CHAPTER - V
ELECTROCHEMICAL BEHAVIOUR OF CASHEW NUT SHELL LIQUID (CNSL) RESIN BASED METAL POWDER PIGMENTED PRIMERS AND FINISH COATED SYSTEMS IN CHLORIDE MEDIUM

In this chapter the structure of the CNSL and the resin prepared from this liquid with formaldehyde as described in Chapter III are investigated by I.R. spectroscopic technique. Optimisation of the pigment weight ratio of the metal powder pigments in the binder by potentiodynamic method is carried out. The best primer's physical and electrochemical aspects of protection to the metal surface is described. The surface morphology of the coatings are studied by SEM analysis. The finish coated system's protective behaviour is also studied by electrochemical methods.

5.1. INFRA-RED SPECTRAL ANALYSIS OF THE STRUCTURE OF CNSL RESIN

The structure of CNSL monomer and its constituents were analysed by Symes and Dawson [1]. They reported that the CNSL is similar to meta substituted cresol, but the substituent in CNSL is long unsaturated side chains of mono, di and tri olefins. Gedam et.al [2] examined the structure using NMR spectroscopy reported an average of two double bonds in the alkyl side chain.
Figure 5.1 shows the I.R. spectra of CNSL monomer, the strong broad band between 1000-1200 Cm\(^{-1}\) is due to the presence of C\(_{15}\) side chain in the phenol molecule. The sharp peak present in between 1450-1500 Cm\(^{-1}\) is due to the aromatic ring present in the monomer and the sharp peak that appears in between 1400-1350 Cm\(^{-1}\) is due to the presence of phenolic -OH group in the monomer. The figure 5.2 shows the I.R. spectra of the condensation product obtained from the monomer and the formaldehyde. The peaks obtained are similar to the monomer except a broad band formed between 1200-1270 Cm\(^{-1}\). This band is due to the formation of -CH\(_2\)OH group. This -CH\(_2\)OH broad band is similar to the -CH\(_2\)OH group of benzyl alcohol structure [3]. Further the polymerisation reaction is continued by the reaction of the -CH\(_2\)OH group with the other molecules of CNSL monomers, the possible structure of the condensation polymer of CNSL resin is as follows.
Fig. 5-1 I.R. Spectra of cashew nut shell liquid
Fig. 5.2 I.R. Spectra of cashew nut shell liquid resin
The CNSL polymerised product is a highly viscous resin and it is soluble in all kinds of solvents [4] which can be used for primer formulations [5]. The side chain present in the molecule acts as internal plasticizer and the properties of the resin is similar to that of phenolic resins. For these reasons this resin is used for many primer formulations.

5.2. OPTIMISATION OF PIGMENT WEIGHT PERCENTAGE IN PRIMERS BY ELECTROCHEMICAL TECHNIQUE

As the corrosion protection quality of the polymer coatings increases, the electrical resistance of paint is also increased. Michel Joly et.al [6] optimised the CPVC value of primers through polarisation resistance method. Similarly in this investigation, the critical pigment weight concentration (CPWC) of the metal powder pigments in primers has been optimised by the corrosion current determined from the Tafel extrapolation technique.

5.2.1. Optimisation of Nickel pigment

The figure 4.3a shows the polarisation behaviour of mild steel in 3% NaCl solution. Fig. 5.3 shows the polarisation behaviour of 60% Nickel pigmented primer coated mild steel in 3% NaCl solution for different durations. The shape of the polarisation curve as shown in
Fig. 5.3. Potentiodynamic polarisation of CNSL based NiRP on M.S. plate in 3% NaCl solution for different duration.
@ -1 day, ⑥ - 7 days, ② - 15 days, ④ - 30 days, ⑧ - 60 days.
the figure is mixed control reaction type. This behaviour depends upon the protective capability of the paint film due to the delaying of the transit of reactive species into the substrate. The corrosion current and the shape of the curve give the qualitative information about the primer. It is seen from the figure 5.3 that the curves are steadily changing in both the directions and there is no greater change in corrosion current upto 30 days of study. This shows that the primer is still intact on the surface without the formation of any passage to the corrosive ions. The shape of the polarisation curves are equated with the protection offers by the primer [7]. After 60 days, a slight change in the behaviour of the polarisation curve is observed, which shows that the coating has allowed to diffuse the corrosive ions through the film, and so the corrosion current increases with duration.

Similarly the corrosion current derived from the polarisation curves of 20% to 80% nickel pigmented primer coated mild steel plates in 3% NaCl solution for different duration is plotted against various PWC as shown in the figure 5.4. It is seen from the figure that the corrosion current slowly increases from 20% pigment weight concentration (PWC) to 40% PWC and thereafter slowly decreases
Fig. 5.4. Relationship between the corrosion current and the PWC of nickel pigmented CNSL resin in 3% NaCl

- 1 day, - 7 days, - 15 days, - 30 days, - 60 days.
upto 60% PWC. After 60% PWC, the corrosion current is steadily increased with an increase in pigment concentration. This behaviour of the corrosion current with time is observed throughout the period of this study.

These results indicate that the increasing trend of corrosion current at lower concentration of nickel in Cashew Nut Shell Liquid (CNSL) resin is due to the barrier effect of the binder. This barrier effect decreases by the addition of the pigment upto 40% PWC. This is due to the insufficient pigment particles in the medium, which leads to the voids in the continuous binder film on the surface. Further addition of the nickel powder will increase the particle to particle contact within the primer coat to reduce the possibility of porous coating, which leads to the decreasing trend of the corrosion current. The corrosion current is very low at 60% PWC primer and thereafter the corrosion current is increased with the addition of the pigment. This shows that further addition of nickel lead to non-continuous coating on the surface and subsequently the primer failed to protect the surface. This study indicates that the 60% nickel pigmented primer gives very low corrosion current compared with the other primers, and so 60% nickel is chosen as the critical pigment weight concentration in CNSL medium.
5.2.2. Optimisation of stainless steel pigment

Similar to the nickel rich primers, the polarisation curves of stainless steel pigmented primers are also mixed control protection type. The slope of the cathodic and anodic polarisation curves are changed, but not much change in the corrosion potential is observed. This shows that the shifting of the slope either in anodic or cathodic direction does not occur during the course of the study. The values of corrosion current obtained from the polarisation curves of stainless steel pigmented CNSL coated mild steel in 3% NaCl solution for various duration is plotted against different pigment weight concentration as shown in the figure 5.5. It is clearly seen from the figure that the corrosion current decreases with the addition of pigment upto 60% pigment weight concentration and thereafter the corrosion current is increased with the addition of the pigment.

These results show that the addition of stainless steel pigment in the binder will decrease the corrosion current which indicates that in addition to the barrier effect of the binder, the pigment will give protection to the surface. This trend is observed upto 60% of stainless steel pigment in the binder, afterwards by the addition of the pigment resulted in an increase in the corro-
Fig. 5.5. Relationship between corrosion current and the pwc of stainless steel pigmented CNSL resin in 3% NaCl

- 1 day, ○ 7 days, ○ 15 days, △ △ 30 days.
sion current. This shows that further addition of the pigment will lead to the pores formation on the surface of the coating. The behaviour of stainless steel pigment in CNSL binder medium shows that at 60% pigment weight concentration gives better protection than the other percentage of the pigment in this medium.

5.2.3. Optimisation of zinc pigment

At the beginning stage of the polarisation curves of the zinc pigmented primers show that the corrosion process is controlled by the cathodic reaction characterised by the large cathodic over potential. This trend is observed upto 30 days of the polarisation studies. Sixty days of this study indicates that the corrosion process is largely controlled by the mixed protection type. This is due to the formation of the zinc corrosion products, that simultaneously act as a barrier coat. The values of corrosion current obtained from the zinc pigmented primers in 3% sodium chloride solution at various time duration is plotted against different pigment weight percentage as shown in the figure 5.6. It is seen from the figure that the corrosion current increases with the addition of zinc pigment in the CNSL binder. This trend is observed upto 80% pigment weight concentration, thereafter the corrosion current is decreased with the addition
Fig. 5-6. Relationship between the corrosion current and the p.w.c of zinc pigmented CNSL in 3% NaCl solution for different duration.

- - - 1 day,
- - - 7 days,
- - - 15 days,
- - - 30 days,
- - - 60 days.
of the zinc pigment. The 90% and 95% ZRP shows almost same corrosion current with duration.

These results show that low percentage of zinc in the CNSL medium gives protection by the effect of the binder. At the lower percentage of zinc in the binder medium, the zinc particles are not exposed to the electrolyte and also the particle to particle contact is not possible. This leads to the lower corrosion current for the lower percentage of zinc in the CNSL medium. From 60% zinc pigmented primer onwards the corrosion current is steadily increased with the addition of the pigment. This indicates that the particle to particle contact is increased and also the zinc particles on the surface are exposed to give cathodic current to protect the surface.

A slight potential difference between crystal faces promotes the formation of corrosion cell and thereby more corrosion products are formed, however, such a little difference in the corrosion rate in the initial corrosion process is lost by the formation of a secondary barrier of corrosion product layer [8]. This effect is observed in the case of 90% and 95% zinc pigmented primers on mild steel substrate and so the corrosion current is decreased. The corrosion current is almost equal in the case of 90% and 95% ZRP, this shows that further addition of zinc
will not affect the protection of the surface. So the 90% ZRP is chosen as the optimum level in the CNSL medium. The lower percentage of zinc in CNSL medium gives low corrosion current in the electrolyte, the protective action of these primer is due to the barrier effect of the binder and this effect to protect the substrate for shorter duration than the high ZRP. Because the zinc corrosion product formed will not cover throughout the surface and subsequently leads to failure of the primer to protect the surface.

5.2.4. Optimisation of manganese pigment

The diffusion of the electrolyte through the surface is prevented by the primers at the beginning stages and so it is not possible to polarise the primers. After 30 days of immersion only, the electrolyte diffuses through the primer and gives the polarisation response. The behaviour of the polarisation curves indicates that the corrosion process is controlled by the cathodic reaction due to the large cathodic over potential. But this trend is changed after 60 days. This shows that the protective action of the primers are controlled by mixed control reaction. This change in behaviour may be explained by the formation of manganese corrosion products such as manganese oxide, manganese carbonate and manganese hydroxide
over the surface [9]. The values of corrosion current measured from the tafel polarisation curve for various ratios of manganese pigmented primers in 3% NaCl solution with different duration is shown in the figure 5.7. It is seen from the figure that the corrosion current decreases with the addition of the pigment in the binder upto 70% pigmentation. Afterwards the corrosion current increases with the addition of manganese powder to the medium. This result shows that the 70% manganese pigmented primer in CNSL medium gives better protection than the other primers.

All these four metal powder pigmented primers in CNSL medium are subjected to salt spray test, the results are in comparison with the Tafel polarisation method results.

5.3. PHYSICAL PROPERTIES OF THE PRIMERS

The experimentally observed mechanical properties of the primers on mild steel substrate are given in the table 5.1. The abrasion resistance of all the primers are good except the stainless steel pigmented primer. This may be due to the cohesive bond between the binder and the stainless steel flake pigment, which is weaker than the other primers. The elongation properties of all the primers are better than the butyl titanate based
Fig. 5.7. Relationship between the corrosion current and the p.w.c of manganese pigmented CNSL resin in 3% NaCl

Δ-Δ 30 days, ○-○ 60 days.
Table 5.1

Physical properties of metal powder pigmented primers in CNSL medium coated M.S. substrate

<table>
<thead>
<tr>
<th>No.</th>
<th>Properties</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Abrasion resistance (Taber)</td>
<td>(a) 0.267 m.gms</td>
</tr>
<tr>
<td></td>
<td>weight loss for 1000 gms load/1000 revolutions</td>
<td>(b) 0.28 m.gms</td>
</tr>
<tr>
<td></td>
<td>Extensibility</td>
<td>(c) 0.223 m.gms</td>
</tr>
<tr>
<td></td>
<td>(Conical Mandrel)</td>
<td>(d) 0.329 m.gms</td>
</tr>
<tr>
<td>2.</td>
<td>Extensibility</td>
<td>(a) Passes 0.3174 cm (20% elongation)</td>
</tr>
<tr>
<td></td>
<td>(Conical Mandrel)</td>
<td>(b) Passes 0.3174 cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c) Passes 0.3174 cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d) Passes 1.27 cm (5.9% elongation)</td>
</tr>
<tr>
<td>3.</td>
<td>Impact resistance</td>
<td>(a) 12.6 Kg - Cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b) 18.9 Kg - Cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c) 40.5 Kg - Cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d) 10.8 Kg - Cm</td>
</tr>
<tr>
<td>4.</td>
<td>Cross Hatch Adhesion tester</td>
<td>(a) 100% passes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b) 100% passes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c) 100% passes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d) 60% passes</td>
</tr>
<tr>
<td>5.</td>
<td>Water absorption</td>
<td>(a) 10.96%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b) 6.29%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c) 4.38%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d) 6.83%</td>
</tr>
</tbody>
</table>

a = ZRP
b = Mn RP
c = Ni RP
d = S.S. RP
primers as given in Chapter IV. This behaviour is due to the elongation property of the CNSL binder. The impact resistance of nickel pigmented primer is better than the other primers. This is due to the adhesion of the primer with the surface, which is more stronger than the other primers. The adhesion and water absorption test also indicate that the nickel pigmented primer has better adhesion to the substrate and the water absorption is very low when compared to the other primers. Comparatively the physical properties show that the nickel pigment is suitable for the CNSL binder in chloride environment.

5.4. ACCELERATED TEST (SALT SPRAY [FOG] TEST)

The salt spray test result shows the following order of performance of the primer coated mild steel, (1) Nickel pigmented primer, (2) Zinc pigmented primer, (3) Manganese pigmented primer and (4) Stainless steel pigmented primer. No iron corrosion product is observed in zinc rich primer after 720 hours salt spray test, however zinc corrosion products are covered throughout the surface. In the case of manganese pigmented primer, iron corrosion spots are seen after 720 hours test, the count of corrosion spots found to be 3 to 5. The corrosion spots count for stainless steel pigmented primer is 12 to 15.
In the case of nickel pigmented primer also no corrosion spot is seen after 720 hours of salt spray test.

5.5. ELECTROCHEMICAL TECHNIQUES TO EVALUATE THE PRIMERS

5.5.1. Potential - Time measurements

Figure 5.8 shows the potential - time variation for the four primers on mild steel in 3% NaCl solution. It is seen from the figure that the initial potential of zinc rich primer is more negative than the other primers and it gradually decreases to attain a steady state after 30 days of immersion. The potential drop after a short period is due to the consumption of zinc by cathodic protection, or to the surface coverage of the zinc corrosion product [10]. The potential of the manganese rich primer steadily rises from -50 m.V to -389 m.V for the period of 60 days duration. This shows that the manganese particles are blocked by the binder present in the composition at the beginning stage and so the potential is very low. When the immersion time increases, the particle to particle contact of the manganese powder is increased to attain the potential of the manganese and afterwards it reaches the corrosion potential of the mild steel in the electrolyte. On the other hand the potential of nickel pigmented primer is below -200 m.V after the duration of 60 days. This is the noble potential equal to the nickel in the
Fig. 5-8. Potential behaviour of CNSL based primer coated M.S. plate in 3% NaCl solution for different duration.

- ZnRP
- MnRP
- NiRP
- S.S.RP
same electrolyte and so the behaviour of the primer is similar to the nickel metal. The potential behaviour of stainless steel pigmented primer shows that the potential is increased upto 15 days and afterwards there is not much change in the potential. This indicates that the diffusion of the corrosive electrolyte through the primer is much easier than the other primers in this binder.

5.5.2. Galvanic current measurement

The figure 5.9 shows the galvanic behaviour of the zinc and manganese pigmented primers in 3% NaCl solution. It is seen from the figure that the galvanic current produced by zinc rich primer constantly decreases with time, and after 45 days of duration the current is very negligible. Thus the period of cathodic protection is short for the zinc in CNSL medium. But the protection offered by this primer is of longer term, through the formation of zinc compounds, whose stability in pores is increased by the early formation of hydroxy ions at cathodic region [10]. The galvanic current produced by manganese pigmented primer shows that at the beginning the current increased, remains at this rate throughout the period of 30 days and thereafter it decreases with time. However the current produced by this primer is very low, when compared with butyl titanate manganese rich
Fig. 53. Galvanic current measurement of primer based on CNSL binder in 3% NaCl solution for different duration.

- ZnRP.
- MnRP.
primer. The result indicates that the manganese pigmented organic coatings also protect the surface by galvanic action mechanism. The galvanic current produced by this primer is very much limited when compared with the manganese pigment in inorganic binders such as butyl titanate and ethyl silicate [11].

5.5.3. Polarisation method

Figures 4.3a and 5.3 show the polarisation curves for mild steel and 60% nickel pigmented primer in 3% NaCl solution for various time duration. The corrosion parameters of the primer is given in table 5.2a. It can be seen from the figure 5.3 and the table 5.2a that the corrosion potential is shifted from more negative to positive direction with time upto 15 days. After that the corrosion potential is shifted to the anodic direction with time. The initial more negative potential value indicates that the dissolution process takes place in the first 7 days immersion. This may be due to the dissociation of the binder present on the surface layer of the primer. When the nickel particles are exposed in the electrolyte, the anodic overpotential is increased with time, due to the anodic passivation ability of the nickel powder. The protection of nickel pigmented primer proceeds with a very low corrosion current upto 30 days of immersion. After-
Table 5.2a
Potentiodynamic polarisation values of CNSL resin based primers on M.S. in 3% NaCl solution for different duration

<table>
<thead>
<tr>
<th>Duration (Days)</th>
<th>Nickel rich primer</th>
<th>Stainless steel rich primer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OCP (mV)</td>
<td>Ec (mV)</td>
</tr>
<tr>
<td>1</td>
<td>-71</td>
<td>-93</td>
</tr>
<tr>
<td>7</td>
<td>-76</td>
<td>-108</td>
</tr>
<tr>
<td>15</td>
<td>-65</td>
<td>-83</td>
</tr>
<tr>
<td>30</td>
<td>-22</td>
<td>-28</td>
</tr>
<tr>
<td>60</td>
<td>-182</td>
<td>-196</td>
</tr>
</tbody>
</table>

OCP and Ec values are given with reference to SCE
wards the corrosion current is increased due to the for-
mation of pores on the surface. The behaviour of the nickel
pigmented primer in 3% NaCl solution is some what compa-
rable with the polarisation study of nickel plates in
0.5M sodium fluoride solution by V.M.Carroll and M.B.
Howley [12].

It can be seen from the table 5.2a that the corro-
sion potential of stainless steel pigmented primer is
shifted to more cathodic potential values with time. This
indicates that the dissolution process takes place with
longer period of immersion. The corrosion current also
increases with time and this shows the protective action
of the coating decreases with duration.

From the table 5.2b, it is seen that the corrosion
potential of zinc rich primer is shifted to more cathodic
values with time. This indicates that the dissolution
process followed by diffusion process takes place in this
primer system. It can also be seen from the table that
the values of corrosion current increases initially there-
after suddenly decreases. This may be due to the dissolu-
tion process followed by the oxide film formation on the
metal surface [13]. Further increasing of corrosion rate
with time indicates the formation of porous surface follow-
ed by galvanic coupling action in the case of zinc rich
primer.
Table 5.2b
Potentiodynamic polarisation values of CNSL resin based primers on M.S. in 3% NaCl solution for different duration

<table>
<thead>
<tr>
<th>Duration (Days)</th>
<th>Zinc rich primer</th>
<th>Manganese rich primer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OCP (mV)</td>
<td>Ec (mV)</td>
</tr>
<tr>
<td>1</td>
<td>-765</td>
<td>-781</td>
</tr>
<tr>
<td>7</td>
<td>-966</td>
<td>-978</td>
</tr>
<tr>
<td>15</td>
<td>-805</td>
<td>-883</td>
</tr>
<tr>
<td>30</td>
<td>-795</td>
<td>-919</td>
</tr>
<tr>
<td>60</td>
<td>-771</td>
<td>-855</td>
</tr>
<tr>
<td>*Mild steel</td>
<td>-492</td>
<td>-522</td>
</tr>
</tbody>
</table>

OCP and Ec values are given with reference to SCE.
In the case of manganese pigmented primer, it is seen from the table 5.2b that initially the diffusion of the electrolyte in the surface is not possible due to the adhesive character of the primer. After 30 and 60 days of polarisation studies show that the corrosion potential is shifted towards more anodic values. This shows that the manganese powder may form a passive manganese corrosion product layer [9] on the surface of the coatings after 60 days of immersion. The corrosion current also increases with duration. This indicates the formation of pores on the surface and subsequently leads to the formation of galvanic coupling to protect the surface from the corrosive electrolyte.

5.5.4. Impedance method

A.C. impedance measurements are made for mild steel in 3% NaCl solution and the primer coated electrodes in the solution for different durations. The impedance plots of mild steel alone may be explained as a charge transfer semicircle followed by a slow diffusion at lower frequencies. This behaviour is in agreement with the uncoated metals in 3% NaCl solution [14].

The shape of the impedance plots are mainly that of a semicircle followed by a straight line which in most of the cases bends towards Z' axis. This type of behaviour
is ascribed as diffusion control reaction. The impedance plots of nickel rich primer is shown in the figure 5.10 and the $R_t$, $C_p$ values are given in the table 5.3a. From the figure it is seen that at the beginning, the diffusion of the electrolyte is prevented by the primer and so the straight line of capacitive behaviour of the coating has been observed. The plots obtained after 7 days and subsequent days show that the plots slightly bend towards $Z'$ axis and form a straight line. This indicates that the electrolyte has started to diffuse into the surface through the primer. The curve obtained after 7 days are extrapolated to form a semicircle and the significance of $R_t$ and $C_p$ values are identified. It is seen from the table that the $R_t$ value is increased upto 30 days of exposure and then decreases with duration. This increase in the value of $R_t$ with time indicates that the pore blockage is due to the passivation of the nickel or the corrosion products [15]. The capacitance value also decreases upto 30 days and then increases. This is in agreement with the general trend of $R_t$ and $C_p$ values which are inversely proportional to each other.

The figure 5.11 shows that the Nyquist plots of stainless steel pigmented primer and the $R_t$, $C_p$ values are given in the table 5.3a. It is seen from the figure
Fig. 5.10. Nyquist plots of CNSL based NiRP on M.S. plate in 3% NaCl solution for different duration.

- 1 day, - 7 days, - 15 days,
- 30 days, - 60 days.
Fig. 5-11. Nyquist plots of CNSL based S.S.R.P on M.S. plate in 3% NaCl solution for different duration.

- 1day,  7days,  15days,
- 30days,  60days.
Table 5.3a
Charge transfer resistance and interfacial capacitance of CNSL based primer on M.S. in 3% NaCl solution for different duration

<table>
<thead>
<tr>
<th>Duration (Days)</th>
<th>Nickel rich primer</th>
<th>Stainless steel rich primer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rt ohms Cm²</td>
<td>Cp F</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>5.9 x 10⁵</td>
<td>4.56 x 10⁻⁸</td>
</tr>
<tr>
<td>15</td>
<td>9.0 x 10⁵</td>
<td>1.35 x 10⁻⁷</td>
</tr>
<tr>
<td>30</td>
<td>1.25 x 10⁷</td>
<td>1.89 x 10⁻⁹</td>
</tr>
<tr>
<td>60</td>
<td>5.25 x 10⁶</td>
<td>6.05 x 10⁻⁸</td>
</tr>
<tr>
<td>*Mild steel</td>
<td>127.00</td>
<td>4.56 x 10⁻⁴</td>
</tr>
</tbody>
</table>
that the shape of the curves are diffusion control reaction type. The table also indicates that the Rt values constantly decrease with time and the $C_p$ values reach almost constant value from 7 days exposure. The significant of the $C_p$ value depends upon the water permeability of the coating [16]. The early failure of the stainless steel pigmented primer may be due to the poor bonding character of the primer with the substrate.

Figure 5.12 shows the impedance plots of zinc rich primer in 3% NaCl solution and the corresponding Rt, $C_p$ values are given in the table 5.3b. The shape of the plots are diffusion control system. After 15 days immersion, a high frequency semicircle followed by a low frequency semicircle and then the formation of Warburg diffusion tail has been observed. It is also seen from the table that the Rt value decreases with duration upto 15 days and thereafter the Rt value increases with time. This shows that at the beginning, CNSL binder is covered on the surface to prevent the exposure of the zinc particles to the electrolyte, and so the Rt value is much high. After that the zinc particles in the primer protects the surface by galvanic current mechanism upto 30 days and so the Rt value decreases with time. This is further supported by the galvanic current measurement as given in the figure 5.9. Thereafter the surface is covered by zinc
Fig. 5-12. Nyquist plots of CNSL based ZnRP on M.S. plate in 3% NaCl solution for different duration. 
-1 day, -7 days, -15 days, 
-30 days, -60 days.
Table 5.3b
Charge transfer resistance and interfacial capacitance of CNSL based primer on M.S. in 3% NaCl solution for different duration

<table>
<thead>
<tr>
<th>Duration (Days)</th>
<th>Zinc rich primer</th>
<th>Manganese rich primer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rt  ohm cm$^{-2}$</td>
<td>C$_p$ F</td>
</tr>
<tr>
<td>1</td>
<td>4.2 x 10$^6$</td>
<td>6.0 x 10$^{-9}$</td>
</tr>
<tr>
<td>7</td>
<td>3400</td>
<td>1.0 x 10$^{-7}$</td>
</tr>
<tr>
<td>15</td>
<td>300</td>
<td>2.1 x 10$^{-8}$</td>
</tr>
<tr>
<td>30</td>
<td>530</td>
<td>7.5 x 10$^{-9}$</td>
</tr>
<tr>
<td>60</td>
<td>1125</td>
<td>3.6 x 10$^{-9}$</td>
</tr>
</tbody>
</table>
corrosion product [13,17] to form a barrier coating and so the Rt value further increases with duration. Thus the zinc rich coatings protect the surface for a long time.

Figure 5.13 shows the impedance plots of manganese rich primer in 3% NaCl solution for different duration and the corresponding Rt, C values are given in the table 5.3b. The shape of the plots are depressed semicircle followed by a diffusion tail. The diffusion tail in all the curves are more than 45° angle with Z' axis. This shows that the diffusion reaction takes place in a controlled manner through the primer. The Rt value decreases with duration upto 30 days and thereafter the Rt value increases. This behaviour is similar to the zinc rich primer because the manganese primer also protect the surface at the beginning by galvanic current mechanism. This study indicates that the manganese rich primer also protect the surface upto 30 days by galvanic current effect. But the current produced by the coating is very low (see the figure 5.9) and so the Rt value is higher than the ZRP coatings. When the galvanic current becomes low, the manganese corrosion products [9] block the pores and form a barrier coating over the surface, that is why the Rt value increases further and protect the surface for longer duration.
Fig. 5.13 Nyquist plots of CNSL based MnRP on M.S plate in 3% NaCl solution for different duration.

- 1 day, - 7 days, - 15 days, - 30 days, - 60 days.
5.6. SURFACE MORPHOLOGY BY SCANNING ELECTRON MICROSCOPY (SEM) METHOD

SEM figures 5.14a to 5.17a are for nickel, stainless steel, zinc and manganese rich primers in CNSL medium respectively. The figures of nickel and stainless steel primers show that the flake structured particles closely packed on the surface. The surface is quite rough and many pores are visible to some extent at a short distance into the coating. The SEM photograph of nickel flake pigment in organic binder developed for the production of conductive organic coating is demonstrated by A.C. Hart [18]. He concluded that the effect of particle morphology on the electrical conductivity of organic coatings are quite considerable. Similarly the stainless steel flake pigmented coatings also conduct current through it at higher percentage of pigmentation. The zinc rich primer in CNSL medium indicates that the zinc spherical particles are closely packed with each other and also dispersed uniformly throughout the surface. Here unlike the titanate based ZRP (Fig. 4.14a), there is no crack on the surface. This may be due to the good wetting character of the binder. Figure 5.17a of manganese rich primer shows the presence of manganese dioxide and some filler materials as white patches on the surface.
Fig. 5.14a, Scanning Electron Micrograph 1000:1 of CNSL-NiRP coated M.S.

Fig. 5.14b, Scanning Electron Micrograph 1000:1 of CNSL-NiRP coated M.S. after immersed in 3% NaCl solution for 60 days.

Fig. 5.15a, Scanning Electron Micrograph 1000:1 of CNSL-5.5J.R.P. coated M.S.

Fig. 5.15b, Scanning Electron Micrograph 1000:1 of CNSL-5.5J.R.P. coated M.S. after immersed in 3% NaCl solution for 60 days.
Fig. 5.16a, Scanning Electron Micrograph 1000x1 of CNSL-ZRP coated M.S.

Fig. 5.16b, Scanning Electron Micrograph 1000x1 of CNSL-ZRP coated M.S. after immersed in 3% NaCl solution for 60 days.

Fig. 5.17a, Scanning Electron Micrograph 1000x1 of CNSL-MnRP coated M.S.

Fig. 5.17b, Scanning Electron Micrograph 1000x1 of CNSL-MnRP coated M.S. after immersed in 3% NaCl solution for 60 days.
The SEM photographs 5.14b to 5.17b show the surface of the corresponding primers after immersion in 3% NaCl solution for 60 days. From the nickel rich primer, it is seen that the nickel particles are still intact on the surface and so the impedance and Tafel polarisation resistance values of this primer is higher than the other primers. It is seen from the figure 5.15b that the stainless steel flake pigments are separated from the binder and so it allows the diffusion of the corrosive electrolyte into the surface. The separation of the stainless steel flakes from the binder may be due to the poor wettability of the pigment with binder. The poor performance of the stainless steel rich primer is also supported by the impedance data. With regard to zinc rich primer, it is seen from the figure 5.16b, that the zinc particle starts to disintegrate to form zinc corrosion product and also forms micro cracks within the coating. This micro cracks are formed due to the higher zinc content, which leads to the poor wetting of the zinc particles with the binder [19]. The electrolyte filling the cracks contributes to the ionic conduction and so protects the surface for longer duration. It is seen from the figure 5.17b that the corrosion products of manganese is increased, when compared with the figure 5.17a. Actually the corrosion of manganese particles start from the boundaries of manga-
nese dioxide present in the primer and also the filler materials in the composition. This corrosion product is increased slowly throughout the surface and protect the surface for longer duration.

5.7. ELECTROCHEMICAL BEHAVIOUR OF PRIMER WITH FINISH COATED SYSTEMS

The electrochemical behaviour of Micaceous Iron Oxide (MIO) pigmented chlorinated rubber and Titanium dioxide (TiO₂) pigmented chlorinated rubber finish coats on mild steel substrate are explained in Chapter IV.

5.7.1. Potential - Time relation

The potential - time relationship of CNSL based primers' finish coated with MIO and TiO₂ pigmented chlorinated rubber are given in fig.5.18 and 5.19 respectively. For MIO pigmented finish coated system, it is seen from the figure 5.18 that for nickel and stainless steel primer systems, the potential is decreased with time upto 150 days. Thereafter the potential gradually increases with time. This results show that the potential of these two primers with MIO pigmented finish coat are more noble upto 150 days and afterwards it reaches the potential of the respective primers. The behaviour of the manganese primer with MIO pigmented finish coat shows that the potential is steadily increased with time. This indicates that
Fig. 5-18. Variation of potential with time of CNSL based primer + MIO pigmented chlorinated rubber top coated system in 3% NaCl solution.

- ZnRP
- MnRP
- NiRP
- S,SRP
Fig. 5.19. Variation of potential with time of CNSL based primer + TiO₂ pigmented chlorinated rubber top coated system in 3% NaCl solution.

- ZnRP
- MnRP
- NiRP
- SSRP
the diffusion of the electrolyte through the finish coat is continuous, eventhough the potential of the system is under noble condition for 150 days and afterwards a sudden shift in the potential is noticed. In the case of zinc rich primer coated system, it is seen from the figure 5.18 that the potential steadily rises upto 150 days and then a sudden fall in the potential behaviour is observed. Eventhough in these four systems some potential change is noticed after 150 days, the potential observed is also noble and well below the corrosion potential of iron in the electrolyte.

The TiO₂ pigmented chlorinated rubber finish coated primers also behave some what similar to that of MIO pigmented finish coat systems, except in the case of stainless steel primer system. The stainless steel primer with finish coated system reaches a steady state after 120 days. This value shows that the diffusion of the electrolyte through the finish coat is easier than in other systems. This may be due to the poor intercoat adhesion between the primer and the finish coat. Eventhough the potential behaviour of the MIO and TiO₂ pigmented finish coat systems on the four primers are more or less same, the MIO pigmented finish coat system's potential is much more nobler than the TiO₂ pigmented finish coat systems. The much better pro-
tection of the MIO pigmented systems are due to the unique lamellar platelet orientation properties of the pigment. The long term protective property of this pigment in various coatings are studied by S.Wiktorek [20]. He explained the Lamellar orientation character of the pigment and the SEM studies of the coatings in detailed manner. From these results it is concluded that the potential measurement may be used to determine the trends in paint film performance, but its protective properties should be confirmed by some other corrosion measurement methods [21].

5.7.2. Polarisation method

Fig. 5.20 and 5.21 show the polarisation behaviour of nickel rich primer with MIO pigmented chlorinated rubber and TiO₂ pigmented chlorinated rubber finish coated systems in 3% NaCl solution for different durations respectively. The corresponding Tafel polarisation values are given in tables 5.4 and 5.5. From the figure it is seen that the method of protection of the coating is resistance control reaction type. That is, the coating layer delayed the transists of ions, thereby inhibiting the formation of corrosion cell [9]. The polarisation plots of 30 and 60 days of primer with MIO pigmented finish coat system is not obtained because of the unsteadiness of the potential. This is due to the resistance offered by the top
Fig. 5-20. Potentiodynamic polarisation of CNSL based NiRP+MIO pigmented chlorinated rubber top coated M.S. plate in 3% NaCl solution for 100 days.
Fig. 5.21. Potentiodynamic polarisation of CNSL based NiRP-TiO₂ pigmented chlorinated rubber top coated M.S. plate in 3% NaCl solution for different duration.

@ - 60 days, @ - 100 days.
Table 5.4
Data from potentiodynamic polarisation of CNSL based primers + MIO pigmented chlorinated rubber finish coat on M.S. in 3% NaCl solution for different duration

<table>
<thead>
<tr>
<th>Duration (Days)</th>
<th>Nickel rich primer + Finish coat</th>
<th>Stainless steel rich primer + Finish coat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OCP (mV)</td>
<td>Ec (mV)</td>
</tr>
<tr>
<td>100</td>
<td>-38</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>-223</td>
<td>-285</td>
</tr>
<tr>
<td>100</td>
<td>-235</td>
<td>-273</td>
</tr>
</tbody>
</table>

OCP and Ec values are given with reference to SCE.
Table 5.5

Data from potentiodynamic polarisation of CNSL based primer + TiO₂ pigmented chlorinated rubber finish coat on M.S. in 3% NaCl solution for different duration

<table>
<thead>
<tr>
<th>Duration (Days)</th>
<th>Nickel rich primer + Finish coat</th>
<th>Stainless steel rich primer + Finish coat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OCP (mV)</td>
<td>Ec (mV)</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>-42</td>
<td>-34</td>
</tr>
<tr>
<td>100</td>
<td>-228</td>
<td>-258</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Zinc rich primer + Finish coat</th>
<th>Manganese rich primer + Finish coat</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>-371</td>
</tr>
<tr>
<td>100</td>
<td>-272</td>
</tr>
</tbody>
</table>

OCP and Ec values are given with reference to SCE
coat for the ions to diffuse. Similarly the TiO$_2$ pigmented finish coat system resists the diffusion of the ions through it at the beginning stage, but it allows the ions after 60 days of immersion. This behaviour of delayed response of polarisation study of the coatings are explained by higher resistance of the coating. When the rate of corrosion is low, the time necessary for attaining a stationary state at the working electrode is correspondingly high [22]. From the table it is seen that the MIO pigmented finish coat system gives very low corrosion current than the TiO$_2$ pigmented finish coat system for 100 days duration in the electrolyte. This shows that the MIO pigmented finish coat gives better protection for nickel rich primer in the 3% NaCl solution.

Table 5.4 and 5.5 show the polarisation values of stainless steel rich primer finish coated with MIO pigmented chlorinated rubber and TiO$_2$ pigmented chlorinated rubber system in 3% NaCl solution respectively. In this MIO pigmented finish coated system delays diffusion of the electrolyte into the surface for longer duration than the TiO$_2$ pigmented finish coat system. The shape of the polarisation curve is also similar to the polarisation plots of nickel rich primer with finish coat systems, i.e., resistance control reaction type of mechanisms to protect
the surface. From the table it is seen that the TiO₂ pigmented finish coat system allows the diffusion of corrosive ions into the surface from the beginning stage itself, and the corrosion current slowly decreases with time duration. On the other hand the MIO pigmented finish coat system has not allowed the diffusion of the ions and so the stationary state of the working electrode is obtained after 100 days of immersion. The corrosion current obtained after 100 days of immersion shows that it is lower than that of the TiO₂ pigmented finish coat in the same period. This indicates that the MIO pigmented finish coat system will protect the stainless steel rich primer for long time.

The table 5.4 and 5.5 show the polarisation values of zinc rich primer finish coated with MIO and TiO₂ pigmented chlorinated rubber in 3% NaCl solution for different durations respectively. The shape of the polarisation curve shows that the mechanism of protection of these two coating systems are also by resistance control type. From the table it is seen that both the systems prevent the diffusion of the ions at the beginning and thereafter slow diffusion of the electrolyte in the surface. The corrosion current of both the systems are decreased with the duration of immersion shows that the micro pores in
the finish coats are filled with the zinc corrosion products and prevent the diffusion of the electrolyte into the surface. Further the corrosion current of MIO pigmented finish coated system is lower than the other systems. This indicates that the MIO pigmented finish coat is suitable for the zinc rich primer in chloride electrolyte.

The table 5.4 and 5.5 show the polarisation values of manganese rich primer finish coated with MIO and TiO₂ pigmented chlorinated rubber in 3% NaCl solution for 100 days duration respectively. The behaviour of the polarisation curve is resistance control reaction type as explained before. The stationary state of the system is not obtained before 100 days and so the polarisation plots are obtained only after 100 days immersion. The values of corrosion current from the table indicates that the TiO₂ pigmented finish coated system is lower than the other system. The result shows that the TiO₂ pigmented finish coat performs well for manganese rich primers in chloride electrolyte.

5.7.3. Impedance behaviour of the coating systems

The Nyquist plots of CNSL based nickel rich primer with MIO and TiO₂ pigmented chlorinated rubber finish coated mild steel in 3% NaCl solution for different duration
is shown in the figures 5.22 and 5.23 respectively. The corresponding charge transfer resistance (Rt) and the interfacial capacitance (C<sub>p</sub>) of these systems are given in the table 5.6 and 5.7. It is seen from the figure that the behaviour of the coating system is mainly diffusion control reaction type in both the systems. In the case of MIO pigmented finish coated system, during 30 and 60 days a capacitive behaviour of the plot is observed. This indicates that the paint film is not grossly defective and intact on the surface. With an immersion period of 100 days, a high frequency semicircle followed by a diffusion 'tail' is observed, which shows that there is some degradation of the coating. But the Rt values of the system is in the order of 10<sup>8</sup> ohms Cm<sup>2</sup>. This indicates that the paint film is intact on the surface after 100 days immersion. Fastrup et al.'s [23] study of intact painted and scribed painted panels reveals that an intact paint coating always produce the electrical properties of the coating, whereas the damaged coatings produce a complicated impedance behaviour of the coating system in the corrosive electrolyte. In the case of TiO<sub>2</sub> pigmented finish coated system, the diffusion of electrolyte takes place from the beginning itself but the Rt values are high enough to a pore free intact coating. Table 5.7 shows that the Rt value decreases with duration which indicates the
Fig. 5-22 Nyquist plots of CNSL based NiRP+MfO pigmented chlorinated rubber top coated M.S. plate in 3% NaCl solution for different duration.

- 30 days, - 60 days, - 100 days.
Fig. 5.23. Nyquist plots of CNSL based NiRP+TiO₂ pigmented chlorinated rubber top coated M.S. in 3% NaCl solution for different duration.

⊙ - 30 days, ✡ - 60 days, ☼ - 100 days.
Table 5.6
Charge transfer resistance and interfacial capacitance of CNSL based primer +
MIO pigmented chlorinated rubber finish coated M.S. in
3% NaCl solution for different duration

<table>
<thead>
<tr>
<th>Duration (Days)</th>
<th>Nickel rich primer + finish coat</th>
<th>Zinc rich primer + finish coat</th>
<th>Manganese rich primer + finish coat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rt ohms Cm²</td>
<td>C_p F</td>
<td>Rt ohms Cm²</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>-</td>
<td>6.25 x 10^7</td>
</tr>
<tr>
<td>60</td>
<td>-</td>
<td>-</td>
<td>2.5 x 10^8</td>
</tr>
<tr>
<td>100</td>
<td>1.45 x 10^8</td>
<td>2.67 x 10^{-10}</td>
<td>4.7 x 10^8</td>
</tr>
</tbody>
</table>
Table 5.7

Charge transfer resistance and interfacial capacitance of CNSL based primer +
TiO₂ pigmented chlorinated rubber finish coated M.S. in
3% NaCl solution for different duration

<table>
<thead>
<tr>
<th>Duration (Days)</th>
<th>Nickel rich primer + Finish coat</th>
<th>Stainless steel rich Zinc rich primer + Finish coat</th>
<th>Manganese rich primer + Finish coat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R_t ) ohms Cm²</td>
<td>( C_p ) F</td>
<td>( R_t ) ohms Cm²</td>
</tr>
<tr>
<td>30</td>
<td>( 1.0 \times 10^7 )</td>
<td>( 1.6 \times 10^{-10} )</td>
<td>( 1.2 \times 10^8 )</td>
</tr>
<tr>
<td>60</td>
<td>( 9.4 \times 10^7 )</td>
<td>( 6.76 \times 10^{-11} )</td>
<td>( 1.03 \times 10^8 )</td>
</tr>
<tr>
<td>100</td>
<td>( 1.85 \times 10^7 )</td>
<td>( 6.6 \times 10^{-9} )</td>
<td>( 3.36 \times 10^7 )</td>
</tr>
</tbody>
</table>

210
diffusion of the electrolyte as a continuous process and the increase in $C_p$ value points out that the water uptake of the coating is increased with duration. The $R_t$ value after 100 days study of the system is in the order of $10^7$ ohms Cm$^2$ shows that the coating has some minor pores on the surface when compared with the MIO pigmented coating.

Purely capacitive behaviour of stainless steel rich primer with MIO pigmented finish coat system is observed throughout the period of 100 days. The $R_t$ and $C_p$ values of stainless steel rich primer with TiO$_2$ pigmented finish coated system in 3% NaCl solution are given in the table 5.7. The behaviour of the coating is normal diffusion control reaction of high frequency semicircle followed by a diffusion 'tail'. The table shows that the $R_t$ value decreases with time, which means the corrosion process at the interface enhances conduction through pores in the coating. The $C_p$ value is increased with time indicates the degree of water uptake of the coating [24,25]. After 100 days of immersion the $R_t$ value is in the order of $10^7$ ohms Cm$^2$ shows that the coating is still intact on the surface with minor defects.

The $R_t$ and $C_p$ values of ZRP with MIO and TiO$_2$ pigmented chlorinated rubber finish coated specimens in 3% NaCl solution for different duration is given in the table
5.6 and 5.7 respectively. In both the systems, the behaviour of the Nyquist plot is in normal diffusion control reaction type of high frequency semicircle followed by a diffusion 'tail'. It is seen from the table 5.6 that the \( R_t \) value increases with time and the \( C_p \) value decreases with duration. The increase in \( R_t \) value is explained by the pores or the defect present in the finish coat is completely blocked by the zinc corrosion product of the primer. Similar explanation is applicable to the \( \text{TiO}_2 \) pigmented finish coated system. The values of the system is given in the table 5.7. In this system the \( R_t \) value is in higher order than the MIO pigmented finish coat system. But both the systems have very high \( R_t \) values after 100 days of immersion. This indicates that these finish coat systems are intact on the surface.

The \( R_t \) and \( C_p \) values of manganese rich primer coated with MIO and \( \text{TiO}_2 \) pigmented chlorinated rubber on M.S. surface in 3\% NaCl for different duration is given in the table 5.6 and 5.7 respectively. The impedance behaviour of the plots are in normal diffusion control reaction type. At the beginning stages, both the systems behaviour are purely capacitive. This indicates that the coating system is not grossly defective even after 60 days of immersion. After 100 days, \( R_t \) values shows that the \( \text{TiO}_2 \)
pigmented finish coat is in the order of $10^9$ ohms $\text{cm}^2$ and MIO finish coated system is in the order of $10^7$ ohms $\text{cm}^2$. This results indicate that TiO$_2$ pigmented chlorinated rubber finish coat is suitable for manganese rich primer in the chloride electrolyte.

The electrochemical behaviour of the finish coated system shows that the MIO pigmented chlorinated rubber finish coat is suitable for nickel, zinc and stainless steel rich primers and the TiO$_2$ pigmented chlorinated rubber finish coat is suitable for manganese rich primer.
References


