many signals and the two most often used to produce images are secondary electrons (SE) and back-scattered electrons (BSE). These electrons are collected through the detectors and converted into an electrical signal. The electron beam traverse the sample surface point-by point along a line and the back-scattered electron signal is collected and generated into an image.

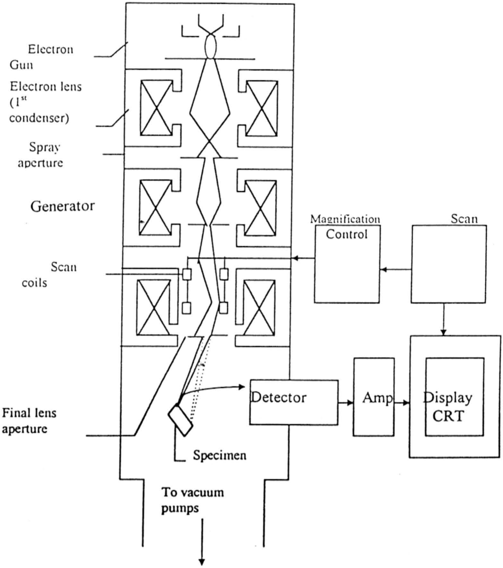


Figure 2.7 : Schematic drawing showing the electron column, the deflection system and the electron detectors [98]

X-rays emitted from a specimen bombarded with the finely focused electron - beam of the SEM can be used to identify which elements are present in the sample. This technique is known as energy dispersive X-ray analysis. EDAX was performed with a Philips 9800 equipment to analyze the chemical composition of the sample surface. X-Ray microanalysis can be considered as a quantitative and non-destructive technique that allows insitu detection of elements as low as 10^{-19}g.

Its limitations are that it cannot distinguish between ionic, non-ionic and isotopic species and EDAX in particular cannot detect the low atomic number elements. EDAX fitted with beryllium window detectors can detect elements with Z>11 while EDAX with windowless detection can detect elements with Z>5. EDAX is a surface analytical technique and because of the vacuum requirements of the SEM, it is not suitable for hydrated samples. To explain X-Ray production, consider figure 2.8 below:

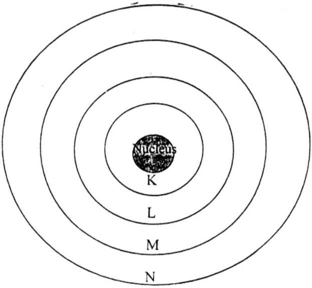


Figure 2.8 : Energy shells for orbiting electrons

The orbiting electrons are arranged in distinct energy bands or shells. In X-Ray work, these shells are designed as K,L,M,N etc. The electrons in the innermost K shell will need the most energy compared to the electrons in the L,M,N etc. Shells to be removed from the atoms.

If an incident electron from the electron gun knocks one of the K shell electrons a vacancy is created in the K shell of the silver atom. Since the vacancy is created at a higher energy, an electron from an outer shell L, M, N, etc. can fill in this vacancy, restoring the atom of the 'ground' or non-excited state. An amount of energy equal to the difference in energy between the shells involved in the transition is released as a photon of electromagnetic radiation. If the ejected electron was from an inner shell (K,L,M) then the energy is such that the photon is an X-Ray.

Although shells have distinct energies, within these shells the energy of the electron differs with the atomic number. This is because the positive charge on the nucleus is also dependent on the atomic number. Even between elements of adjacent atomic number this variation in energy is significant. Hence whenever an electron transition occurs the energy released is characteristic for each atomic number and therefore characteristic to each element.

The techniques for quantifying results is called ZAF. ZAF is an acronym from three separate effects, atomic number (Z), absorption (A) and fluorescence (F) which the method compensates for. The compositional results were reported as atomic percentage (AT%) and in weight percentage (WT%).

2.10 SEM AND EDAX STUDIES ON COATINGS

The thermal degradation of the coatings were studied using a scanning electron microscope [PHILIPS 515] equipped with an energy dispersion chemical analysis [EDAX - PHILIPS MODEL PV 3800] on heat treated panels (according to ASTM D 2485) to identify the microcracks and microchemical composition in the coatings. Prior to SEM analysis, all the heat treated panels were coated with carbon using a Bio-rad high-vacuum sputter coating unit model E5100 Series II.