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EVALUATION OF CORROSION PROTECTION PERFORMANCE OF CONDUCTING POLYANILINE/NANO-ZINC PHOSPHATE COATED LOW CARBON STEEL BY IMPEDANCE SPECTROSCOPY

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Conducting polyaniline nano zinc phosphate composite was prepared by chemical oxidative method. The epoxy based paint containing 2 wt % conducting polyaniline nano zinc phosphate composite pigment was applied on low carbon steel samples. Corrosion protection performance the painted low carbon steel samples in 3.5 wt % sodium chloride solution was evaluated by impedance spectroscopy and alternating immersion testing machine. Conducting polyaniline nano zinc phosphate based paint can protect low carbon steel up to 48 hours in 3.5 wt % NaCl aqueous medium and withstand drying - wetting cycles in the atmosphere. The protection is based on simultaneously operating mechanisms viz. enhanced barrier protection, passivation and release of inhibiting phosphate ions when in contact with corrosive media.

Keywords: Conducting Polyaniline, Nano Zinc Phosphate, Impedance spectroscopy, Alternating immersion testing, Corrosion protection, Pigments, Low carbon steel

1. Introduction

Low carbon steel products get corroded when the relative humidity in the atmosphere exceeds sixty percent. Organic coatings or paints are commonly used to protect low carbon steel products in commercial practice. However, inhibitive coatings, the most effective anti-corrosion organic coatings contain environmentally hazardous pigments. Conducting polymers such as polyanilines have been emerged as an alternative to the toxic pigments in paint formulations [1]. However, the extent of using this conducting polymer coating for commercial applications becomes limited in presence of relatively large defects in the coating [2]. One of the strategies, recently adopted, for improving performance of the

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conducting polymer coating is the use of nano composites [3]. S. Radhakrishnan et al. synthesized conducting polyaniline - nano TiO_2 composite based paint and evaluated its corrosion resistance in 3.5 wt% NaCl by electrochemical methods. In these investigations, the open- circuit potential was found to shift with time from 0.38 V SCE to anodic side [4]. P. P. Deshpande et al. synthesized polyaniline/ multi wall nano-tubes (PANI- MWCNT) composite based paint and observed that the corrosion rate of low carbon steel painted with this composite in 3.5 wt % NaCl, was ~ 0.037 mm per year, which is about 5.2 times lower than that of un painted low carbon steel and 3.6 times lower than that of epoxy coated steel [5]. Al. Dulami et al. used TiO_2 andSiO_2 in an acrylic sheet to prepare conducting polyaniline based paints. In this work, it was found that the acrylic paint containingSiO_2wasmore effective for corrosion protection of steel [6]. P.P. Deshpande et al. recently reported the corrosion protection performance of conducting polyaniline nano zinc phosphate based paint on low carbon steel. The corrosion rate of low carbon steel coated with 2 wt % PANI-Zn_3 $(PO4)_2$ based paint, in 3.5 wt % NaCl, was found to be 5.1×10^{-4} mm per year, which is about34 times lower than that of unpainted low carbon steel and 10timeslower than that of epoxy coated steel [7]. For commercial use, however, paint coating should be able to protect the desired metal for long term duration. To investigate long term performance, conducting polyaniline-nano zinc phosphate painted low carbon steel samples were investigated in 3.5wt % NaCl by using electrochemical impedance spectroscopy as well as alternating immersion testing and results are reported in this paper.

2. Experimental Procedure

2.1 Synthesis of nano zinc phosphate crystals

Nano zinc phosphate crystals were synthesized as per the similar method described by Jin Ku Liu et al. [8]. Tri sodium phosphate (0.1 M of $Na_3PO_4.12 H_2O$) was added in 100 ml distilled water. This solution along with another solution containing zinc nitrate (0.1 M of $Zn (NO_3)_2 .6H_2O$) was added in 500 ml of distilled water. The reaction system was put in the ultrasonication machine-Equitron (Supplied by Medico Instrument Manufacturing Co, Mumbai, India) with continuous stirring until complete precipitate was formed. The precipitate was sonicated for15 minutes and filtered by using conical flask with 41 numbered what man filter paper. The powder was dried in a simple oven at 100°C for 45 minutes and crushed in a mortar for 10 minutes. Finally, it was dried in a microwave oven for homogenization. The nano zinc phosphate pigment particles, so obtained, were subsequently used for making conducting polyaniline nano zinc phosphate composite.

2.2 Synthesis of conducting polyaniline nano zinc phosphate composite and paint preparation

Conducting polyaniline was synthesized by addition of 0.94 ml 0.1 Maniline in to 0.1M 100ml ortho - phosphoric acid using 0.1M ammonium persulphate as an oxidizing agent. Aniline (AR grade supplied by Loba Chemicals, India) was double distilled prior to use. Orthophosphoric acid and ammonium persulphate (AR grade supplied by Loba Chemicals, India) were used without further purification. Two grams of nano zinc phosphate powder were added during chemical polymerisation of aniline in the ortho- phosphoric acid solution to get conducting polyaniline nano zinc phosphate composite. Conducting polyaniline based paint was prepared by following the technique described by Deb et al. [9]. Conducting polyaniline-nano zinc phosphate composite paint formulation is given Table 1.

Table 1

Conducting polyaniline -nano zinc phosphate composite paint formulation

Sr no	Chemical name	Weight in gram (gm)
1	Epoxy resin G Y 250 Araldite	70
2	Xylene solvent LR grade	12
3	Dioctyl phthalate (2-ehyalhexyl)	8
4	Titanium di oxide (TiO_2)	8
5	PANI - nano zinc phosphate ($Zn_3(PO_4)_2$)	2

One hundred grams of the paint was ball milled for 16 hours (Ball Mill supplied by Indo- German Industries, Daman, India, Crompton Make Drive 2 HP motor with 1440 rpm, 415 Voltage, 50 Hz frequency). The purpose of adding titanium dioxide and Di-octyl phthalate in epoxy resin to improve viscosity and elastic properties of paint. Xylene was used as a solvent for paint formulation. The paint was filtered through fine cotton and applied on the low carbon steel samples (AISI 1015 supplied by Rajasthan steels, India) by film applicator to keep paint thickness ~ 60 µm uniform on the entire surface. Finally, the painted low carbon steel samples were cured in air at ambient temperature for 24 hrs.

2.3 Electrochemical impedance studies

A corrosion cell having three-electrode geometry, in which paint coated sample acts as working electrode (8 cm^2), platinum as counter electrode and saturated calomel electrode (SCE; pH Products, Hydrabad, India) as a reference electrode was used. The cell was coupled with Gamry reference system 1000 (Wilmington, USA) for electrochemical impedance measurements. The corrosion protection performance of epoxy containing 2 wt % nano zinc phosphate, epoxy containing 2 wt % polyaniline and 2wt % polyaniline- nano zinc phosphate painted low carbon steel was assessed by electrochemical impedance spectroscopy in 3.5 wt % NaCl aqueous solution. All measurements were carried out five times to obtain good reproducibility of the results, over frequency range 100 KHz to 0.1 Hz using amplitude signal 10 mV rms as per ASTM G106 and ASTM 2005b.

2.4 Alternating immersion studies

In order to evaluate resistance of the coating to withstand drying and wetting cycles in the atmosphere, A home-made alternating immersion testing machine set up as shown in Fig. 1 was used. It consists of 300 mm diameter wheel and 20liters capacity plastic tank. The painted samples were suspended from the spokes of the wheel in 3.5 wt% NaCl aqueous solution by a thread. The speed of rotation of the wheel was kept constant~ 0.2 rpm. During each rotation, the sample gets partially immersed in the solution and also exposed to the atmosphere. The potential was measured immediately after its immersion in the medium against SCE and at regular intervals of 24 hours up to 96 hours of immersion. In addition to potential, capacitance values of the painted samples were also noted by using Digital LCR meter (Rhydo Technologies Private Ltd, India, Model, V5 300 M)

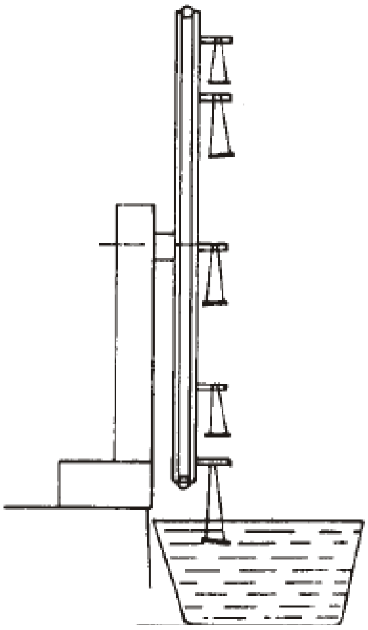

Fig.1. Schematic of home-made alternating immersion chamber

3 Results and Discussion

3.1 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopic investigations of painted samples just after immersion and by the end of 24 hours, 48 hours, 72 hours and 96 hours of immersion in 3.5 % wt NaCl solution were carried out and reported here in terms of bode plots depicted in Figs. 2 to 7. The impedance values obtained from these figures are recorded in Table 2.

Table 2

Zinc phosphate coated samples: Impedance values

Sample	Immersion time (Hrs)	Z_{mod} (kΩ-cm^2)	Z_{real} (kΩ-cm^2)
Zinc phosphate painted low carbon steel	Just after immersion	26.11	24.99
	24	1.30	1.28
	48	814	585
	72	0.41	0.38
	96	0.48	0.45
PANI painted low carbon steel	Just after immersion	3.91	4.01
	24	9.29	8.72
	48	3.59	3.32
	72	9.05	8.66
	96	5.32	4.92
PANI -2% zincphosphate painted low carbon steel	Just after immersion	29.13	28.55
	24	151.7	149.0
	48	724.3	645.1
	72	51.03	50.63
	96	7.47	7.35

Bode plots for epoxy containing 2 wt % nano zinc phosphatecoated low carbon steel just after immersion, 24 hours of immersion, 72 hours of immersion and 48 hours of immersion are shown in Figs. 2 and 3 respectively.

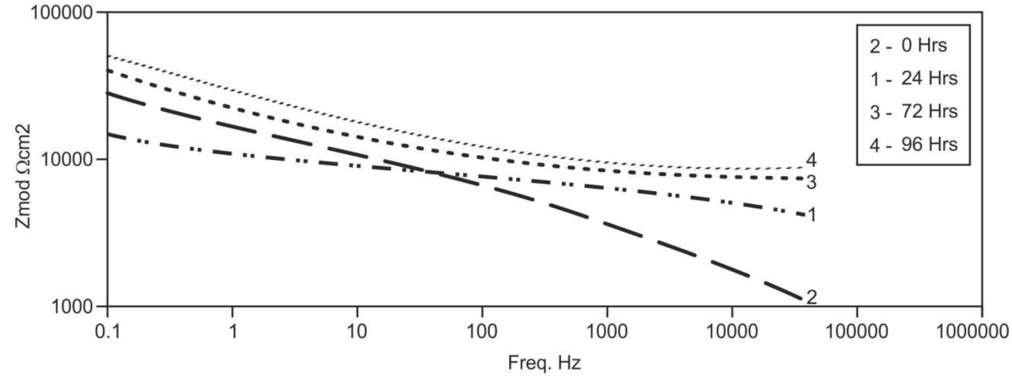

Fig. 2. Bode plot for epoxy coating containing 2 wt % nano zinc phosphate

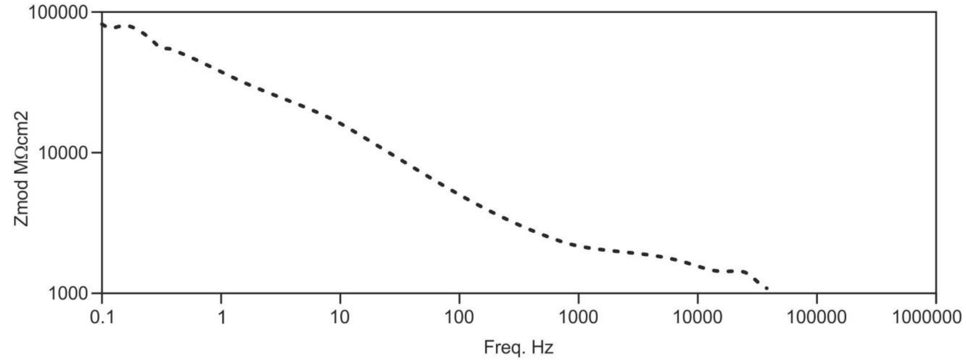

Fig. 3. The bode plot for epoxy containing 2 wt % nano zinc phosphate after 48 hours of immersion

The impedance (z $_{mod}$) is found to be decreased from 26.11 kohms-cm^2 just after immersion to 1.30 kohms-cm^2 at 24 hours of immersion. This can be assigned to dissolution of steel in chloride medium. Subsequently, it increased to 814 Kohms-cm^2 at 48 hours of immersion. This can be attributed release of phosphate ions from the zinc phosphate pigment and their inhibition effect. However, it again decreased to 0.41 kohms-cm^2 at 72 hours of immersion and 0.48 Kohms-cm^2 at 96 hours of immersion.

Bode plots for epoxy containing 2wt % polyaniline, just after immersion and for 24, 48, 72 and 96 hours of immersion are shown in Figs. 4 and 5 respectively.

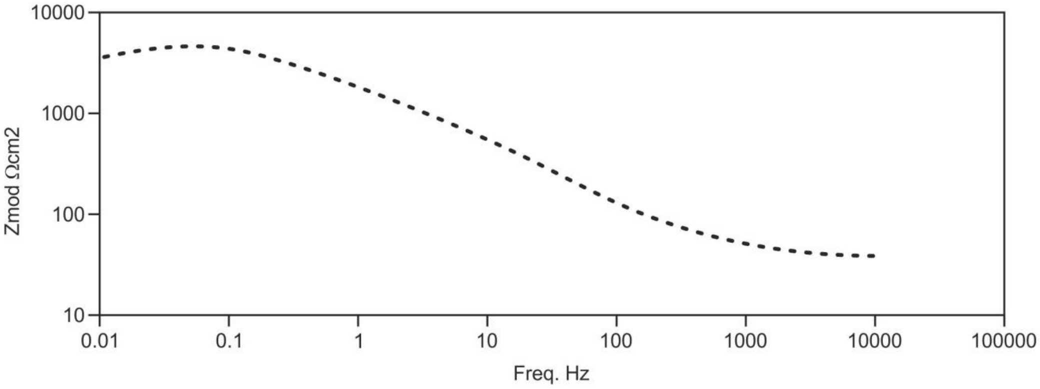

Fig.4. The bode plot for epoxy containing 2 wt % polyaniline, just after immersion

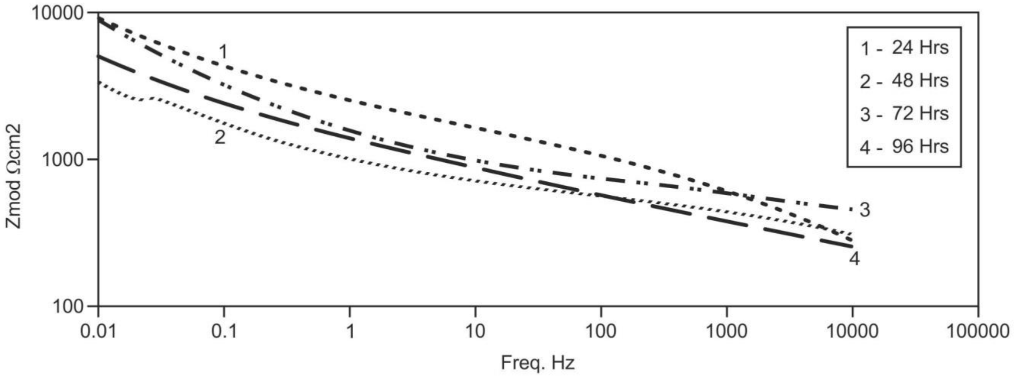

Fig.5. Bode plot for epoxy containing 2 wt % polyaniline for 24, 48, 72 and96 hours of immersion

The impedance (z_{mod}) is found to be increased from 3. 99 kohms-cm^2 just after immersion to 9.29 kohms-cm^{2}by the end of 24 hours of immersion. Subsequently it decreased to 3.59 kohms-cm^{2}after 48 hours of immersion. However, it again increased to 9.05 kohms-cm^2 by the end of 72 hours of immersion and then decreased to 5.32 kohms-cm2 after 96 hours. Increased impedance values can be assigned to the passivation of steel due to redox behaviour of conducting polyaniline. The impedance values in case of conducting polyaniline coated samples are significantly lower than that of nano zinc phosphate coated samples. Bode plots for epoxy containing 2 wt % conducting polyaniline-nano zinc phosphate just after immersion and for 24, 48, 72 and 96 hours of immersion are shown in Figs. 6 and 7.

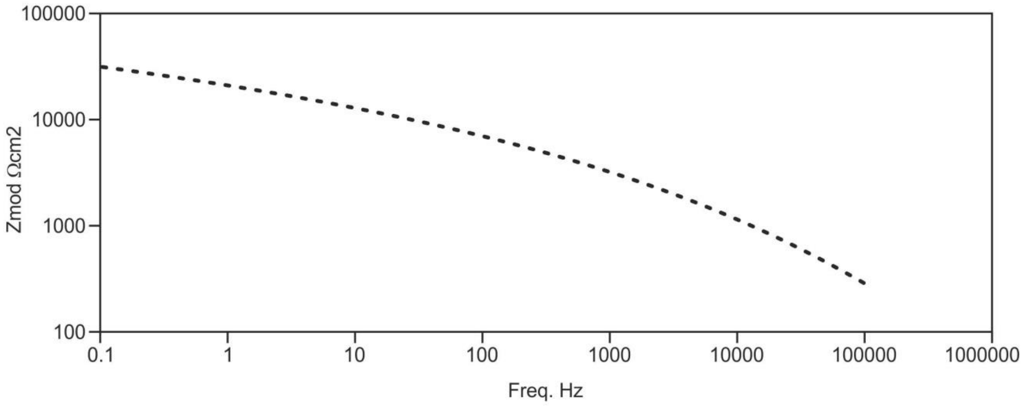

Fig.6. Bode plot for epoxy containing 2 wt % conducting polyanilinenano zinc phosphate just after immersion

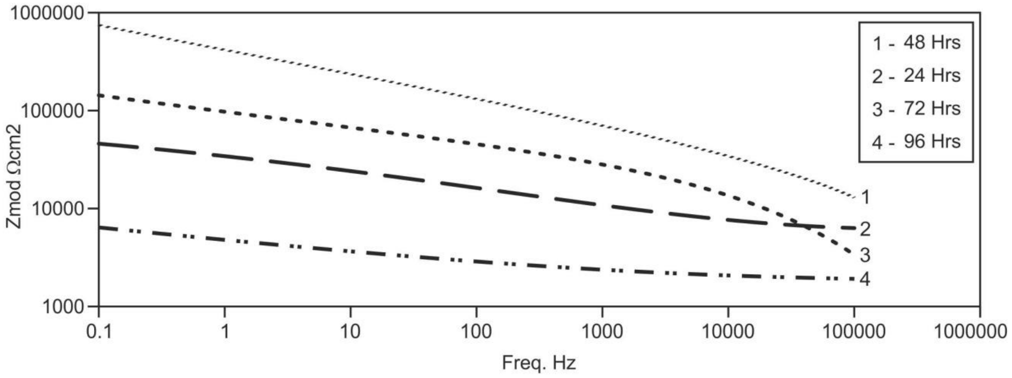

Fig.7. Bode plot for epoxy containing 2 wt % conducting polyaniline nano zinc phosphate for 24, 48, 72 and 96 hours of immersion

The impedance (z_{mod}) is found to be increased from 29.13 kohms-cm^2 just after immersion to 151.7 kohms-cm^2 by the end of 24 hours of immersion and to 724.3 kohms-cm^2 by the end of 48 hours of immersion. It decreased to 51.03kohms/cm^{2}by the end of 72 hours of immersion and to 7. 47 k ohms-cm^{2}after 96 hours of immersion. Electrochemical impedance investigations, therefore, substantiate previous potentio dynamic polarization results [7]. It was demonstrated that steel in contact with conducting polyaniline gets oxidized and subsequently protected due to the formation of iron oxide at the polyaniline -steel interface as shown in Fig. 8 [10].

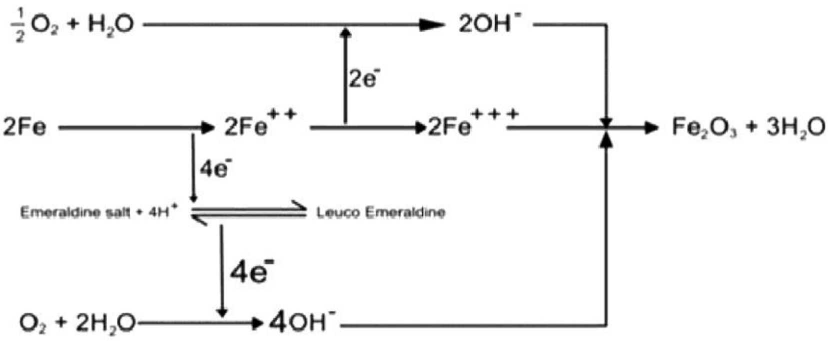

Fig. 8. Formation of iron oxide

3.2 Alternating immersion studies

Potential and capacitance values observed during alternating immersion testing are recorded in Table 3.

Table 3

Potential and capacitance measurements during alternating immersion

Sample	Immersion time (Hrs)	Potential (mV)	Capacitance (nF)
Zinc phosphate painted low carbon steel	Just after immersion	0	0.02
	24	-0.07	0.30
	48	-0.06	0.65
	72	-0.09	2.5
	96	-0.12	3.0
PANI painted low carbon steel	Just after immersion	0	0.02
	24	-0.08	0.70
	48	-0.09	0.80
	72	-0.16	20
	96	-0.18	21
PANI -2% zinc phosphate painted low carbon steel	Just after immersion	0	0.01
	24	-0.06	0.04
	48	-0.05	0.03
	72	-0.08	0.04
	96	-0.08	0.05
Uncoated low carbon steel.	Just after immersion	-0.43	-
	24	-0.55	-
	48	-0.60	-
	72	-0.62	-
	96	-0.63	-

As seen from the recorded values in the Table 3, uncoated steel attains potential of - 0.43 mV just after immersion, whereas all other coated samples show zero potential measurements. This indicates that all the coatings were practically intact at the time of immersion. Potential of uncoated steel decreased continuously and attained potential of - 0.63 mV after 96 hours of alternate immersion. The painted sample containing 2 wt % conducting polyaniline exhibited increase in the potential from 0 mV to-0.084 mV, - 0.09 mV, - 0.16mV and - 0.18 mV after 24, 48, 72 and 96 hours of immersion respectively. This increase in active or negative direction reveals polyaniline coated samples could not withstand alternating drying and wetting cycles in atmosphere. However, an increase in the potential in positive direction from -0.079 mV to -0.065 mV and - 0.06 mV to - 0.052 mV is observed in case of epoxy coating containing 2 wt % zinc phosphate and 2 wt % polyaniline nano zinc phosphate during 24 to 48 hours of immersion respectively. This indicates capacity of these two coatings to withstand alternating drying and wetting cycles in atmosphere. It must be noted that 2 wt % polyaniline nano zinc phosphate painted sample is better than 2 wt % zinc phosphate painted sample. Capacitance measurements of all painted samples exhibited continuous increase from just after immersion to 96 hours of alternate immersion. Paint coating, when immersed, absorbs water as a function of time which is reflected in the increased value of coating capacitance. However, 2 wt % polyaniline nano zinc phosphate coated sample, after 96 hours showed only 0.056 nF as compared to 3 nF and 21 nF, in case of 2 wt % nano zinc phosphate coated sample and 2 wt% polyaniline coated sample respectively. This supports electrochemical impedance studies results and revels that 2 wt % polyaniline nano zinc phosphate composite coating exhibit excellent corrosion resistance properties as compared to that of 2 wt % polyaniline coated and 2 wt % zinc phosphate coated samples. This can be assigned to barrier action due to epoxy based paint, passivation due to conducting polyaniline and self- healing effect due to release of phosphate ions from the pigment.

4. Conclusions

Conducting polyaniline nano zinc phosphate based paint can protect low carbon steel up to 48 hours in 3.5 wt % NaCl aqueous medium. Also, this paint can withstand drying - wetting cycles in atmosphere. As such it can be applied in the applications such as ballast tank. The protection is based on simultaneously operating mechanisms viz. enhanced barrier protection, passivation and release of inhibiting phosphate ions when in contact with corrosive media.

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