Corrosion protective performance studies of coating systems in soda ash chemical industry

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ABSTRACT

Organic coatings are widely used to protect steel structures. The performance of the coating system depends upon the atmospheric conditions prevailing in the chemical industry. Before selecting a protective system, the corrosivity of the atmosphere has to be determined. A study has been made for selecting a good protective system for a soda ash chemical industry where chemicals such as soda ash, sodium chloride and hydrochloric acid are produced by using sea water as a raw material. Under these conditions, after collecting the corrosivity rate at various places of industrial areas, coated steel panels with various paint combinations were exposed in different sites for a period of 2 years. The performance of the coatings was monitored by EIS studies besides visual inspection. The corrosion protection performance of the various coating systems of zinc rich primer with different types of under coats and top coats has been studied and the results are reported.

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1. Introduction

Chemical plants are exposed to wide range of corrosive environment. Corrosion is the most serious problem associated with chemical and marine industries. The degradation of steel, alloys and non-metallic materials can be avoided by using suitable coating systems. Three coat systems are widely used to protect structures from this environment for the past 30 years. The three coat system of zinc rich primer/epoxy middle coat/polyurethane top coat has been designed as an excellent protective coating system. Zinc rich primer gives good adhesion and cathodic protection to the surface; epoxy system gives maximum barrier properties to the substrate and the polyurethane system has good resistance to UV radiation [1,2]. Nowadays high build coatings with normal thickness have also been used to protect structures. Further two coat systems of zinc rich primer followed by siloxane coating perform as well as that of three coat systems. The two coat systems decrease the cost and also the total painting time. In addition to this, the two coat systems offer faster recoats, faster handling and reduce labour cost [3]. Polyvinyl coating and fluorinated polymers with low thickness are also recommended for chemical processing industries [4].

In this study, the corrosion protective performance of five different schemes of three coat systems was evaluated at two highly corrosive areas and one clean atmosphere of the industrial site. The atmospheric performance of these coatings at site and the electrochemical behaviour of these coatings in the laboratory were compared and the corrosion protective performance of the coatings is reported.

2. Experimental

2.1. Atmospheric corrosivity studies

The climatic conditions prevailing in the industrial area are as follows:

Average relative humidity: 60–95%
Average temperature: 20–45 °C
Average rainfall: 350 mm

The chloride levels in the atmosphere have been found out by wet candle method [5] and the levels are given in Table 1.

The corrosivity of the industrial atmosphere has been evaluated by gravimetric method. Weighed polished mild steel specimens of 10 cm × 15 cm were exposed in the factory site on stands. After 6 month duration a set of panels were removed from the stand and the rust were completely removed by using Clark solution. The panels were reweighed and the difference in weight gave the weight loss due to corrosion. Corrosion rate of mild steel have been calculated from the weight loss data. Similarly the corrosion rate of mild steel has been calculated after 6 months, 12 months, 24 months

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Table 1
Corrosion rate of mild steel in different locations of the chemical industry.

No.	Location	Chloride concentration mg/dm^2/day	Corrosion rate (mmpy)			Remarks
			6 months	12 months	24 months	
1	Garden area	70	0.0800	0.1549	0.1817	Negligible to moderate corrosion.
2	Near cold process plant	300	0.4973	0.5406	Fully corroded	Moderate to severe corrosion.
3	Near HCl plant	550	0.8420	Fully corroded	Fully corroded	Severe corrosion
4	Near soda ash plant	250	0.3600	0.3486	0.3668	Moderate corrosion.

Table 2
Coating system on mild steel plates exposed in the soda ash factory.

Coating system	Primer				Undercoat				Top coat				Total thickness (μm)
	Binder	Pigment	PVC (%)	Thickness (μm)	Binder	Main pigment	PVC	Thickness (μm)	Binder	Main pigment	PVC	Thickness (μm)	
1	Ethyl silicate	Zinc	88	50 ± 5	Polyvinyl chloride	Red iron oxide	20	40 ± 5	Polyvinyl chloride	Rutile titanium dioxide	12	40 ± 5	130 ± 5
2	Ethyl silicate	Zinc	88	50 ± 5	Liquid epoxy Liquid polyamide hardener	Glass flakes	35	110 ± 5	Aliphatic polyurethane	Rutile titanium dioxide	20	40 ± 5	200 ± 5
3	Ethyl silicate	Zinc	88	50 ± 5	Epoxy resin E.E = 450 polyamide hardener A.V = 225	Micaceous iron oxide	30	90 ± 5	Aliphatic polyurethane	Rutile titanium dioxide	20	40 ± 5	180 ± 5
4	Ethyl silicate	Zinc	88	50 ± 5	Chlorinated rubber resin chlorinated paraffin as plasticizer	Red iron oxide and anatase titanium dioxide	30	100 ± 5	Chlorinated rubber resin chlorinated paraffin as plasticizer	Rutile titanium dioxide and chromium oxide	18	100 ± 5	250 ± 5
5	Ethyl silicate	Zinc	88	50 ± 5	Epoxy resin and hardness similar to system – 3	Anatase titanium dioxide	30	90 ± 5	Aliphatic polyurethane	Rutile titanium dioxide	20	40 ± 5	180 ± 5

E.E. = Epoxy Equivalent, A.V = Amine Value.

exposure. The corrosion rate was calculated from the following equitation.

$$\text{Corrosion rate (mmpy)} = \frac{87.6 \times \text{weight loss (mg)}}{\text{Area (cm}^2) \times \text{Time (h)} \times \text{Density}}$$

The calculated corrosion rate values are given in the Table 1

2.2. Coating systems

The details of high performance three coat systems which were applied on sand blasted steel surface (Sa 2.5) are given in Table 2. They were exposed near chemical processing area, hydrochloric acid plant and the clean environment area. The protective performance of these coating systems was periodically observed.

2.3. EIS Studies

Impedance spectroscopy is a tool to assess the degradation of the coating system quantitatively in shorter duration than by the accelerated experiments. In this study, it gives the information about the unaffected area of the exposed panels. A set of scratched specimens were removed from the exposure stand at the factory site after 24 months and subjected to AC impedance tests.

The AC impedance measurements were carried out by using an EG&G instrument model 6310 AC impedance analyzer with a computer for data acquisition and analysis. The impedance analysis of all the panels was carried out over a frequency range of 10^5 Hz to 10^{-1} Hz using a 10 mV peak to peak sinusoidal voltage. A computerized Bode plot was used to analyze the experimental data. The test was carried out in an aerated 0.5 M sodium chloride solution. A three electrode configuration was formed by fixing a glass tube on the surface of the non-corroded area of the exposed specimen (working electrode) where the coating was intact without any under film corrosion and filling it with the NaCl solution. A Platinum mesh and a saturated calomel electrode (SCE) were used as the counter and reference electrodes respectively. EIS studies were carried out after 30 min exposure of coated area to 0.5 M NaCl solution.

The impedance data were analysed with different equivalent circuits. However, the best fit of the impedance data was obtained with the following equivalent circuit with one time constant only.
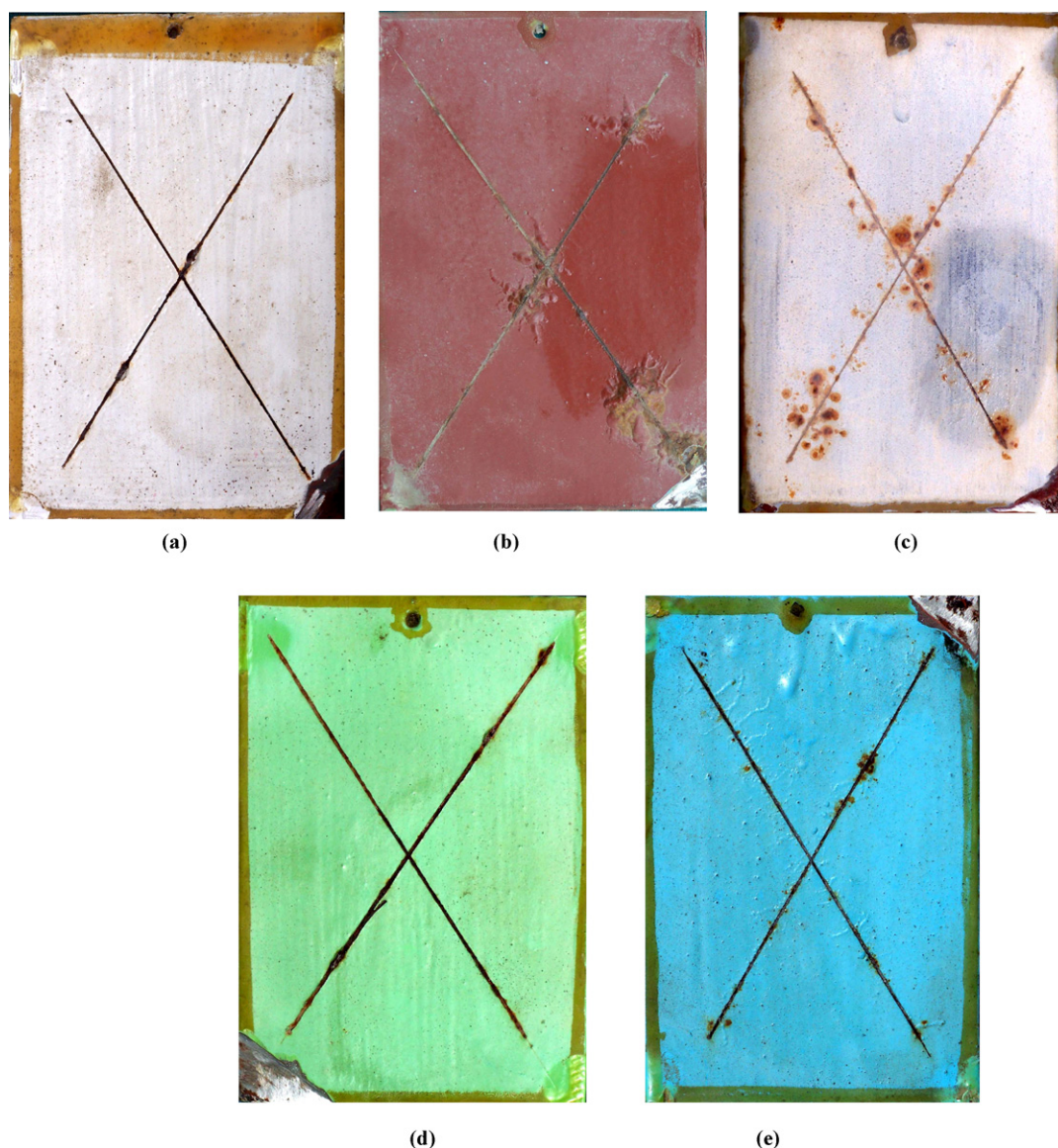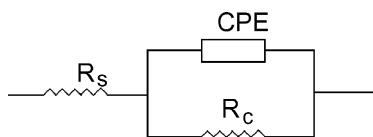

Fig. 1. Coated panels after 2 years of exposure in the garden area of the industry (a) coating system – 1, (b) coating system – 2, (c) coating system – 3 (d) coating system – 4 and (e) coating system – 5.

The relative error of curve fitted circuit element values was less than 5%.

In the above equivalent circuit, R_s is the solution resistance, R_c is the coating resistance and CPE is the constant phase element (Capacitance of the coating C_c).

Assumption of a simple $R_c - C_c$ is usually a poor approximation especially for systems showing depressed semi circle behaviour due to non-ideal capacitive behaviour of solid electrodes [6]. For the description of a frequency independent phase shift between an applied AC potential and its current response, a constant phase element (CPE) is used which is defined in impedance representation as

$$Z(CPE) = Y_0^{-1}(j\omega)^{-n} \tag{1}$$

where Y_0 is the CPE constant, ω is the angular frequency (in rad s^{-1}), $j^2 = -1$ is the imaginary number and n is the CPE exponent. Depending on n, CPE can represent resistance ($Z(CPE) = R_c$, $n = 0$), capacitance ($Z(CPE) = C_c$, $n = 1$), inductance ($Z(CPE) = L$, $n = -1$) or Warburg impedance for ($n = 0.5$) [7]. The equation used to convert Y_0 into C_c is [8],

$$C_c = Y_0(\omega_m'')^{n-1} \tag{2}$$

where C_c is the coating capacitance and ω_m'' is the regular frequency at which Z'' is maximum.

3. Results and discussion

3.1. Atmospheric exposure study [9–12]

Table 2 gives the corrosion rates of mild steel panels exposed at different sites of the factory along with the chloride present in the atmosphere. This table indicates that the panels in the garden area are not affected much due to the clear atmosphere and so this area is in mild corrosive environments. It is observed from the table that
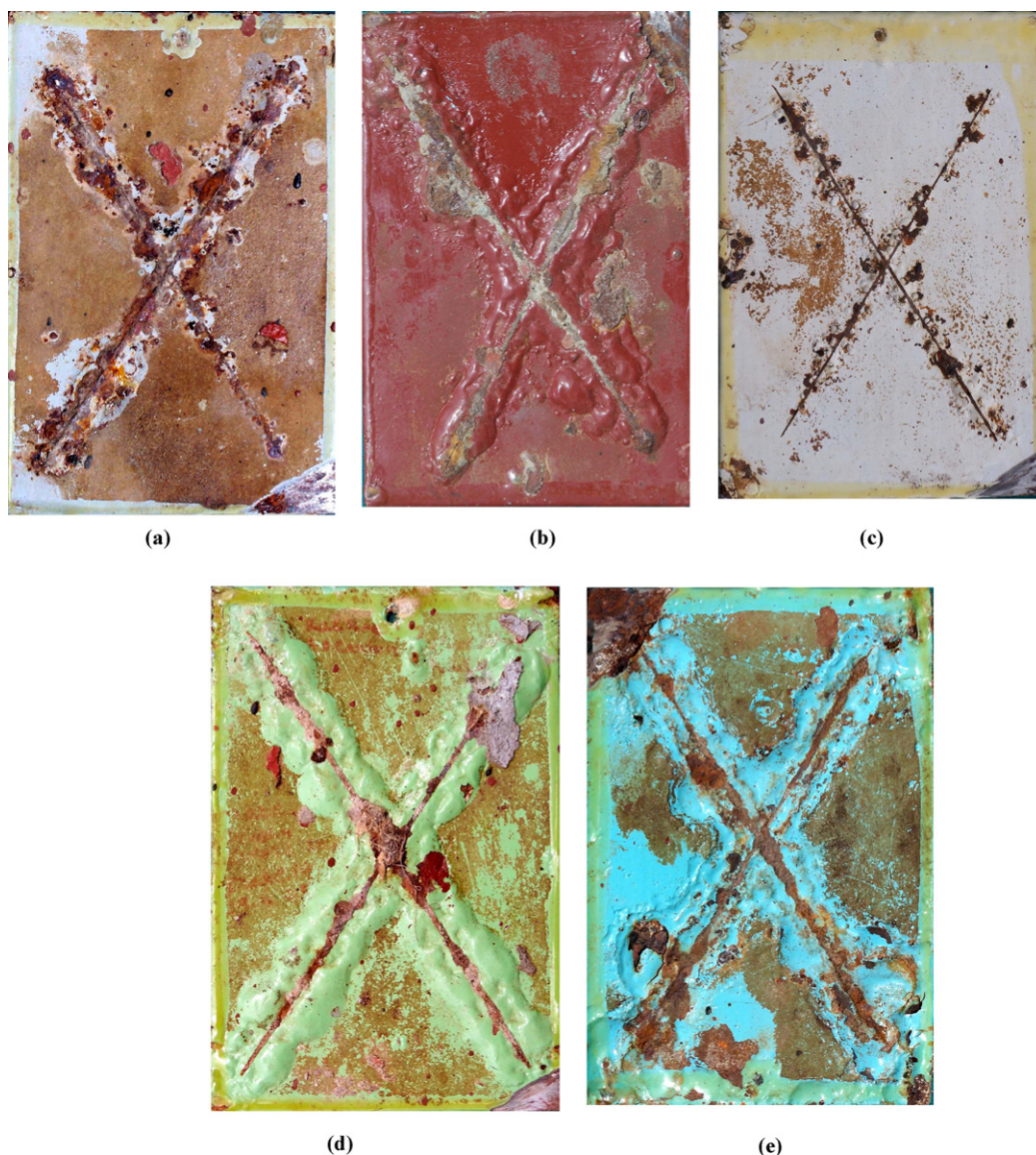

Fig. 2. Coated panels after 2 years of exposure in the processing plant area (a) coating system – 1, (b) coating system – 2, (c) coating system – 3 (d) coating system – 4 and (e) coating system – 5.

the 2 mm plates were completely corroded in the highly corrosive hydrochloric acid plant area and the processing plant site. After 6 month duration of exposure, it is found that the corrosion rate in the acid plant area (0.842 mmpy) is much higher than that of processing plant area (0.497 mmpy). This very high corrosion rate is due to the presence of hydrogen chloride acid vapours as well as high humidity atmosphere. Corrosion rate of mild steel near the soda ash plant area is moderate and the measured corrosion rate is 0.366 mmpy. Thus this study indicates that the structures near the hydrochloric acid plant require highly protective coating systems. The chemical processing plant, soda ash plant and similar processing area required moderate protective coating system.

The periodic examination of coated panels exposed in these areas indicated that there was no corrosion or blisters on the surface of the panels upto 6 months exposure. But corrosion products were seen on the surface of system 1 in hydrochloric acid plant area. Rust spots were seen along the scratched area of all the systems after 1 year exposure, except the specimens near the garden area. Fig. 1(a)–(e) show the appearance of the coating systems after exposure for 2 years in the chemical plant environment near the garden area. It is observed from the figure that the systems 2 and 3 were affected severely by this environment. On the surface of specimens coated with system 3, corrosion spots are seen near the scratched areas, whereas on the surface coated with system 2, blisters are formed along the scratched area. Small corrosion spots are seen on the scratched area of the panels coated with system 5. The coating systems 1 and 4 have better protective efficiency than the other systems with no corrosion spot formation on the surface of the panels.

Fig. 2(a)–(e) show the appearance of coated specimens in the processing area after exposure for 2 years. It is observed from these figures that the corrosion process started from the scratch area and penetrated into the coating. The propagation of the blisters is high for all the coating systems except the coating system 3 (Fig. 2c). This may be due to the effect of the flaky structured micaceous iron oxide present in the middle coat which has restricted the penetration of the corrosive ions. It is also observed that the corrosion is initiated only through the scratched area and has propagated into the coated region. But no corrosive spots are seen on the surface of the plate. This shows that all the coating systems are intact on the surface unless a holiday or damage occurs on the surface. Once damage occurs on the coating, it propagates and leads to failure.
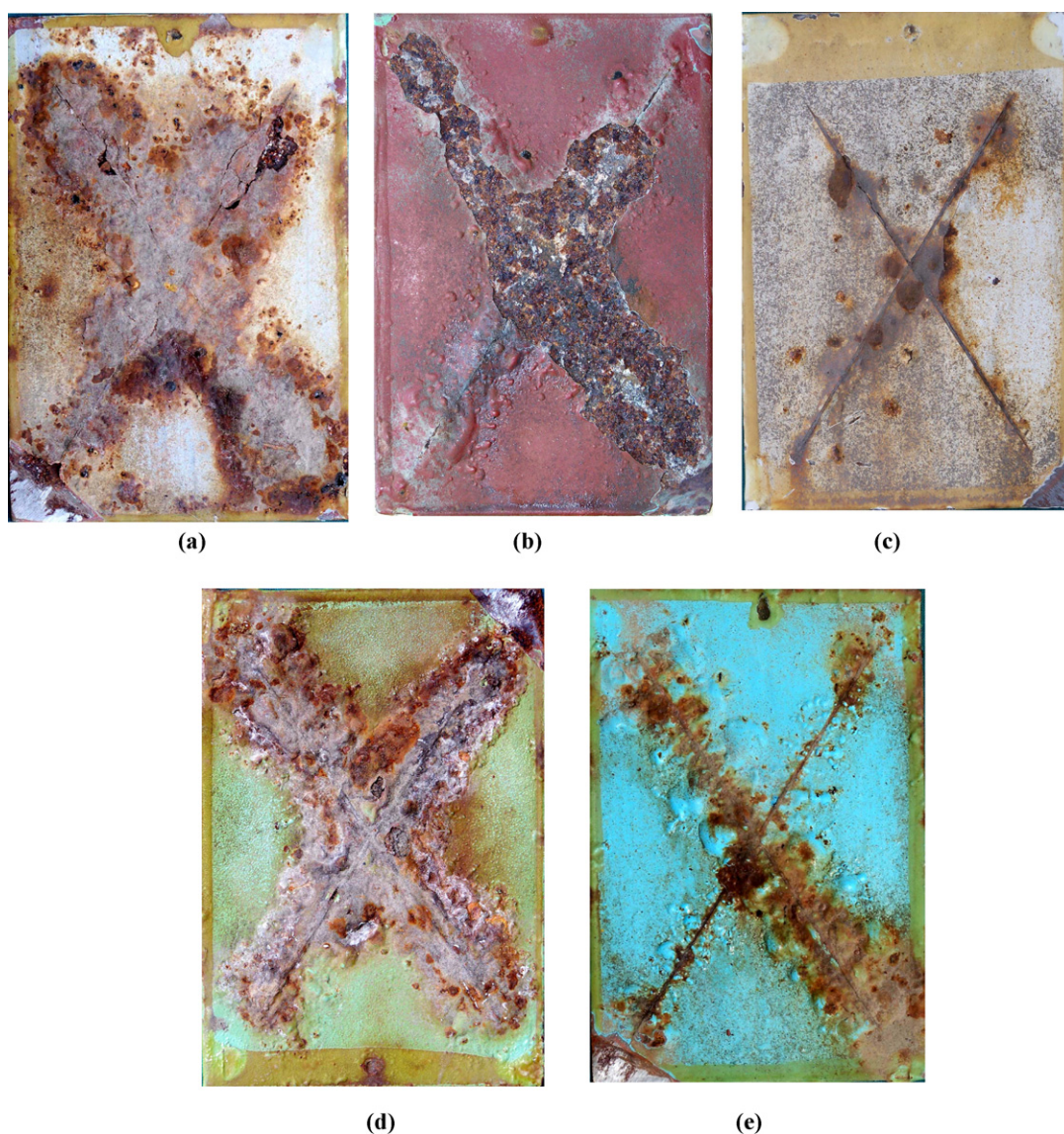

Fig. 3. Coated panels after 2 years of exposure in the hydrochloric acid plant area (a) coating system – 1, (b) coating system – 2, (c) coating system – 3 (d) Coating system – 4 and (e) coating system – 5.

Fig. 3(a)–(e) show the performance of the coating system after exposure in the hydrochloric acid plant area for 2 years. It is seen from the figures that all the coating systems allow the corrosive ions through the scratched area which heavily corrode at the centre of the panels and propagate into entire area. Unlike all other coating systems, no blister formation and propagation was observed along the scratch of the panels coated with system 3 (Fig. 3c). This result indicates that the coating system 3 adhere better on the surface than the other coating systems. But pitting corrosion spots are seen on the surface of this coated panels. This pit formation is mainly due to the attack by the hydrochloric acid fumes of the micaceous iron oxide present in the middle coat to form iron chloride, which is washed away from the surface. Thus the surface is turned to the colour of the zinc rich primer surface. No pit formation is observed on the surface of the system 1, 4 and 5. This shows that these coating systems protect the steel structures from acid atmospheres, provided no damage occurs on the surface. The coating system 2 (Fig. 3b) fails miserably in this atmosphere, which is not recommended for acid environment. In general vinyl coating system are recommended for chemical environments. But our study indicates that it is able to protect the steel structures from corrosive chemical environments, except the acidic atmosphere.

3.2. Impedance measurements

Fig. 4 shows the impedance response for all the coating systems 1–5 before exposure in the chemical plant. In general Bode plots exhibit the different stages of degradation of coatings on metal surface. The unexposed coating systems act as a pure dielectric, separating the steel substrate from the corrosive sodium chloride solution. This character of the coating system results in pure capacitive behaviour [13]. The resistances produced by all the coating systems are in the range of $3 \times 10^9 \, \Omega \, cm^2$–$1 \times 10^{10} \, \Omega \, cm^2$. This high resistance value is characteristic of well protective coatings on steel surface [14].

Fig. 5 shows the impedance spectra for coating systems exposed in the garden area of the chemical industry for 2 years. It is observed from Fig. 5 that the impedance behaviour is purely capacitive in nature for all the coated panels except the panels coated with system 1. Further the resistance produced by all the coated panels is above $10^9 \, \Omega \, cm^2$ except the coating system 1, which shows $2 \times 10^7 \, \Omega \, cm^2$. This indicates that all the coating systems are well suitable for this area of the chemical industry. Even though the

Fig. 5. Impedance spectra of coated panels after exposure for 2 years at the Garden area of the industry. (●) Coating system 1, (○) Coating system 2, (□) Coating system 3; (■) Coating system 4, (◇) Coating system 5.

coating system 1 exerted low resistance after 2 years of exposure at this site, the resistance exerted by this system is within the range of highly protective coating systems. This is also supported by Fig. 1(a), in which there is no corrosion spot on the surface. Thus, the change in the resistance may be due to the poor interlayer adhesion between the primer and the subsequent vinyl coating on the system. The vinyl coating system gives a resistance of $2 \times 10^{10} \, \Omega \, cm^2$ in the garden area of this industry, which is higher than the other coating systems. This is mainly due to the barrier effect of protection offered by the low thickness vinyl coating system. The vinyl coatings are well known for chemical and marine environment resistance properties [15]. If the thickness of the coating system is increased to the range of 200 μm level, then this vinyl system will protect the steel structures for longer duration. Fig. 6 shows the impedance response for the coated specimens exposed in chemical processing area of the industry after 2 years of exposure. It is observed that the behavior is capacitive except for the coating system 1. Further these coatings show very high resistance in the order of $10^9 \, \Omega \, cm^2$ after 2 years of exposure. This is due to the pore free packing of MIO pigments in the middle coat followed by the polyurethane sealant coat for coating system 3. Similarly the
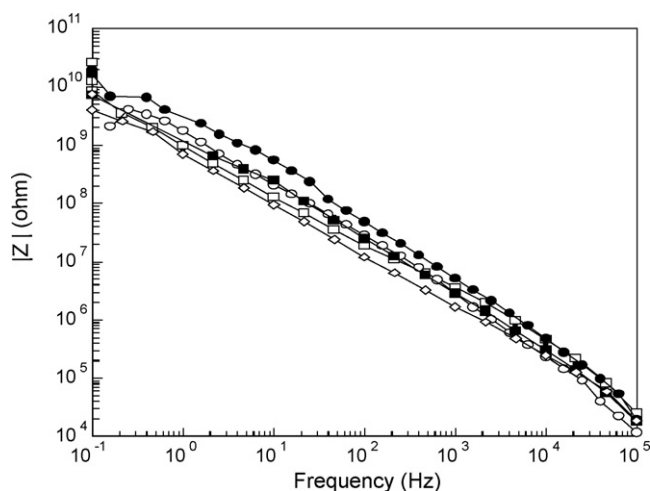

Fig. 4. Impedance spectra of coated panels before exposure in the industrial area. (●) Coating system 1, (○) Coating system 2, (□) Coating system 3; (■) Coating system 4, (◇) Coating system 5.
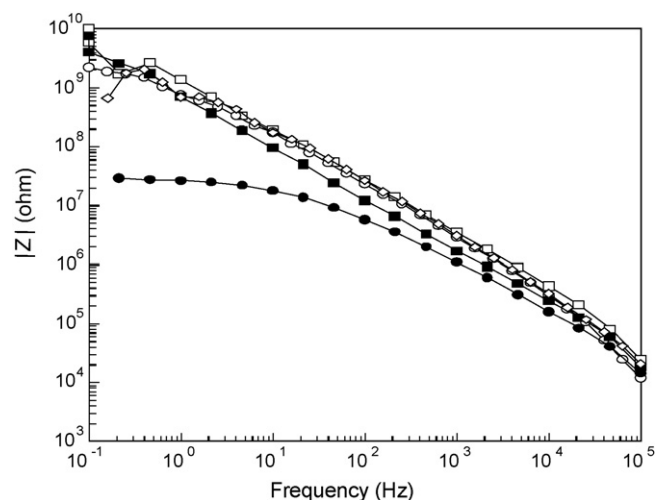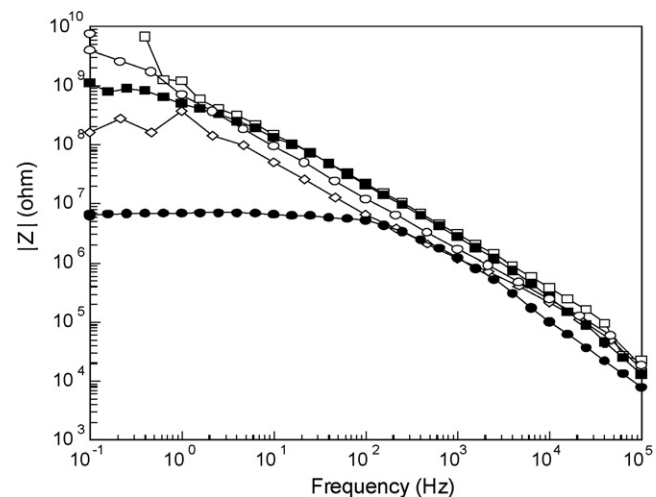

Fig. 6. Impedance spectra of coated panels at chemical processing area of the industry after exposure for 2 years. (●) Coating system 1, (○) Coating system 2, (□) Coating system 3; (■) Coating system 4, (◇) Coating system 5.
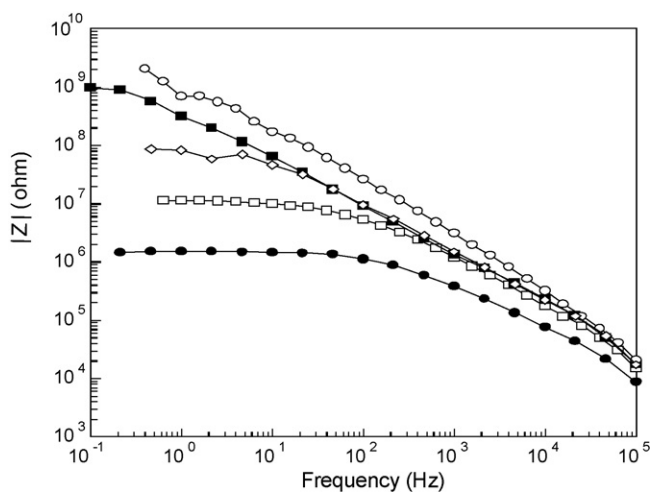
Fig. 7. Impedance spectra of coated panels exposed at Hydrochloric acid plant site after 2 years. (●) Coating system 1, (○) Coating system 2, (□) Coating system 3; (■) Coating system 4, (◊) Coating system 5.

high thickness glass flake filled intermediate coat is highly resistant to the penetration of corrosive ions for the coating system 2. The low resistance offered by the panels coated with system 1 is mainly due to the low thickness of the vinyl formulation. The higher resistance for systems 4 and 5 indicates that these systems have sufficient thickness to protect the structure from corrosion by a barrier mechanism.

Fig. 7 shows the impedance spectra for the coated panels in the hydrochloric acid plant area after 2 years of exposure. It is seen from the figure that the behavior of the coating systems are purely capacitive for systems 2,4 and 5 with the straight line inclined towards the low frequency area. The resistance exerted by these coating systems is in the order of $10^9 \, \Omega \, cm^2$. This high resistance is due to the high thickness of these formulations. In general, the chlorinated rubber based formulations (system 4) are recommended for chemical and acid environments [16], which is proved in our study. Similarly glass flake filled high build coatings (system 2) also have higher resistance to acid fumes atmosphere [17]. The system 5 protects the steel surface due to the protective nature of the epoxy –titanium dioxide combination of the middle coat followed by the polyurethane sealant coat. The low thickness vinyl coating (system 1) has resisted the penetration of hydrochloric acid fumes. But this resistance shows a decreasing trend for long-term exposure. The resistance is reduced from $7 \times 10^9 \, \Omega \, cm^2$ for unexposed panels to $9 \times 10^5 \, \Omega \, cm^2$ for the exposed panels in the acid atmosphere. The resistance $1 \times 10^7 \, \Omega \, cm^2$ exhibited by system 3 in this acid area is mainly due to the penetration of acid fumes. These vapors readily attack the micaceous iron oxide pigment in the undercoat and accelerate the corrosion process. Unlike the MIO middle coat, the titanium dioxide pigmented middle coat does not react with the

acid fumes and so the protective ability of this system is higher than that of the coating system.

4. Conclusion

This study reveals that the zinc rich primer coating provides strong adhesion on the steel plates and gives anchoring to subsequent coats. The coating resistances values of all the five systems are high, in the range of $10^9 \, \Omega \, cm^2$. This resistance decreases for the system with polyvinyl iron oxide under coat and poly vinyl–TiO_2 top coat and for the systems with epoxy micaceous iron oxide under coat and polyurethane topcoat exposed in the hydrochloric acid plant site. The photographic comparison of the exposed panels shows that the corrosion started at the scratched area and penetrates under the coated area. There is no pitting corrosion seen on the surface of the coated panels, except for the coating system of zinc rich primer with iron oxide under coat and polyurethane top coat. Thus the coating systems are able to protect the steel structures for long duration unless a damage occurs. The low thickness poly vinyl system protects the chemical industrial structures, soda ash plants and other building structures. The glass flake filled epoxy under coat with polyurethane top coat system and the system based on chlorinated rubber-TiO_2-iron oxide under coat with chlorinated rubber – Cr_2O_3 top coat are equally good to protect the entire structures of the chemical industry for longe duration. Thus the electrochemical impedance studies are able to differentiate between the protective performance of the coating systems exposed in chemical industrial environment.

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