

Study on Electrochemical Behavior of Nano-ZnO Modified Alkyd-Based Waterborne Coatings

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ABSTRACT: A nano-composite coating was formed using nano-ZnO as pigment in different concentrations, to a specially developed alkyd-based waterborne coating. The nano-ZnO modified composite coatings were applied on mild steel substrate by dipping. The dispersion of nano-ZnO particles in coating system was investigated by scanning electron microscopic and atomic force microscopic techniques. The effect of the addition of these nanoparticles on the electrochemical behavior of the coating was investigated in 3.5% NaCl solution, using electrochemical impedance spectroscopy. Coating modified with higher concentration of nano-ZnO particles showed com-

paratively better performance as was evident from the pore resistance (R_{po}) and coating capacitance (C_c) values after 30 days of exposure. In general, the study showed an improvement in the corrosion resistance of the nano-particle modified coatings as compared with the neat coating, confirming the positive effect of nano-particle addition in coatings. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2232–2237, 2009

Key words: waterborne coatings; Nano-ZnO; corrosion resistance; EIS; coatings; nanotechnology

INTRODUCTION

The addition of pigments has a pronounced effect on the properties of the organic coatings. However, several limitations and coating defects have been reported for the conventional micro-size pigments.¹ With the advent of nanotechnology and its application on coating, several properties of coatings are being modified with nano-materials as pigments/fillers. Owing to their small particle size, nano-materials exhibit special properties, and addition of these nano-materials to the coating system can produce multifunctional coatings.^{2–10} Further, the concentration of nano-particles required to achieve these modifications is far less as compared with the conventional micro-size particles. The main aim of this study is to understand the effect of nano-particles on the anticorrosive efficiency of the waterborne coatings.

In present study, nano-ZnO is used as a pigment to modify waterborne alkyd-based coatings. Nano-ZnO, owing to its characteristic structure possesses unique chemical, biological and semi-conductor properties. Because of its non-toxic nature as compared with ordinary zinc oxide (particle size ≥ 100 nm) and the ability to block UV radiation, it has

found vast applications in cosmetics, textile, and in many coatings systems. ZnO has a wide bandgap (3.37 eV) and large excitation binding energy of 60 meV; therefore, it can absorb light that matches or exceeds their band gap energy and which lies in the UV range of the solar spectrum.^{11,12} Nano-ZnO does not degrade over time because of its enhanced photostability providing long product life. Low photocatalytic activity of ZnO suppresses free radical formation thus preventing the damage of co-used organic components. It also possesses natural anti-fungal properties. Using these special properties of nano-ZnO, an environmental friendly and multifunctional coating was developed. Waterborne alkyd-based coatings pigmented with nano-ZnO particles in different concentrations were prepared by direct mixing method and their corrosion behavior was determined by electrochemical impedance spectroscopy (EIS). The corrosion characteristics of the coatings were investigated through immersion in 3.5% NaCl solution.

EXPERIMENTAL

Raw materials

Low-molecular weight, waterborne alkyd resin and other additives were procured from Worlee-Chemie, Germany and were used as received. Nano-ZnO (average size of 35–40 nm and specific area $29 \text{ m}^2 \text{ g}^{-1}$) was procured from Horsehead Corporation, USA.

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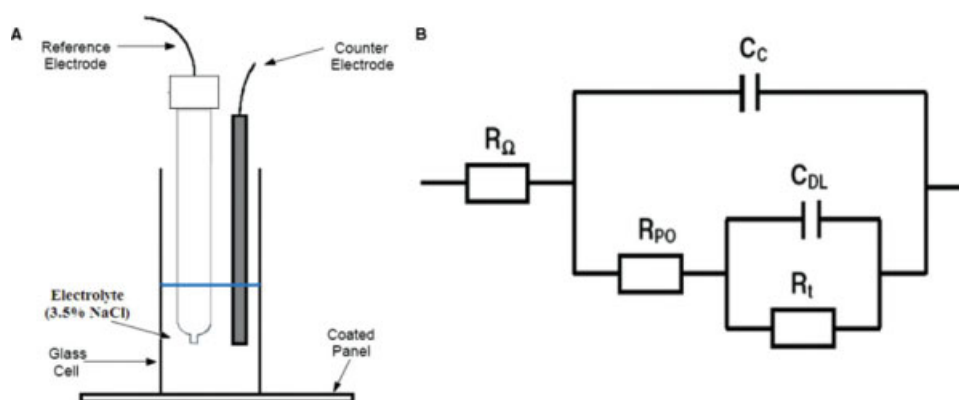


Figure 1 (a) EIS test apparatus and (b) equivalent electrical circuit for the corrosion behavior of the polymer-coated metal. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Preparation of nano-composite coatings

An alkyd-based waterborne clear coating developed in our laboratory was used as a base matrix for the preparation of nano-particle based composite coating.¹³ A nano-composite coating was formed by adding nano-ZnO to the base matrix in various concentrations, namely 0.01 wt %, 0.02 wt %, and 0.03 wt %. The particles were dispersed by using a high-speed mechanical stirrer followed by ultra-sonication. The coating was applied on cold rolled mild steel panels (76.2 mm × 152.4 mm × 0.8 mm) by dip-coating. The panels, after coating were cured in oven at 130 °C for 30 min and were cooled to room temperature. The measured coating thickness was 9–10 μm.

Characterization

The powder nano-particles were investigated by transmission electron microscopy (TEM) (Philips CM200) and X-ray diffraction (XRD) (X'Pert Pro Philips) for its shape and size. Analytical techniques like, scanning electron microscope (SEM) and atomic force microscope (AFM) were used to investigate the dispersion of nano-ZnO particles. Scanning electron microscopic studies were carried out using software controlled SEM, (Hitachi S-3400N). For this, a small piece of sample was cut from the test panel and was used for the SEM study. Surface topography information was obtained for samples by cutting a 12 mm × 12 mm size sample from the coated panel, and using a Digital Instrument Nanoscope IV Multimode Scanning Probe Microscopic controller, Veeco Metrology Group, operated in contact Mode with etched silicon probe. Scan size of 5 μm × 5 μm, was used to collect topography (height) images. EIS was used to evaluate the protective properties of the coatings. A classical three-electrode system was used: coated panel with an exposed area of ~3.2 cm² as working electrode, Ag/AgCl₂ as reference electrode and a platinum auxiliary electrode. Figure 1(a)

represents the typical test setup for the EIS study of the polymer coated metal. The measurement was conducted at room temperature in 3.5% NaCl solution for periods up to 30 days. Electrochemical impedance measurement was performed under the open circuit potential (OCP). EIS spectra were acquired using a software controlled CH Instrument system, Model 600C series, in the frequency range of 1 Hz–100 KHz with 5 mV applied ac (versus E_{ocp}). The results of EIS analysis for the nano-composite coatings is presented as Bode plot which comprises of a graph between the log magnitude versus frequency, measured over a range of frequencies. The high-frequency region of the Bode plot provides information about coating defects and other changes in surface area; the low-frequency region provides information about processes occurring near the metal surfaces. The interpretation of impedance

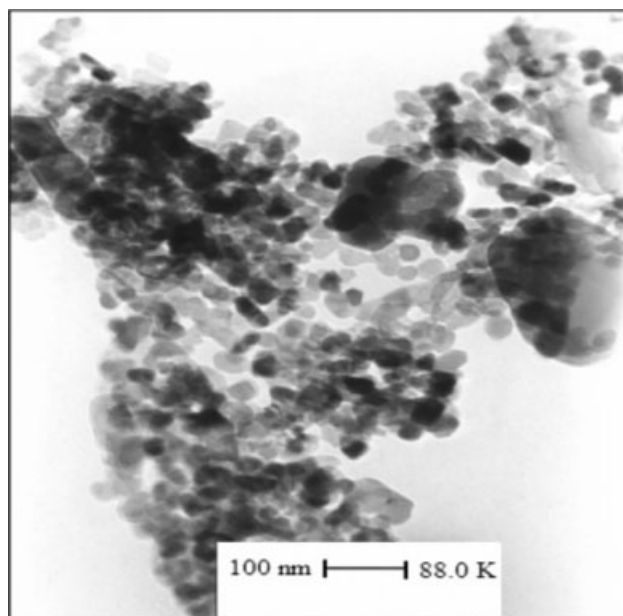


Figure 2 TEM photograph of nano-ZnO powder.

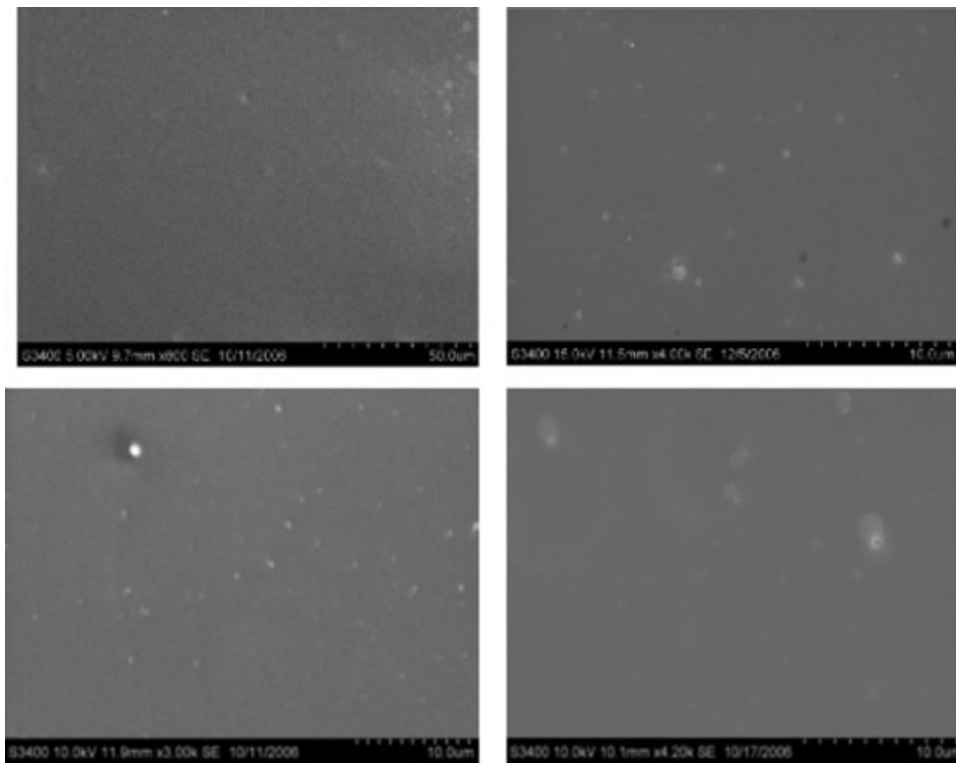


Figure 3 SEM surface micrographs of unexposed samples (a) neat sample and modified with (b) 0.01% nano-ZnO, (c) 0.02% nano-ZnO, and (d) 0.03% nano-ZnO.

spectra was performed after numerical fitting using the equivalent circuit presented in Figure 1(b).^{14,15} In this equivalent circuit R_{Ω} is the uncompensated resistance, C_c is the coating capacitance, which depends on its dielectric constant and its thickness, R_{po} is pore resistance owing to the formation of ionically conducting paths in the polymer, R_t is the charge transfer resistance and C_{dl} is the corresponding double layer capacitance.

RESULT AND DISCUSSION

TEM study of nano-particles

Figure 2 shows the TEM photograph of nano-ZnO. From this figure, it can be seen that the particle appears more or less spherical with an average particle size of $\approx 35\text{--}40$ nm.

Microstructure analysis

The surface of the neat and modified coatings was studied by SEM and AFM techniques, for any application or curing defects and also to investigate the dispersion of nano-ZnO particles in the coatings. Figure 3 shows the SEM surface micrographs of unexposed neat and nano-ZnO modified coatings at different loading levels. Figure 3(a) represents SEM surface micrographs of unexposed neat coating. It can be clearly seen that the coating formed is uni-

form and free from any application and curing defect. The surface micrographs of coatings modified with nano-ZnO particles [Fig. 3(b–e)] show no surface defects, indicating that the nano-ZnO particles are well dispersed except for a few agglomerations. This is well supported by the AFM topography height images as shown in Figure 4. Figure 4(a)

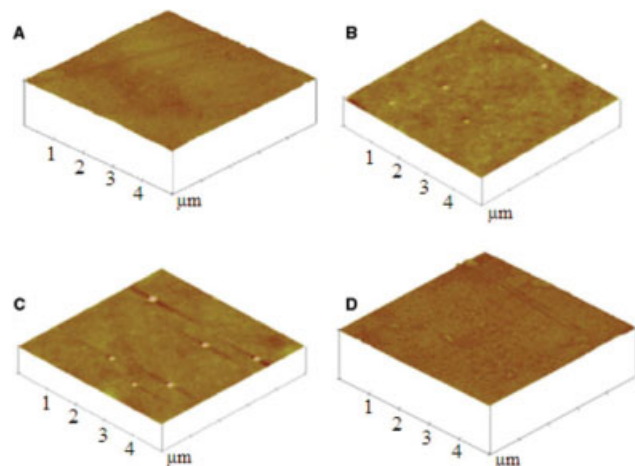


Figure 4 AFM topographic height images of an unexposed coating surface at a scan size of $2\ \mu\text{m} \times 2\ \mu\text{m}$ (a) Neat sample and modified with (b) 0.01% nano-ZnO, (c) 0.02% nano-ZnO, and (d) 0.03% nano-ZnO. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

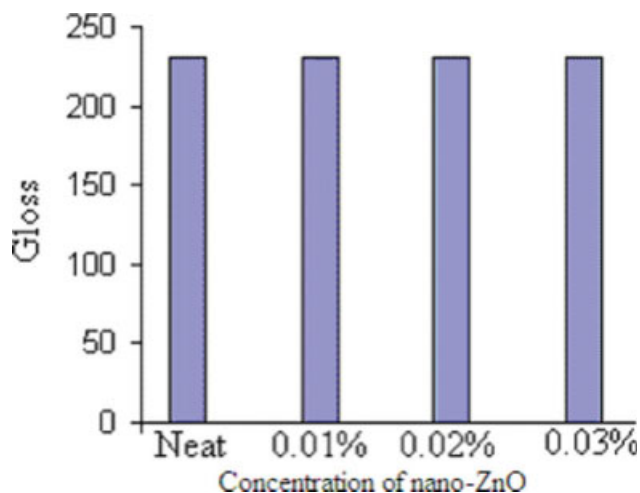


Figure 5 Gloss values for neat and nano-ZnO modified coatings at different concentrations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

represents the AFM topography height image of unexposed neat sample indicating that the coating surface before exposure was smooth with nanoscale roughness. Figure 4(b–d) demonstrates that the particles are evenly dispersed in polymer matrix. The polymer matrix surrounding the particles makes them appear bigger than as presented in AFM picture. The surface roughness measurement by AFM also supports the aforementioned discussion. Surface roughness of neat coating (4.17 nm) and nano-ZnO modified coatings (0.01% nano-ZnO (4.32 nm), 0.02% nano-ZnO (4.73 nm), and 0.03% nano-ZnO (4.95 nm)) shows no appreciable changes in their values after modification. This suggests that the particles in the coating are well-dispersed.

Dispersion of nano-ZnO particles in the coatings was further investigated by measuring the change in gloss of the coating. The measurement was carried out as per ASTM G523. Figure 5 shows the gloss values of the neat coating and nano-ZnO modified coatings. It can be seen that the gloss values are more or less the same for all the coating systems. This is attributed to the inherent property of the base matrix; also, the particle size is very small so there is no protrusion on the film surface followed by good dispersion, which provides a surface roughness of very small amplitude. Further, the concentration of nano-ZnO particle is so small that the well-dispersed particles in the coating do not protrude above the surface and therefore do not influence the surface glossiness.^{16,17}

Corrosion analysis of alkyd/nano-ZnO composite coatings

Figures 6 and 7 represent the bode plot for dry coating and coating exposed for 30 days in 3.5% NaCl solution, respectively. The OCP, R_{po} and C_c values

for the coatings at 0 days and after 30 days exposure are shown in Tables I and II, respectively. OCP is a summation of the half-cell reaction potentials in a specific electrolyte, which can be used as a measure of the spontaneity of the reaction and a rough indication of tendency to corrode.¹⁸

During the first hour of exposure, the coating modified with nano-ZnO shows a higher open-circuit potential, indicating a noble characteristic as compared with the neat coating. It can be seen that, with the increase in the concentration of nano-particles, the OCP shifts to noble direction as compared with the neat coating. Initially, the coating exposed to an electrolyte shows an excellent barrier property and acts as perfect capacitor. This is because the coating film does not allow water molecule to enter or penetrate the substrate. At this stage, the R_{po} is extremely high. This is evident from the bode plot (Fig. 6), which shows a straight line of slope-1 with high impedance at low frequency. The R_{po} for neat coating was found to be less as compared with those modified with nano-ZnO. The R_{po} in general increased as the concentration of nano-ZnO particles is increased from 0.01% to 0.03%. It can be attributed that the presence of well-dispersed nano-ZnO in the coating acts as a barrier for the penetration of electrolyte and increases the coating resistance as compared with the neat coating. Also, the C_c , which is associated with the uptake of water by the coatings has been found to increase during the initial stage of immersion. It can be noted that the C_c for neat coating (3.32×10^{-9} F/cm²) is much higher as compared with the C_c for nano-ZnO modified coatings. The ZnO-based coatings, show a relatively less increase in C_c as compared with neat coating and the value is the least for 0.03% nano-ZnO incorporated coating (6.9×10^{-10} F/cm²), indicating that the uptake of water by the composite coating is slow owing to its improved barrier property by the addition of nano-ZnO.

After 30 days of exposure, the OCP becomes more negative due to diffusion of the chloride ions at the metal/coating interface.^{19–21} The OCP for neat coating and nano-ZnO-based coatings has shifted to negative potential. However, the OCP of the neat coating has moved toward more negative potential (–620 mV vs. Ag/AgCl₂) as compared with 0.03% nano-ZnO modified alkyd coatings (–534 mV vs. Ag/AgCl₂), which is in positive direction as compared with the neat coating, indicating that the coating has maintained its integrity. Further, after 30 days of coating exposure, the R_{po} values for neat coatings as well as nano-ZnO composite coatings were found to decrease followed by an increase in the corresponding C_c . The R_{po} for neat coating had shown large decrease in its value when compared with its initial value for 0 days of exposure, whereas, nano-ZnO modified composite coatings show less

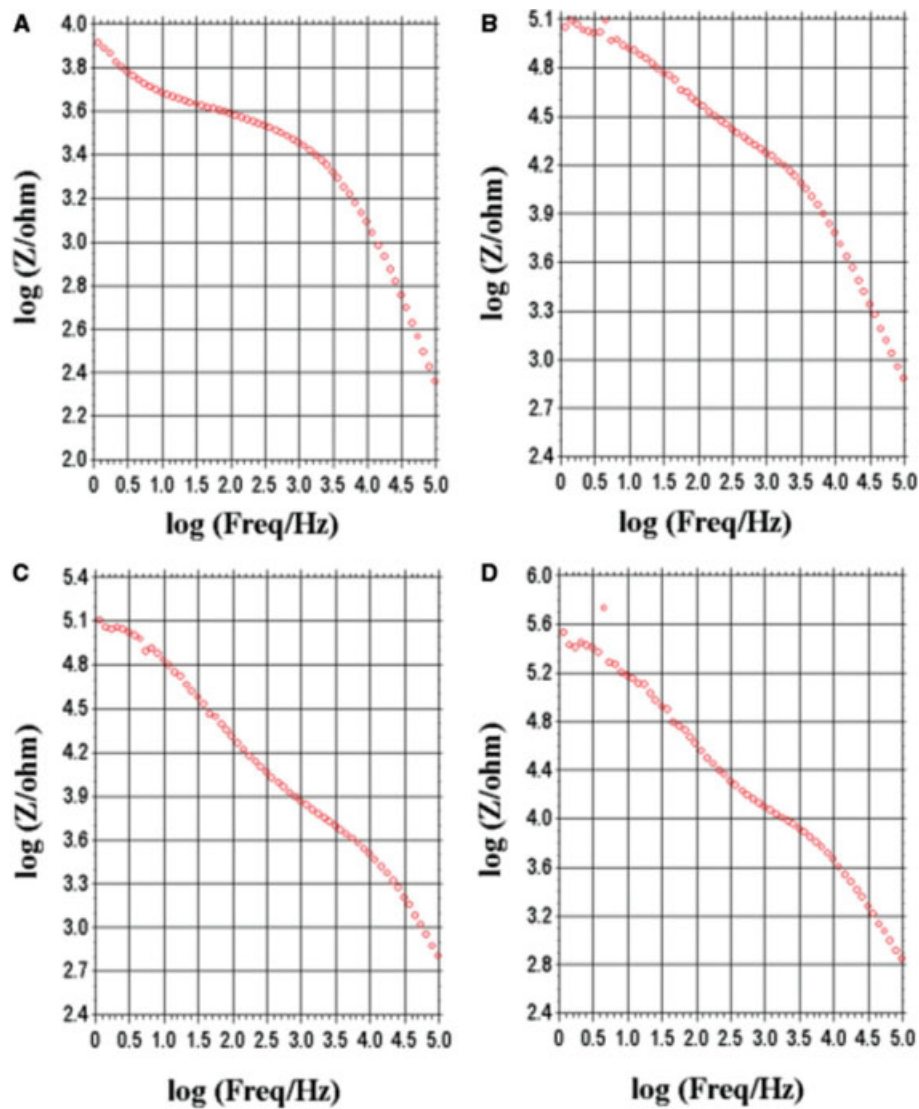


Figure 6 Bode plot for the coated sample (a) neat and modified with (b) 0.01% nano-ZnO, (c) 0.02% nano-ZnO, and (d) 0.03% nano-ZnO, at the first day of immersion in 3.5% NaCl solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

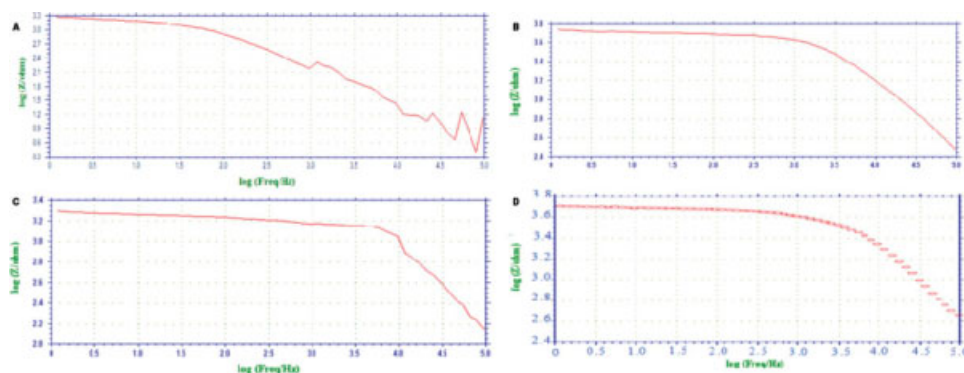


Figure 7 Bode plot for the coated sample (a) neat and modified with (b) 0.01% nano-ZnO, (c) 0.02% nano-ZnO, and (d) 0.03% nano-ZnO, after 30 days of immersion in 3.5% NaCl solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

decrease in their R_{po} values as compared with their corresponding initial values. The R_{po} value for 0.03% nano-ZnO modified coating showed least change in its R_{po} value, suggesting the effective performance toward corrosion resistance property. A significant increase in the C_c value for neat coating, $\sim 3.09 \times 10^{-7}$ F/cm², was seen after 30 days of exposure, which is 100 times more than that in the initial stage. This may be due to the structural changes occurring in the polymer network structure. It can be attributed that the electrolyte solution had penetrated into the coating through macro pores leading to the electrochemical process on the metallic interface which resulted into the loss of coating adhesion and breakdown of the polymer network structure, whereas, the increase in C_c for nano-ZnO modified coating was not much significant as compared with the neat coating. The 0.03% nano-ZnO modified coating showed the least increase in the C_c value (2.00×10^{-9} F/cm²) which is less as compared with the neat coating.^{22–25}

In general, it can be suggested that the coating without nano-ZnO showed significant decrease and increase in R_{po} and C_c values as compared with their initial values, respectively. But, with the increase in the concentration of nano-ZnO, the decrease in R_{po} value and increase in C_c value was not much significant indicating the improvement in the corrosion resistance of the coatings. The improvement in the corrosion resistance of nano-ZnO incorporated coating is attributed to the small size and large surface area of the nano-particle. Because of their small size, the free space between the particle and the resin is less and thus restricts the penetration of electrolyte through the pores in the coating film. The large surface area allows more amount of resin to adsorb on their surface and improves the interaction between the particle and the resin.

CONCLUSION

Nano-ZnO modified alkyd-based waterborne coatings were developed on a mild steel substrate. Although, the neat and nano-modified coatings show effective barrier against corrosive environment in the first stage of immersion, the protection seems

TABLE I
OCP, R_{po} , and C_c of Neat and Nano-ZnO Modified Alkyd-Based Waterborne Coatings at 0 Days of Immersion

Coating system	OCP	R_{po} (Ω/cm^2)	C_c (F/cm ²)
Neat	-0.535	876.3	3.32×10^{-9}
0.01% Nano-ZnO	-0.504	942.8	7.90×10^{-10}
0.02% Nano-ZnO	-0.513	1172	8.21×10^{-10}
0.03% Nano-ZnO	-0.500	1358	6.96×10^{-10}

TABLE II
OCP, R_{po} , and C_c of Neat and Nano-ZnO Modified Alkyd-Based Waterborne Coatings at 30 days of Immersion

Coating system	OCP	R_{po}	C_c
Neat	-0.620	373	3.09×10^{-7}
0.01% Nano-ZnO	-0.561	500	3.98×10^{-9}
0.02% Nano-ZnO	-0.559	925	2.63×10^{-9}
0.03% Nano-ZnO	-0.534	1190	2.00×10^{-9}

to reduce owing to the diffusion of corrosive electrolyte through the coating film, after 30 days of testing. However, nano-particle modified coatings showed delay in corrosion process as evident from the R_{po} and C_c values after the 30 days of exposure. The improvement in the corrosion resistance of the nano-modified coatings was much significant at the higher loading level (0.03%). This suggests the positive effect of nano-pigments, addition on alkyd-based waterborne coatings. However, optimization in the loading level of nano-particles and development in dispersion technique can further improve the performance of the coating.

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