Evaluation of Protective Ability of High Solid Novolac Clear Coatings Through Electrochemical Techniques

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Solvent free high solid coatings are increasingly used as they posses number of advantages such as, lower cost per unit film thickness, better performance and eco-friendliness. In the present study polymeric film-forming materials such as aniline-novolac (ANS), cresol-novolac (CNS) and acrylic copolymer blended cresol-novolac (ACNS) coating materials have been prepared. The corrosion resistance properties of the prepared high solid coating materials have been evaluated through potential-time, potentiodynamic polarization and electrochemical impedance studies (EIS). Among the three coating systems, cresol-novolac polymer coated substrates offer better corrosion resistance property and the order of the performance was found as CNS 〉 ACNS 〉 ANS. We can recommend these systems for use in automobile applications.

Keywords : Novolac, high-solid, acrylic blended coatings, EIS and polarization measurements.

1. Introduction

Variety of materials have been used both for the protective and decorative purpose in various industries. As per materials available in the literature the non-volatile materials present in the coating system is around 30-40% and the rest will be organic solvents. The environmental regulations, in several countries insist that volatile organic content (VOC) present in the coating should be minimum. In mid seventies stimulated the technological development of high solid and solventless coatings for the high performance protective coating industry. Since the slow and steady transition from conventional solvent based anti-corrosive coatings having volume solids ranging between 30-40% to high solid coatings having volume solids in the range of 80-90% for structural steel protection has been effected primarily to derive the benefit of high film build application in less number coats for enhanced service life as well as reduced emission.[1] With steep increase in labour cost, pressure was mounted on the painting contractors to reduce the overall application cost and improve productivity to sustain competitiveness for which they demanded rapid curing coatings that can be applied in single coat without any detrimental effect on film performance.

The growing popularity of solventless high solid coating for the protection of structural steel and concrete may be attributed to the series of benefits offered by such coatings with respect to application safety, environmental control, productivity improvement and performance benefits. Some of the salient advantages of such coatings are summarized below.[1]

• Capabilities to produce high film build in single coat or less number of coats.

• Less possibility of coating failure due to absence of interlayer contaminants, solvent entrapment, intercoat adhesion problem when applied in single coat.

• Faster curing- minimum disruption and down time curing after application

• Environment-No VOC ensures ecological and worker safety.

• Reduced application cost due to reduced labour, inspection and QC cost and automated application.

In response to these restrictions the coating industries have developed the products having low VOC. Some of the newly developed coating systems are as.[2-4]

• Water-borne coatings
• High-solid coatings

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• Powder coatings

The solventless 100%volume solids are being recommended by many companies as high performance internal tank lining for ballast tanks, crude, solvent, acid and water storage tanks, offshore application as well as self-leveling coatings on industrial flooring concrete. Properly formulated 100% solid coatings can offer excellent elongation properties ranging from 50%-200% but at the same time maintaining higher tensile strength (100-200Kg/cm^2). With appropriate choice of hardeners these coatings can also be made light stable. The pot life of such coatings may be varied between 5 minutes-40 minutes with proper balance of reactivity's between base and hardener and catalyst component to suit various types of applications.[1),4)]

The high solids are becoming more and more accepted as an alternative to traditional systems, not only because of their environmental effects but also for their technical performance and economical benefits. This is of importance for the maintenance sector and can also lead to lower labour costs because of fewer layers. Another important argument in favour of the high solids approach is that high solids resemble conventional systems. Switching to high solid coatings is therefore easier and cheaper because standard equipment and knowledge built up over the years can be used. Professional coaters will accept these products more readily.[4)]

In this present work, a family of novolac resins has been synthesized for the preparation of high-solid novolac coatings to meet the environmental regulations. The novolac resins generally have wide range of commercial importance, mainly in molding compounds, coatings, wood binders due to their high-temperature tolerance with ablative properties.[5)] The ability of the corrosion resisting property of these novolac's coatings in 5% NaCl have been examined through electrochemical techniques. Visual inspections have also been made during the period of exposures.

2. Experimental details

2.1 Sample preparation

The synthesized aniline/cresol-formaldehyde (ANS & CNS) and already polymerized carboxylic acid ended acrylic co-polymer blended with cresol-formaldehyde (ACNS) novolac were applied over pre-treated mild steel specimens which is mechanical polished and decreased with acetone[2)] The preparation procedures was established in earlier literature.[6)] The carboxylic-ended acrylic copolymer was established by author in earlier.[2)] The coating was cured at 100°C for 30 minutes in hot air-oven, to

obtain the coatings having average dry film thickness of 25±5μm, which was measured by using a magnetic gauge.

Three cylindrical glass tubes (5cm length and 1cm dia) were fixed on the coated flat surfaces with the aid of epoxy adhesives to get good adhesion to the flat metallic coated substrates, which create a specially arranged cell set up.[7)-9)] The 5% NaCl electrolyte was filled in the tube up to 3.5 cm height; the exposed area of the coated substrates was 1 cm^2.

3. Electrochemical methods and equipments

3.1 Potential-time measurement

The 5% aq.NaCl aggressive solution was filled in the specially arranged cell[7)-9)] and the exposed area of coated substrate was 1 cm^2. Change in potential of high solid material coated specimens was noted with an interval of 24 hours for a period of 240 hours. Electronic multimeter Philips model PM 2518 was employed to monitor the potential change against saturated calomel electrode (SCE). This measurement was taken to discuss about the correlation between the corrosion potential of the coating and real behavior of the system.

3.2 Electrochemical impedance measurement

EIS measurements were carried out for ANS, CNS and ACNS coated specimens at ambient condition, open to air in 5% NaCl solution with different exposure times (48, 84, 120, 240 hours). The coated steel substrate with 1 cm^2 area was served as the working electrode. A platinum foil and SCE were used as auxiliary and reference electrodes respectively. All measurements were carried out at the open circuit potential, with 15 minutes interval to reach steady state potential. The EIS measurements were performed by using an EG & G Princeton Applied Research (PAR) Model 6310 electrochemical impedance analyzer with Equivcurt 398 software.

Impedance spectra were recorded in the frequency range of 100 KHz - 10 mHz with 10 mV AC amplitude was super imposed over the steady state potential. Impedance measurements were carried out for all the coated substrates immersed in aggressive electrolyte for 240 hours with periodic intervals.

The coating resistance was obtained from the lower frequency end of the corresponding Bode/Z/ (impedance Vs frequency) plots and coating capacitance (Cc) values were calculated using the following equation,[2)]

$$Cc = 1//Z/''$$

Where,

Cc - Coating capacitance

/Z/'' - imaginary part of impedance

3.3 Tafel polarization measurement

Polarization measurement for the high solid coated materials in 5% NaCl were carried out using BAS 100A Bio-electrochemical at different time interval for a period of 240 hours. The electrochemical cell setup was same as that used for the EIS measurements. A time interval of 15 minutes was given for each experiment to get constant open circuit potential (OCP) and the changes of potential were recorded until its stabilization at a value referred to as the corrosion potential (E_{corr}). The coated substrates were polarized 300 mV anodically and 200 mV cathodically with respect to OCP of the system at a sweep rate of 1 mV/Sec. Log current Vs potential plots were recorded. The corrosion current (i_{corr}) and corrosion potential (E_{corr}) were calculated from their respective plots.[10]

4. Results and discussion

4.1 Potential-time and Polarization measurements:

Monitoring the electrode potential (E_{oc}) and corrosion potential (E_{corr}) against exposure time provides a means for estimating the corrosion tendency of the specimens of various categories. Fig. 1 the E_{oc} of the coated substrates was plotted against immersion time. From the Fig. 1 it is clearly evident that among the 3 formulations studied, the formulation with CNS has minimum potential change towards negative side compared to other two formulations in 5% NaCl of continuous exposure. The high positive potential is explained as due to anodic passive effect.[11] Any negative shift of either E_{oc} or E_{corr} is explained as due to permeation of moisture or water through the pores of the films and initiates active corrosion in the metal film
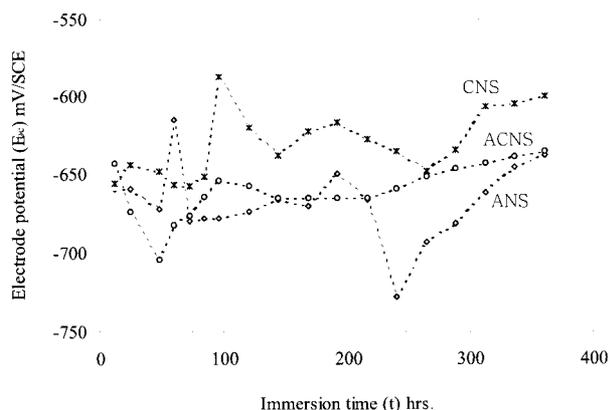

Fig. 1. Plots of electrode potential (E_{oc}) Vs immersion time (t) of various protective coated specimens exposed in 5% NaCl solution.
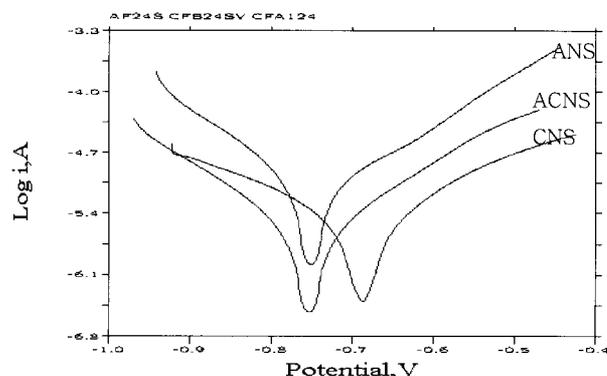

Fig. 2. Potentiodynamic polarization plots of specimens exposed in 5% NaCl solution after 24 hours exposure
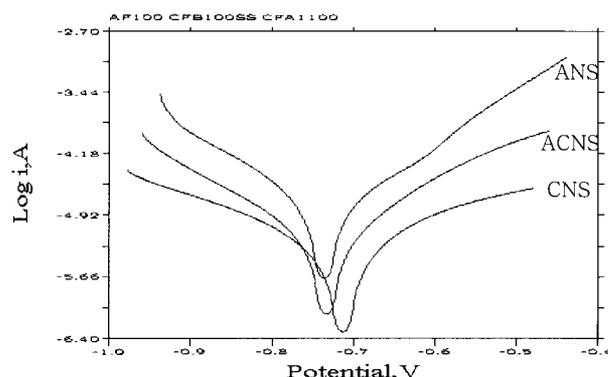

Fig. 3. Potentiodynamic polarization plots of specimens exposed in 5% NaCl solution after 120 hours exposure
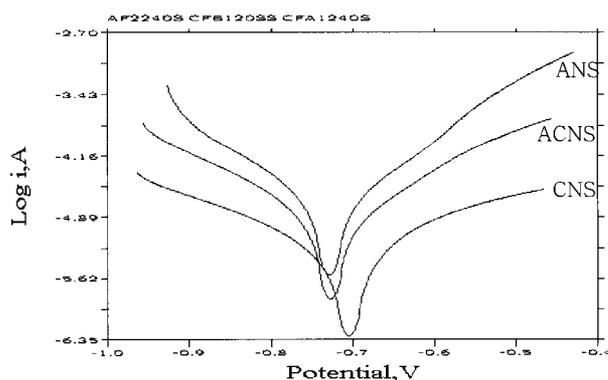

Fig. 4. Potentiodynamic polarization plots of specimens exposed in 5% NaCl solution after 240 hours exposure

interface.[12)-14)] The ANS and ACNS formulations having more negative potential shift than CNS formulation indicate that the CNS formulation has better permeation resistance than other two.

The plots of all potentiodynamic polarization diagrams for coated substrates immersed in 5% NaCl solution are given in Figs. 2~4. The corrosion rate expressed in corro-
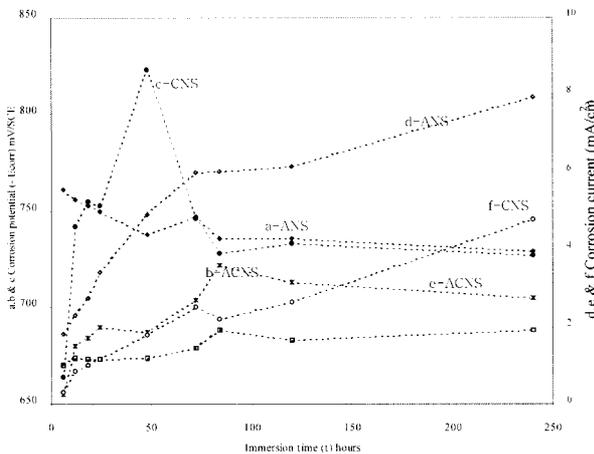
Fig. 5. Plots of corrosion potential / current Vs immersion time (t) of various protective coated specimens exposed in 5% NaCl solution.

sion current density (i_{corr}) was comparatively lower than the bare (uncoated) substrate. The Tafel plots of all formulations move towards negative (more cathodic) direction with in the experimental study duration of 240 hrs. The more negative shift of the corrosion potential with increased time of exposure indicates the more susceptible nature of the underlying steel surface to corrosion.[15] The CNS coating has more noble potential compared with the other systems. It is evident from the shifting of potential towards cathodic region and exhibition of lower corrosion potential (shown in fig. 5) in corrosive atmosphere, even after 84 hrs of exposure. The corresponding value was -650 mV and it remain constant throughout the exposure.

It can be concluded that, the E_{oc} of CNS is nobler than ANS & ACNS and the CNS coating has maintained an almost constant E_{oc} & E_{corr} (value variance less than ± 10mV between them) of low electronegative (more noble) values. It demonstrates that coating with free cresol-formaldehyde coating (CNS) provides relatively low permeability to moisture and other corrosive agents.

On the contrary ANS and ACNS coated specimens having the more active potential and the potential decay to more negative are confirmed from figs. 1&6, suggest that, they have less corrosion protection property. After 240 hrs of exposure, the icorr of ANS and ACNS coated substrates increase to 7.94 $\mu A/cm^2$ and 4.78 $\mu A/cm^2$ respectively. But CNS coating has maintained its protective character, providing lower values of i_{corr}, i.e., from 0.03-1.90 $\mu A/cm^2$. The corrosion protection property of the coating systems could be graded based on the parameters such as E_{oc}, E_{corr} and i_{corr}, values, which leads to the following order.

CNS > ACNS > ANS

4.2 Electrochemical impedance (EIS) measurements

This method offers a convenient way for evaluating the performance of organic exposed coatings. Generally, the resistance of the coatings gets degraded with time in aggressive environment. The resistance is associated with water penetration in to the coatings, transport of ions through the coating and the subsequent electrochemical reaction takes place at the polymer-metal interface.[16] The EIS has proven to be the most successful and informative analytical tool to analyze the coatings in recent years.[17]-[23] The properties of organic coatings were examined through electrochemical impedance (EIS) measurements. The total coating resistance (R_f) yes correct this is a film resistance & capacitance (Cc) was obtained at low frequency tail end of respective Bode/Z/ impedance plots. The R_f value will be considered as total coating resistance, since it represent the sum of the coating resistance, charge transfer resistance and solution resistance.[24]

R_f values of all coatings were lower than 10^5 Ωcm^2 ranging from 3.76×10^5 to 7.78×10^2 Ωcm^2), respectively. These low resistance values indicate that the coatings possessed an inherent porosity, substantial amount of electrolyte penetration through the pores of the coating, lower film thickness of unpigmented coating and adherence of the coatings etc., [25]-[27]. This suggests that the electrolyte has penetrated through the coatings and that corrosion of the metallic substrate has taken place vigorously. It also indicates that the unpigmented organic coatings are no longer act as protective layer.[28]

The variations of paint film resistance (R_f) and coating capacitance (C_c) are plotted with respect to time represented in Figs. 6&7. It shows that the R_f value
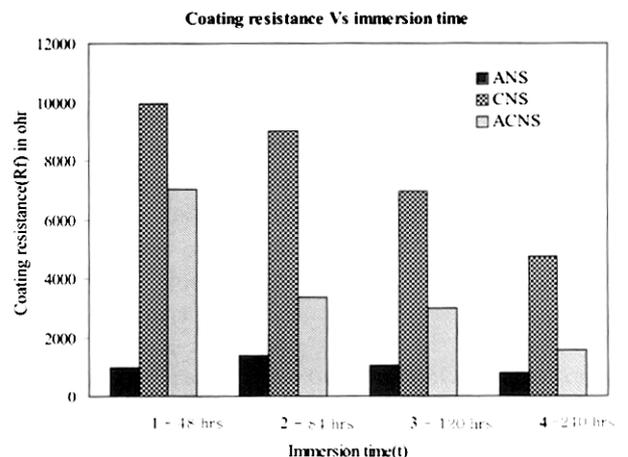

Fig. 6. Plot of coating resistance (R_f) against immersion time (t) of 3-different Novolacs coated specimens exposed in 5% NaCl solution
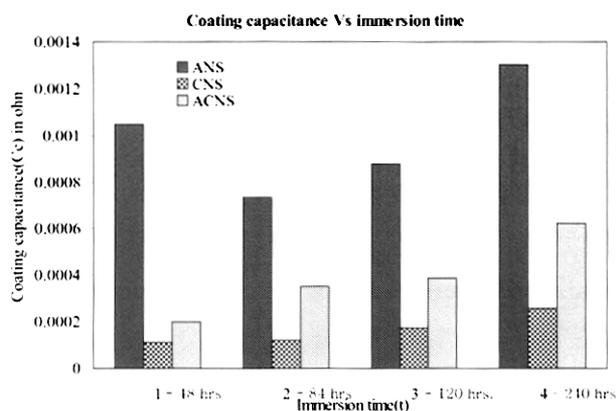
Fig. 7. Plot of coating capacitance (Cc) against immersion time (t) of 3-different Novolacs coated specimens exposed in 5% NaCl solution

Fig. 8. Electrochemical impedance plots of specimens exposed to 5% NaCl solution for 240 hours

decreases gradually with increasing time of exposure, suggesting that water ingress was uniform through out the coating and not localized.[27]

Comparatively, in CNS coating having a higher resistance than the other two systems. ACNS system has initially higher R_f value (700 ohm), but decreases rapidly to 1.58 x 10^3 Ωcm^2 due to having blended with long chain carboxylic acid ended polymer matrix. But occurrence of hydrolysis in aqueous medium due to high polarity of the polymer causes the degradation of the coating.[28] This is responsible for the minimum R_f values during longer exposure in the case of ACNS system. As a result of this, the film becomes more permeable to water, oxygen and ions, which enhance the conductivity of the solution and facilitates the cathodic reaction of oxygen ionization, complementary to the metallic dissolution process.[29] The R_f value of CNS system is 9.95 x 10^3 Ωcm^2 at initial, however it decays slowly through long exposure (4.74 x 10^3 Ωcm^2 - after 240 hrs exposure). The slow decay of R_f values is due to the more anchoring behavior of methyl and hydroxyl groups. In the earlier literature, it has been observed that epoxy cresol-novolac resins exhibit excellent chemical as well as physical properties including acids and alkali resistance. It has better flexibility and hardness than epoxy phenol novolac and epoxy resins.[6]

Further, increasing the capacity values, associated with the penetration of water in to the coating as well as an increase in the area of pores. The water uptake causes an increase of the relative dielectric constant of the coating.[30] The Fig. 7 shows the variation of coating capacitance with immersion time. It is evident that the best performance of CNS coating was due to attainment of saturation in capacitance value up to end of exposure.

The Nyquist plots of impedance spectra were recorded for the coated steel substrates exposed in 5% aq. NaCl
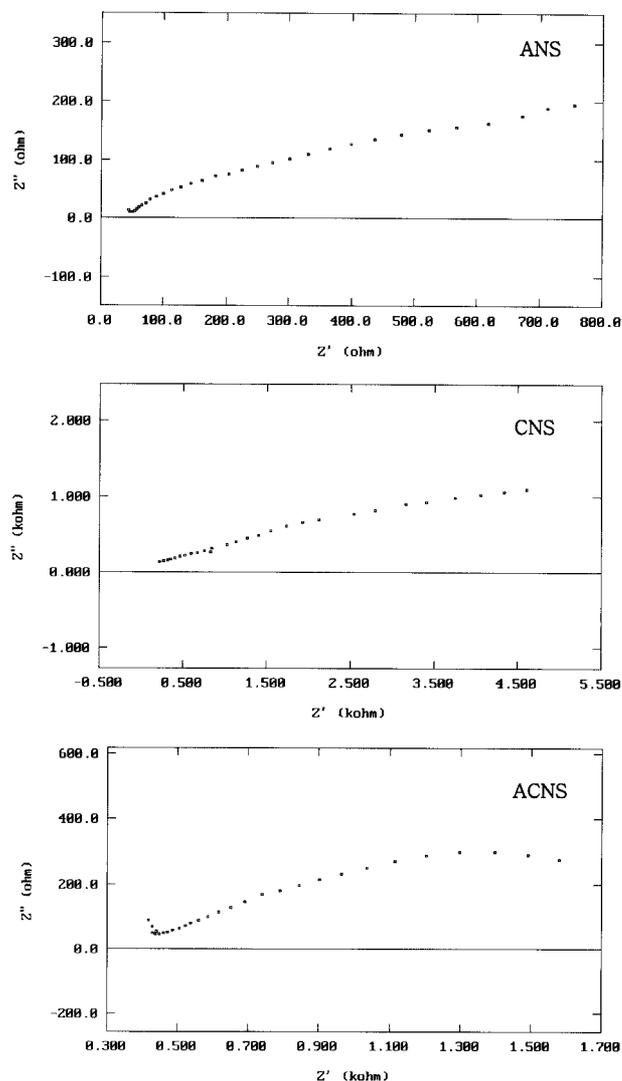
solution and presented in Fig. 8. Nyquist plots show the coatings depict the Warburg impedance (diffusion tail) as a consequence of a diffusion controlled corrosion process occurring at the protective coating interface.[28] The system response in terms of impedance in EIS can be interpreted by means of appropriate equivalent circuit called as Randles simple circuit,[25),31)-34)] represented as follows,

Equivalent Circuit
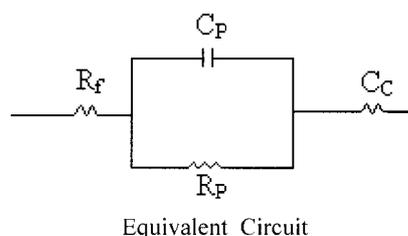
R_f represents the combined resistance of the solution, the adsorbed layer, yes correct and the corrosion products on the metal surface, R_P and C_P, the ionic resistance and capacitance and C_c is the coating capacitance.

As per ASTM,[34] visual inspection of specimens was observed during their exposure in 5% NaCl solution for 360 hours. Blisters and rust spots have not been observed through out the exposure (up to 360 hrs) of all protective coatings. Hence, all the coating systems performed well during shorter immersion periods. The order of the performance based on the capacitance and resistance values is same as that predicted in the previous studies. This result reiterates the CNS coated system offered high corrosion resistance property in the 5% NaCl aggressive environment over a period of the study.

5. Conclusions

The corrosion protection behavior of ANS, CNS, ACNS high solid (having lower VOC) organic coatings on mild steel were studied as electrochemically in 5% NaCl and following conclusions have been drawn.

1) All the three systems perform well to provide best protection during shorter duration of immersion. CNS system has higher corrosion protection than the other systems. It is evident from lower corrosion potential (noble region) and maintains the lower corrosion current density through out the exposure time.

2) From the EIS study, it is inferred that the CNS system maintains higher coating resistance than the others, due to the anchoring nature of $-CH_3$ and $-OH$ groups present in it. On prolonged exposure, slowly increased capacitance and decreased R_f values were obtained for the CNS coated substrate.

3) Visual examination showed there was no blistering and rusting formation during the period of exposure for all the coated substrates.

4) The protective performance of the coating systems based on the corrosion potential, corrosion current, total coating resistance and capacitance leads to the following order.

CNS $>$ ACNS $>$ ANS

5) Evident from these studies, protective coating of these systems could be recommended to develop enamel coatings, for use in automobile applications.

Acknowledgements

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