Chapter 4

RESULTS AND DISCUSSION II

CHAPTER 4 : HEAT AND CORROSION RESISTANT PROPERTIES OF SILICONE-TITANATE (PAINT II) AND RHODORSIL SILICONE (PAINT III) WITH CERAMIC PIGMENTED COATINGS

4.1 Introduction

The protective nature of silicone coatings allows their use on mild steel structures exposed to high temperature environments [119-122]. These coatings are considered to be important technological developments; they improve the thermal stability of the materials ; avoid the need for replacing steel structures ; reduce workmanship and energy costs; and prolong the life expectancy of new structures.

The wide diversity of commercially available coatings raises questions as to their thermal stability for high temperature environment. These type of coatings age rapidly above 333 K (60° C) with the loss of elasticity, adhesion and protective value. In the temperature range of 473 K (200° C) to 573 K (300° C), the majority of organic film forming bases are carbonised and, in some cases, with the evaluation of aggressive gases such as hydrogen chloride from PVC. The purpose of high temperature protective coatings is two fold. On the one hand, these maintain the external appearance and heat resistance for extended periods at high temperatures, and, on the other, possess anti corrosion properties [123].

William Finzel [124] describes that silicone resins with reduced levels of volatile organic compounds (VOC) can be used on coatings without sacrificing chemical , heat and weather resistance. Earlier work has discussed how the heat and chemical resistance of silicone resins can be increased by adding manganese ore type pigments to them [125].

In chapter 3, the results of silicone-titanate based paint (paint I) incorporated with TiO_2 , mica and silica pigments were described and it was found that they were able to withstand the thermal stability upto 315°C on mild steel surfaces . Heat resistant paints are required for use on surfaces such as exterior of steel chimney, interior of furnace doors, cooking stoves, space heaters, exhaust pipes, boiler motor , etc. , besides their use in aircraft, rockets and launching pads.

In this chapter, two types of coatings (silicone -titanate resin and rhodosil silicone resin) are prepared with the pigments such as titanium di-oxide, mica, zirconium oxide and quartz which are coated on the mild steel substrates and are exposed to muffle furnace at different temperatures [80] . The preparation procedure of these coatings are given in the chapter 2. The thermal degradation of the coatings due to hot corrosion was analysed by EIS measurements and SEM with EDAX analysis. The physico-mechanical properties of the painted panels before and after exposure to the effect of heat were studied. The corrosion and solvent resistance properties of these coatings are also analysed.

4.2 Visual evaluation

The heat resistance test shows that the Si-Ti (paint II) and rhodrosil silicone coatings (paint III) will protect the surface up to 863 K (590° C) and thereafter cracking of the coatings could be observed on a visual examination. After 918 K (645° C) the coatings flake off, but there is no decolourisation of the coatings. This fact is further substantiated by observing the heat treated panels using high resolution light microscope. The coated structures are shown in the photographs [fig4.1(a-b) and 4.2(a-b)]. From the figure, it can be seen that these coatings develop cracks at 918 K (645° C).

Figure 4.1.a : Light microscopic image of Si-Ti (paint II) panels after annealing at 863 K [590 °C] with the magnification 30X

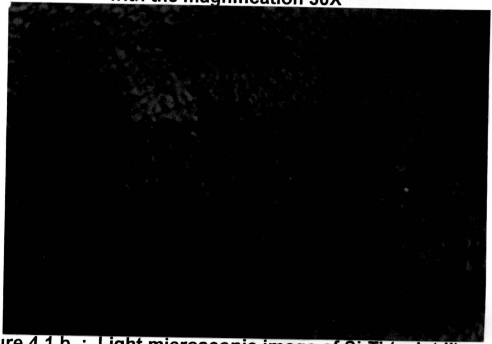

Figure 4.1.b : Light microscopic image of Si-Ti (paint II) panels after annealing at 918 K [645 °C] with the magnification 30X

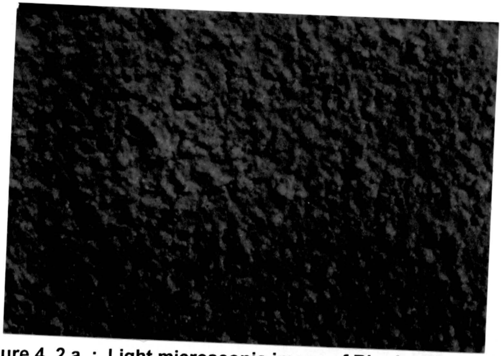

Figure 4. 2.a : Light microscopic image of Rhodorsil Silicone (paint III) panels after annealing at 863 K [590 °C] with the magnification 30X

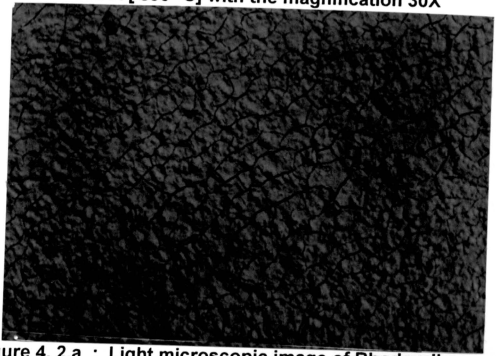

Figure 4. 2.a : Light microscopic image of Rhodorsil Silicone (paint III) panels after annealing at 918 K [645 °C] with the magnification 30X

4.3 EIS Studies

Electrochemical impedance responses obtained from the heat treated coated panels after 1 day of immersion in the 3 percent sodium chloride electrolyte are shown in the Fig. 4.3(a-f) - 4.4(a-c). These Bode plots (plotted in log |z| Vs. log f) exhibit several important features. For the two types of paints at different temperatures, the Bode plot exhibits a linear increase of log |z| versus log f. Where log |z| is invariant with frequency, this is indicative of the response expected of a pure resistor. Overall, these two segments of the plot can be considered representative of the response owing to the coating and can be modeled in terms of simple parallel resistance - capacitance (RC) equivalent electrical circuit.

In practice, as the coatings degrade , the charge transfer resistance of the coating decreases and the double layer capacitance of the coating increases. This behaviour of the coatings are due to the transport of electrolyte through the coating to the metal substrate and the formation of ionically conducting paths.

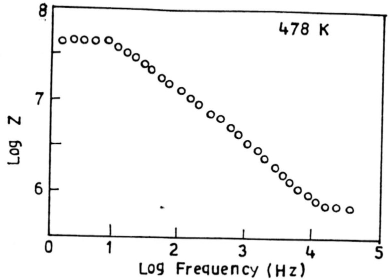

Figure 4.3.a

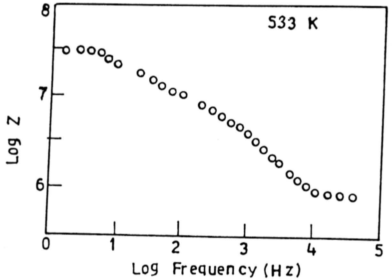

Figure 4.3.b

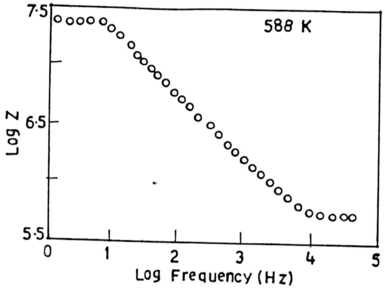

Figure 4.3.c

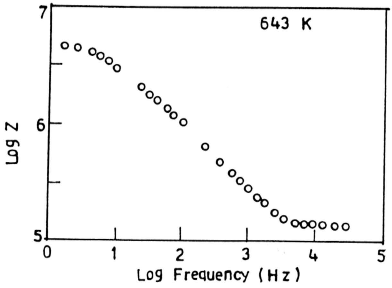

Figure 4.3.d

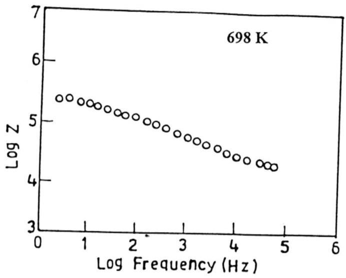

Figure 4.3.e

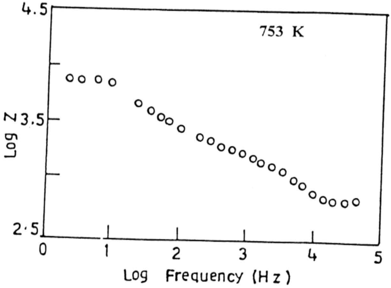

Figure 4.3.f

Figure 4.3 : Electrochemical responses for Si-Ti (paint II) coating on M.S. panels heated at (a) 478 K, (b) 533 K, (c) 588 K, (d) 643 K, (e) 698 K and (f) 753 K [one day immersion in 3 % NaCl solution]

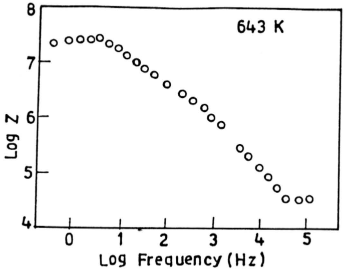

Figure 4.4.a

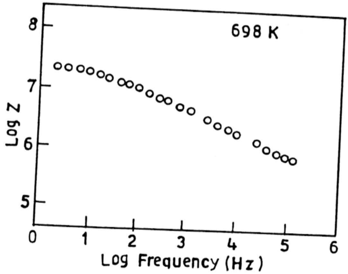

Figure 4.4.b

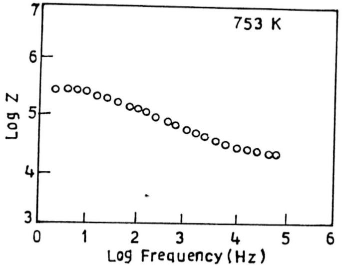

Figure4.4.c

Figure 4.4 : Electrochemical responses for Rhodorsil Silicone (paint III) coating on M.S. panels heated at (a) 643 K , (b) 698 K and (c) 753 K [one day immersion in 3 % NaCl solution]

The impedance diagrams shown in Figs. 4.3 & 4.4 indicate that with increasing annealing temperatures the impedance of the coatings get a high value in the order of 10^7 - 10^8 ohm.cm^2 and thereafter decreases considerably to low values below 10^5 ohm.cm^2 (Fig. 4.5).

In the case of Si-Ti coating system, the charge transfer resistance (Rct) of the coating is of the order of 10^7 - 10^8 ohm cm^2 at temperatures up to 643 K (370° C), beyond which the impedance drastically decreases. In the case of the Rhodrosil Silicone coating , the Rct is also of order of 10^{7} - 10^{8} ohm cm^2 upto 698 K (425° C), and decreases thereafter (figure 4.5).

These studies indicate that EIS technique can be used as a rapid method of determining the thermal degradation for heat resistant protective coatings. It can also be noted from the above systems that, at thermal stability, these coatings give a maximum value of 10^{6} - 10^{8} ohm cm^2, which is often denoting a good protection [83,115,116]. Conversely, Rct values showing a value in the order of 10^{5} ohm cm^2 can be considered a very poor protection.

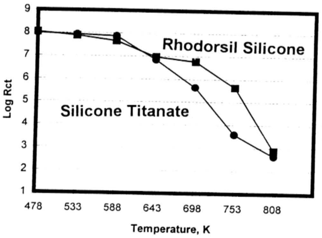

Figure 4.5 : Charge transfer resistance vs. Temerature after one day immersion in 3 % NaCl solution

From these impedance data , it is also possible to calculate values of double layer capacitance according to the following relationship:

$$C_{dl} = 1 / 2\pi f Z_{img}.$$

Where Z_{img} is the imaginary component of the impedance in a region of the spectrum where $Z_{img} \sim z$ and $Z_{img} \alpha 1/f$ [126] . Increasing double layer capacitance values are indicative of an increased water uptake (electrolyte).

C_{dl} values thus obtained are shown in the figure 4.6, plotted as a function of temperature. From these data, it can be seen that each system exhibits [Si-Ti coating at 698 K and Rhodorsil silicone coating at 753 K] the corresponding C_{dl} values increases, indicating the absorption of electrolyte. Electrolyte in the coatings substrate affects the dielectric behaviour of the coating polymer[127]. This is reflected by the change transfer resistance values which decreases in the order of 10^5 as shown in figure 4.5, where the charge transfer resistance values have been plotted against annealing temperatures.

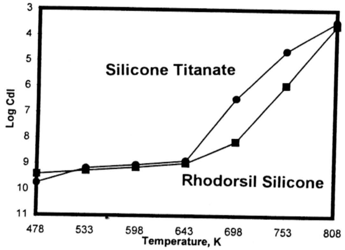

Figure 4.6 : Calculated Double layer capacitance values Cdl vs. Temerature after one day immersion in 3 % NaCl solution

Impedance responses obtained from the painted panels after 7 days exposure are shown in figure 4.7(a-f) - 4.8(a-c). The responses are very similar at temperature of 643 K (370° C) for Si - Ti coating surface (10^{6} - 10^{7} ohm cm^{2}) and of 698 K (425° C) for Rhodorsil silicone coating surface (10^{6} - 10^{7} ohm cm^{2}). Analysis of these data confirm that the electrolyte has penetrated through the pores into the coating whereas at 698 K [Si-Ti coating] and 753 K [Rhodorsil silicone coating] the low resistance values ($5.3x10^{5}$ & $4.3x10^{5}$ respectively) indicate that these could be probably microcracks present in the coated mild steel substrate. The electrolyte penetrated through these microcracks thereby resulting in the decrease of the resistance values of the coatings. This shows that the coatings are progressively deteriorated with increase in temperature.

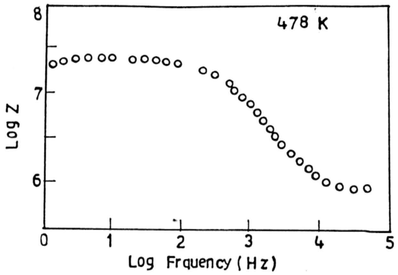

Figure 4.7.a

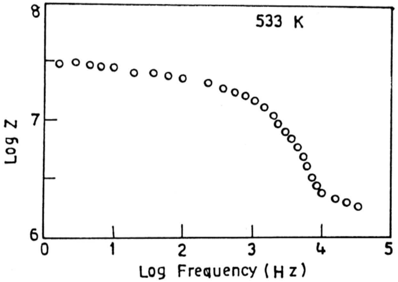

Figure 4.7.b

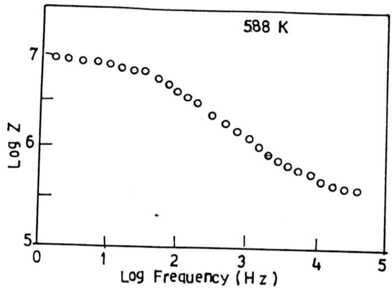

Figure 4.7.c

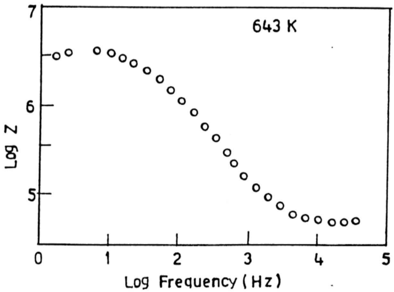

Figure 4.7.d

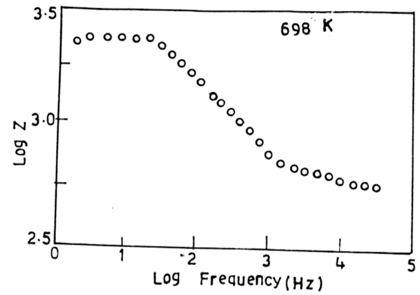

Figure 4.7.e

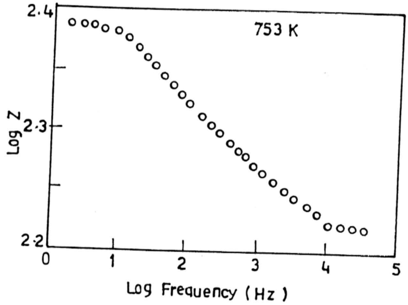

Figure 4.7.f

Figure 4.7 : Electrochemical responses for Si-Ti (paint II) coating on M.S. panels heated at (a) 478 K, (b) 533 K, (c) 588 K, (d) 643 K, (e) 698 K and (f) 753 K [seven days immersion in 3 % NaCl solution]

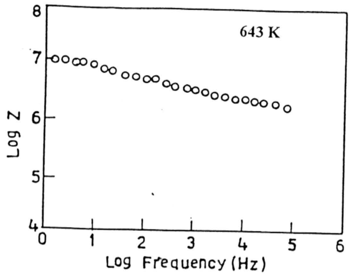

Figure 4.8.a

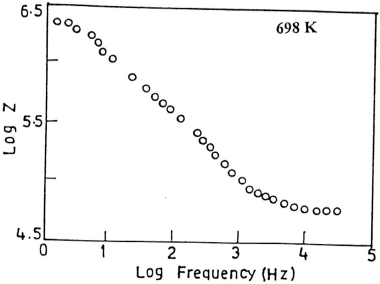

Figure 4.8.b

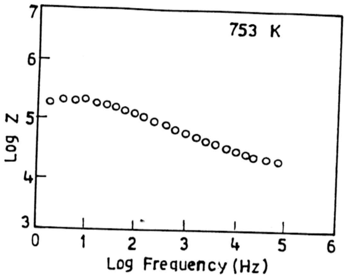

Figure 4.8.c

Figure 4.4 : Electrochemical responses for Rhodorsil Silicone (paint III) coating on M.S. panels heated at (a) 643 K , (b) 698 K and (c) 753 K [seven days immersion in 3 % NaCl solution]

4.4 SEM Studies

SEM investaigations are summarised in figs. 4.9(a-d) - 4.10(a-d). From SEM micrographs, it is seen that the pigment particles are dispersed uniformly throughout the surface of the resin coating. The SEM examination illustrates the fact that the pigments in the formulation are well packed on the surface. These studies reveal that the SEM micrographs explicitly provide evidence for microcracks present in the coated heat treated steel structures. These microcrack areas are sites of rapid contact between the corrosive environment and the steel substrate. Further, these micro cracks on the coating surfaces becomes widened as the temperature increases. It has been suggested that the mild steel substrate has been corroded because of the microcracks developed on the steel substrate due to the high temperature.

In the case of Si-Ti coating upto 643 K (370 °C) , the SEM figures 4.9(a-b) depict that no microcracks are observed on the surface of the coating beyond which thermal degradation (microcracks) start appearing on the coating. However, the Si-Ti coating is able to withstand the temperature upto 643 K (370° C) because of the ceramic pigments (zirconium oxide & quartz) which are added into the Si-Ti resin [128,129].

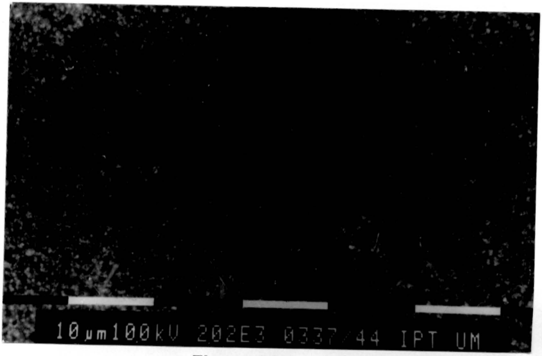

Figure 4.9.a

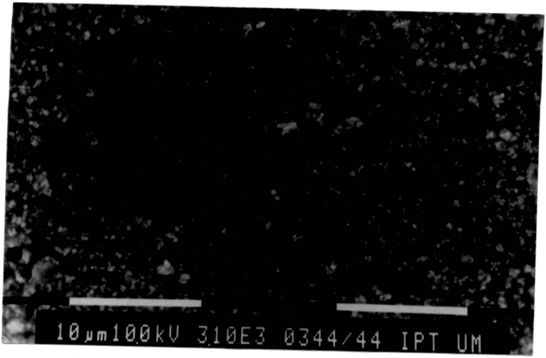

Figure 4.9.b

Figure 4.9.c

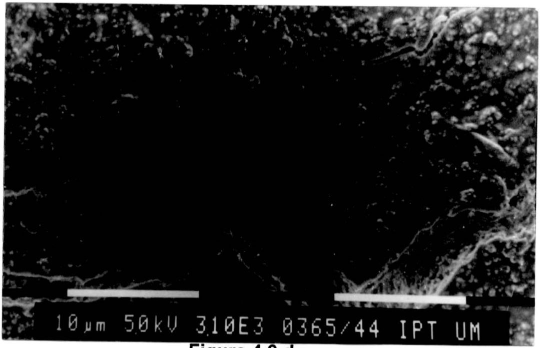

Figure 4.9.d

Figure 4.9 : SEM micrographs of the Si-Ti coating on mild steel panels heated at (a) 588 K , (b) 643 K , (c) 698 K and (d) 753 K

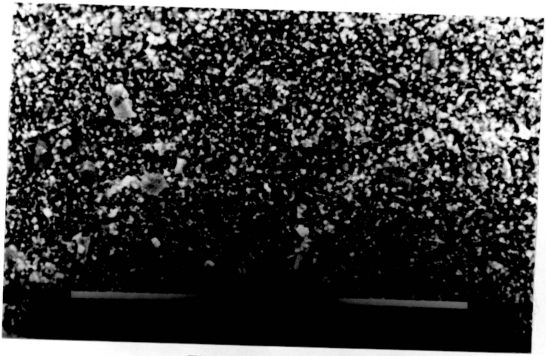

Figure 4.10.a

Figure 4.10.b

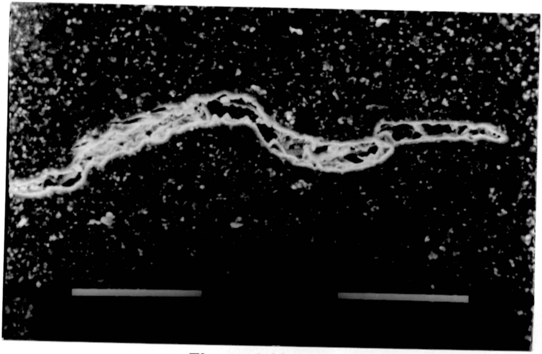

Figure 4.10.c

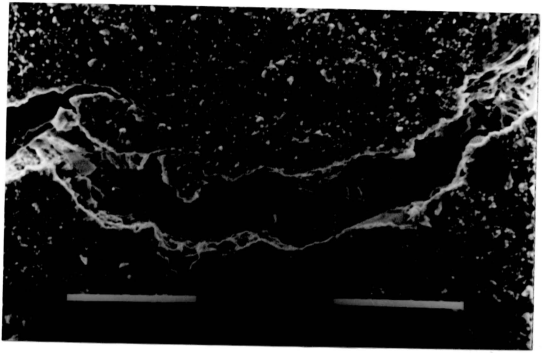

Figure 4.10.d

Figure 4.10 : SEM micrographs of the Rhodorsil Silicone coating on mild steel panels heated at (a) 643K , (b) 698 K , (c) 753K and (d) 808 K

In the case of rhodorsil silicone coating, the SEM micrographs Figures 4.10(a-b) show that the coating has better heat resistance upto 698 K (425°C) (than Si-Ti coating) and thereafter microcracks occur (Fig 4.10 c & d). This is due to the fact that the Rhodorsil silicone resin has high phenyl groups [120].

4.5 EDAX Analysis

To visualize the thermal degradation in silicone coatings after heat treatment [80], specimens were inspected using SEM coupled with EDAX.

Table 4.1 & 4.2 depict the weight % of the microchemical contents of the heat treated panels of the Si-Ti and Rhodorsil coatings by EDAX analysis. The EDAX spectrum of the coatings are shown in figure 4.11(a-c) and 4.12(a-c) respectively.

From Table 4.1 it can be seen that upto 643 K (370° C) no traces of iron are present on the Si-Ti coated panels. But at 698 K (425°C), the EDAX spectrum (Fig 4.11b&c) shows a Fe signal at about 6.3 keV and table 4.1 confirmed a small weight percentage of iron of the surface although the Si-Ti coating is found to be unaffected upto 643 K (370 °C).

In the Rhodorsil coatings, the Fe signal is observed at 753 K (480° C) (figure 4.12c) and the table 4.2 also confirmed a small weight % of iron particles. Therefore the Rhodorsil silicone coating is unaffected by the temperature upto 698 K (425 °C).

The presence of iron is due to the breakdown of the cohesive bond between the steel substrate and the coating followed by the oxidation of the mild steel substrate. This fact which has been confirmed in SEM analysis is supported by EDAX analysis.

Temperature K	Weight percentage of microchemical elements						
	Al	Si	Zr	K	Ca	Ti	Fe
588	4.72	42.76	2.91	2.60	2.40	44.61	-
643	4.95	40.34	2.80	2.73	2.73	46.45	-
698	5.55	37.03	3.03	2.75	2.59	46.94	2.11
753	4.83	32.11	3.91	2.75	2.34	51.56	2.50

Table 4.1 : Microchemical weight percentage of heat treated panels of Paint II [Si-Ti coating]

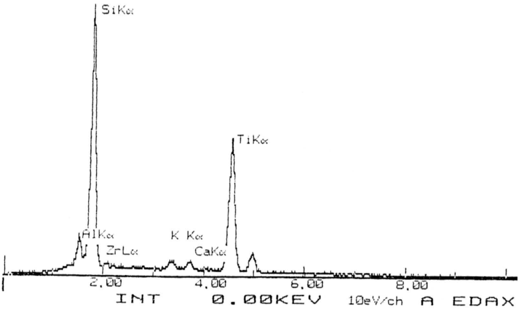

Figure 4.11.a

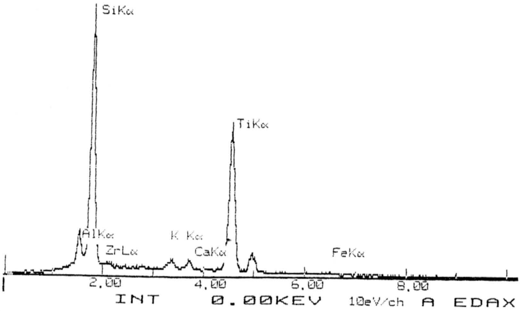

Figure 4.11.b

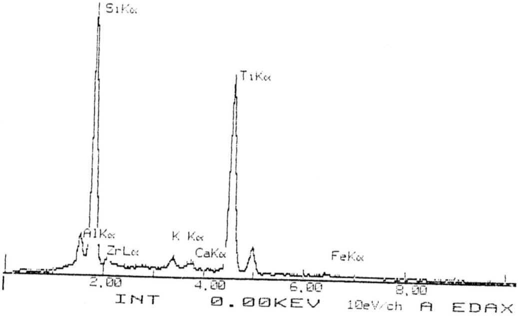

Figure 4.11.c

Figure 4.11 : EDAX pattern of the SI-Ti coating [paint II] on mild steel panels heated at (a) 643 K, (b) 698 K and (c) 753 K

Temperature K	Weight percentage of microchemical elements						
	Al	Si	Zr	K	Ca	Ti	Fe
588	4.95	40.34	2.80	2.73	2.73	46.45	-
643	5.35	36.85	3.06	2.88	2.28	49.58	-
698	5.41	35.98	3.49	2.74	2.35	50.03	-
753	5.98	35.03	3.54	2.86	2.83	47.33	2.43

Table 4.2 : Microchemical weight percentage of heat treated panels of Paint III [Rhodorsil silicone coating]

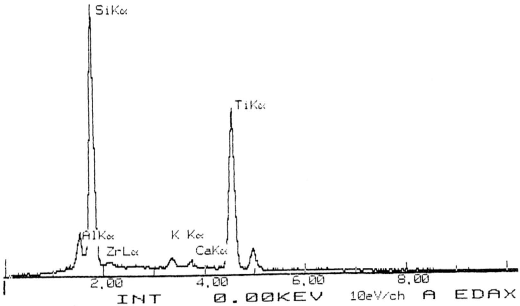

Figure 4.12.a

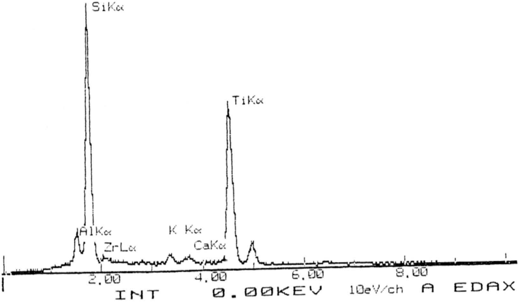

Figure 4.12.b

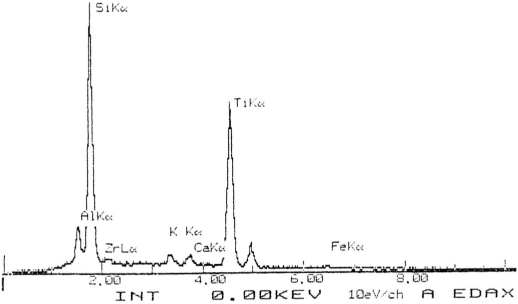

Figure 4.12.c

Figure 4.12 : EDAX pattern of the Rhodorsil Silicone coating [paint III] on mild steel panels heated at (a) 643 K, (b) 698 K and (c) 753 K

4.6 Physical and Mechanical properties

The physical and mechanical properties of the Si-Ti and Rhodorosil silicone coatings were studied. These tests include dry film thickness, drying time , scratch hardness , adhesion, impact resistance and elongation. Table 4.3 and 4.4 reveal that the physical and mechanical properties of the painted panels before exposure to heat testing. From the data of physical and mechanical properties of these coated films based on ceramic pigments (ZrO_2 , quatrz) and the coatings before heating test, it can be seen that all painted films showed moderate drying time , hardness values , good values of impact resistance and elongation property. The adhesion and water absorption tests also indicate that these coatings have better adhesion to the mild steel substrate . The water absorption character of the protective coatings are very important because the water affects the permeation of the ions , oxygen and other corrosive agents [130,131] .

The data showing impact resistance, scratch hardness and adhesion of these coatings after exposure to heating tests are given in table 4.5. From the table, it is clearly seen that after exposure to different heating temperatures [at 643 K for Si-Ti coating , 698 K for rhodorosil silicone coating], these coatings still maintain their mechanical properties and show no significant change in their adhesion, impact resistance and elongation compared with the data before heating.

No	Properties	Paint II		Paint III	
		Primer	Top coat	Primer	Top coat
1	Viscosity	94 minutes	91 minutes	95 minutes	90 minutes
2	Dry film thickness	35-40 microns	30-40 microns	35-40 microns	30-35 microns
3	Drying time	2 hours	2 hours	2 hours	2 hours

Table 4.3 : Physical properties of Liquid Paints

No	Properties	Observation (Paint II)	Observation (Paint III)
1	Extensibility (conical mandrel)	passes 0.3174 (20% elongation)	passes 0.3174 (20% elongation)
2	Scratch hardness	passes 1 kg load	passes 1 kg load
3	Impact resistance	passes 900gms tub fall from a height of 30 cm	passes 950gms tub fall from a height of 20 cm
4	Adhesion	passes 1/8" thickness	passes 1/8" thickness
5	Water Absorption	6.0%	6.2%

Table 4.4 : Mechanical properties data of the Paints

No	Properties	Observation Paint II	Observation Paint III
1	Impact resistance	passes 900gms tub fall from a height of 25cm	passes 950gms tub fall from a height of 20cm
2	Scratch hardness	passes 1kg load	passes 1kg load
3	Adhesion	Passes 1/8" thickness	passes 1/8" thickness

Table 4.5 : Impact resistance, Scratch hardness and Adhesion data of coatings (paint II & III) panels after heating test.

In chapter 3, the formulation of paint (paint I) for the protection of steel substrate were able to withstand only up to 588 K (315° C). In this present study, the heat resistant property of these coatings (paint II & paint III) were enhanced atleast up to 643 K (370° C) and 698 K (425° C) respectively by the addition of zirconium oxide & quartz pigments in place of silica (paint I). This is attributed to the fact that zirconium oxide and quartz are known to have extremely low coefficients of expansion and thermal stability [128,129].

4.7 Corrosion behaviour of the coating by EIS and salt spray test methods

Figure 4.13 shows the resistance values of the coatings which is immersed in 3% NaCl solution for 1, 7, 15 and 30 days. The corresponding impedance values were found to be in the order of 10^6 ohm.cm^2 as obtained from Nyquist plots. These values confirmed the fact that the coatings do not deteriorate under these conditions[132] .

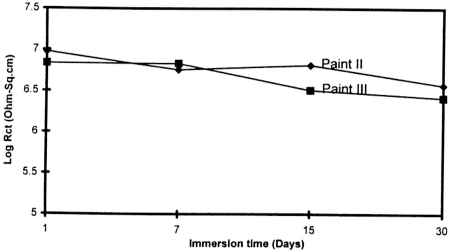

Figure 4.13 : Resistance values for the coatings on mild steel substrate in 3 percent NaCl solution at room temerature

The salt spray test after 720 hours also confirms the above results . At the end of the test, no corrosion products of iron were identified on the surface of the coated panels. Very few iron corrosion spots were seen in the coated panels after 720 hours exposure time in salt spray chamber. Thus from the results of the EIS measurements and salt spray test studies, the coatings (paint II & III) show good corrosion protection properties on the mild steel surface.

4.7 Chemical and Solvent Resistance Test

The Si-Ti and Rhodosil silicone painted panels were immersed in a solution of 5% sodium chloride , 5 % sodium hydroxide and 5% hydrochloric acid for 100 days. Periodic observation was taken after 1,7,15,30 and 60 days of duration and the performance given in table 4.6.

No	Property	Observation Paint II	Observation Paint III
1	Immersion in 5 percent sodium chloride for 60 days	No change	No change
2	Immersion in 5 percent sodium hydroxide solution for 60 days	No change	No change
3	Immersion in 5 % hydro chloric acid solution for 60 days	No change	No change
4	In xylene for 24 hours	No change	No change
5	In butanol for 24 hours	No change	No change
6	In trichloroethylene for 24 hours	No change	No change

Table 4.6 : Chemical and solvent resistance properties of the coatings

From the table 4.6, it can be seen that the chemical resistance character of these paints was good in corrosive atmospheres in acid, alkali and neutral solutions for more than 60 days duration. This is because of inorganic binder-based coatings protect the mild steel substrate by forming strong bond with the metal substrate [118].

The Si-Ti and Rhodosil silicone painted panels were immersed in common solvents like xylene, butanol, and trichloro ethylene and kept for 24 hours. The table 4.6 shows that the resistance to solvents was found to be very good.