CHAPTER - VII

SUMMARY

The resins viz. butyl titanate, cashew nut shell liquid (CNSL), epoxy-polyamide for primer formulation and chlorinated rubber for finish coat have been prepared. The structure of the resins are confirmed by I.R. spectral analysis. The primers are prepared by using these resins with four metallic powder pigments such as Zinc (Zn), Manganese (Mn), Nickel (Ni) and Stainless steel (S.S) in the range of 10 to 95 pigment weight percentage. The critical pigment weight percentage of these primers have been optimised by potentiodynamic polarisation in 3% NaCl solution. On the basis of these studies, for butyl titanate based primers, 80% Zn, 70% Mn, 30% Ni and 30% S.S. have been chosen as critical pigment weight percentage. For CNSL based primers, 90% Zn, 70% Mn, 60% Ni and 60% S.S. have been selected as critical pigment weight percentage and for epoxy-polyamide based primers, 90% Zn, 60% Mn, 40% Ni and 40% S.S. have been chosen as critical pigment weight percentage.

The physical and corrosion resistant (salt spray tests) properties such as abrasion resistance, extensibility, impact resistance, adhesion strength and percentage of water absorption of the three binder based primers
have been determined. The results show that the epoxy-polyamide based primers perform well over the CNSL based primers and the performance of CNSL based primer is better than the butyl titanate based primers.

The electrochemical behaviour of the above primers have been investigated by potential - time measurements, galvanic current studies, Tafel polarisation method and impedance studies in 3% NaCl solution. The results indicate that the manganese and zinc rich primers have better performance in butyl titanate binder medium. This behaviour of these primers are due to cathodic protection of the pigment followed by the barrier protection offered by zinc and manganese corrosion products on the surface of the primers. The galvanic current offered by these two pigments in this binder is in high order and longer duration than the other two mediums. The electrochemical behaviour of CNSL based primers suggest that the manganese, nickel and zinc rich primers have better performance in 3% NaCl solution. This indicates that the zinc and manganese protect the surface by galvanic and barrier effect and the nickel rich primer protects the surface by its passivation behaviour. In the case of epoxy-polyamide based primers electrochemical behaviour in 3% NaCl solution indicates that the nickel and stainless steel rich primers
protect the surface for longer durations than the zinc and manganese rich primers. The reason for this is that the corrosion protection offered by the passivation character of nickel and stainless steel rich primers are superior than the sacrificial and barrier protection offered by zinc and manganese rich primers in epoxy medium.

The surface morphology of the primers are studied through Scanning Electron Micrographic (SEM) analysis. This investigation shows that the surface of zinc and manganese rich primers of the three binder media are covered with the corrosion products of zinc and manganese, which prevent the diffusion of electrolyte into the substrate.

The surface of butyl titanate based zinc rich primer has some microcracks before exposure. But these cracks are filled with electrolyte and continue to protect the surface by galvanic effect followed by barrier mechanism. The SEM micrographs of nickel rich primer indicates that it behaves differently with different binder medium. No change in surface morphology is observed in the CNSL medium, but there is formation of passive layer in the case of epoxy-polyamide medium, while the butyl titanate based nickel rich primer shows formation of pores on the surface. It has been found that the nickel pigments are suitable
in organic binder medium than in the inorganic medium. SEM micrographs of stainless steel rich primer shows that the stainless steel flakes in epoxy-polyamide medium are exposed on the surface and prevent the diffusion of the corrosive ions into the substrate. Whereas in other binder media it leads into pore formation.

Chlorinated rubber based paint formulations pigmented with Micaceous Iron Oxide (25% PVC) and Titanium dioxide (36% PVC) are prepared and they are used as the finish coat for the primers. The electrochemical behaviour of these formulations on M.S. in 3% NaCl solution is thoroughly investigated using polarisation, impedance and potential-time measurements. The results show that the MIO pigmented coating protects the substrate for longer duration than the TiO₂ pigmented coating. The higher protective action of this MIO pigmented coating is due to its lamellar structure, which forms pore free coating on the substrate.

The electrochemical parameters obtained from the alternative and direct current techniques for the finish coated primer systems suggest that the butyl titanate based nickel primer performs well under both the finish coat system, since the charge transfer resistance obtained after 100 days is in the order of $10^8$ ohms Cm² and also the
corrosion current (0.009 μA. Cm\(^{-2}\)) derived from the polarisation method is negligibly small in these finish coated systems. Chlorinated rubber based MIO pigmented finish coat is chosen for manganese rich primers because the corrosion current obtained by the D.C. method after 100 days in 0.0042 μA. Cm\(^{-2}\) and the charge transfer resistance from the A.C. method is also in the order of 10\(^6\) ohms Cm\(^2\) for the above duration. The chlorinated rubber based TiO\(_2\) pigmented finish coat protects the Zn and S.S. rich primers for longer duration than the MIO pigmented finish coat systems. The MIO pigmented finish coat is suitable for CNSL based primers other than the manganese rich primer. The manganese rich primer with TiO\(_2\) finish coat system has high resistance after 100 days, that is in the order of 10\(^9\) ohms Cm\(^2\) and the corrosion current obtained from the D.C. method is very low (0.0004 μA. Cm\(^{-2}\)) for the same duration. While in the case of epoxy-polyamide based primers, the TiO\(_2\) pigmented finish coats perform well over the MIO pigmented finish coat in the chloride medium. The MIO pigmented finish coat equally performs well for stainless steel and zinc rich primers based on this binder.

In the light of the above studies the order of protection of the metal powder pigmented primers and paint systems can be summarised as follows.
a) Primers:
(i) In butyl titanate binder medium, Mn > Zn > Ni > S.S
(ii) In CNSL medium, Mn > Ni > Zn > S.S
(iii) In epoxy-polyamide medium, S.S > Ni > Mn > Zn

b) Finish coats:
MIO pigmented chlorinated rubber finish coat > TiO₂ pigmented finish coat.

c) Total systems:
(i) Butyl titanate based primers + finish coats,  
Ni + MIO/TiO₂ > Mn + MIO/Zn + TiO₂ > S.S + TiO₂

(ii) CNSL based primers + finish coats,  
Mn + TiO₂ > Ni + MIO > Zn + MIO > S.S + MIO

(iii) Epoxy-polyamide based primers + finish coats,  
S.S + MIO/TiO₂ > Ni + TiO₂ > Mn + TiO₂ > Zn + MIO/TiO₂.

From these experimental investigations it has been concluded that butyl titanate binder is more suitable for pigments containing Zn and Mn which protect the surface layer by sacrificial and barrier method. In epoxy medium Ni and stainless steel pigments give better corrosion protection by passivation process. On the other hand, all these pigments offer protection in CNSL binder medium.
The performance of finish coated system shows that MIO pigmented chlorinated rubber finish coat provides best protection in most of the paint scheme in chloride environment. The order of performance changes for butyl titanate based primer and the finish coat system is due to the formation of a passive layer in between the primer and the finish coat.

The protocols presented here is extended to the evaluation of the electrochemical behaviour of these primers and coating systems on other metal substrates, and different pre-treated surfaces as well as in other corrosive media.