

# Corrosion Prevention by Conducting Polyaniline based Paints on Low Carbon Steel

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**Abstract-**Conducting polyaniline powder was synthesized chemically and paints containing conducting polyaniline powder were applied on low carbon steel samples. The conducting polyaniline powder was characterized by UV-Visible absorption spectroscopy and the morphology of paint coating on low carbon steel was studied by scanning electron microscopy. The corrosion protection performance of the coating was evaluated by using electrochemical impedance spectroscopy, alternating immersion and salt spray. It has been found that the 2 wt% polyaniline-hydrochloric acid based paint coating offers significant corrosion protection to low carbon steel in chloride medium. In addition, these paint coatings withstand drying and wetting cycles in atmosphere.

**Keywords:** conducting polyaniline based paint; low carbon steel; corrosion protection; impedance spectroscopy, alternating immersion; salt spray.

## 1. INTRODUCTION

Metals and alloys corrode in environments encountered during their use. Corrosion, being an electrochemical phenomenon, can be tackled through the use of electrochemistry and conducting polymers [1]. Conducting polymer coating on metals or alloys can be obtained using electrochemical deposition techniques [2, 3]. Although, a lot of work has been carried out on electrochemical deposition of conducting polymer on the active metals like iron and steel in recent years, it is difficult to use this approach on massive engineering structures such as ships and bridges. Therefore chemical synthesis route must be explored and extended towards commercial approach. A. Talo et al. studied polyaniline /epoxy blend coatings on mild steel in 0.6 M NaCl and 0.1 M HCl solutions. In this work, the corrosion protective performance was characterized by a shift of corrosion potential by 500 mV in the noble direction and by a decrease of five orders of magnitude in the redox current [4]. P.C. Deb et al. demonstrated use of a paint containing polyaniline-hydrochloride as pigment. Painted panels were exposed in weatherometer chamber, humidity cabinet and salt spray chamber and sea water. Potentiodynamic measurements were also made for finding corrosion current, potential and polarization resistance. It has been observed in this work that paints having lower loading of PANI- HCl is more effective in corrosion prevention of mild steel in 3.5 wt % NaCl [5]. T.K. Rout et al. formulated a coating by dispersing conducting polyaniline powder in a medium oil alkyd resin and evaluated its corrosion resistance. It has been found that the corrosion resistance of PANI

coated samples was 10-15 times higher than the bare steel. In this work, it was also shown that a continuous charge transfer reaction across the metal-coating interface was responsible for the increase in coating capacitance and decrease in polarization resistance [6]. S. Sathiyarayanan et al. investigated the corrosion performance of polyaniline pigmented coating on steel by electrochemical impedance spectroscopy in 3 wt% NaCl and 0.1 N HCl solutions and found out that these coatings were able to protect the steel both in acid and neutral media [7]. A.B. Samui et al. incorporated dioctyl phosphate doped polyaniline as active pigment in various resins and observed that these paints offered protective performance to mild steel for longer period compared to other resins [8]. Jose Ignacio Iribarren Laco et al. studied corrosion protection of steel with thermoplastic coatings and alkyd resins containing polyaniline and showed that the presence of conductive polyaniline in alkyd resin improved the corrosion protection performance [9]. S. Syed Azim prepared conducting polyaniline-aminotrimethylenephosphonic acid (PANI-ATMP), dispersed the polymer in epoxy resin. It has been found out that the open circuit potentials for coated steel have been shifted to noble direction after initial delay in the active direction in 3 wt % NaCl. In addition, the charge transfer resistance values have been found to increase with time due to passivation of steel by PANI- ATMP pigment indicating the protective nature of the coating [10]. S. Touzain et al. used hydrochloride polyaniline powder as a conductive pigment into powder zinc-rich primer formulations in order to enhance the electronic

conduction path between zinc particles inside the coating and the steel. The protective properties and electrochemical behavior of coatings were investigated by monitoring the free corrosion potential versus time and by using electrochemical impedance spectroscopy. It has been shown that this coating exhibits good barrier properties in 3% NaCl solution [11]. Andrea Kalendova et al. tested four pigments of different morphologies - specularite, goethite, talc and graphite with and without polyaniline phosphate coating obtained by epoxy binders on iron plates. In this work, the corrosion tests were carried out in a condenser chamber with continuous water condensation or humidity with sulphur dioxide and in a salt mist cabinet. It has been observed that polyaniline coatings of pigments in all cases improved the anticorrosion properties and graphite coated with PANI performed the best among all the formulations [12]. C. Aleman et al. investigated the corrosion protection imparted by epoxy paints modified by the addition of polyaniline emeraldine base and  $Zn_3(PO_4)_2$  and observed that epoxy with PANI – emeraldine base offered higher protection to mild steel compared to unmodified epoxy paints [13]. E. Armelin et al. employed polyaniline emeraldine salt, polyaniline emeraldine base, polyaniline composite black, polypyrrole composite with carbon black and poly (3,4-ethylenedioxythiophene) doped with poly (styrene sulphonate) and found out that corrosion protection to mild steel offered by formulations modified by conducting polymers and especially polyaniline emeraldine base was significantly higher than that of the unmodified paint [14]. K. Kamaraj et al. found that the vinyl coating containing benzoate doped polyaniline was able to protect steel in neutral media better than in acid media [15]. S. Sathiyarayanan et al. observed that coatings containing 1 wt % and 3 wt % phosphate doped polyaniline and 3 wt % doped chloride doped polyaniline were highly corrosion resistant in 3 % NaCl solution [16]. S. Sathiyarayanan studied corrosion protection performance of sulphonate doped polyaniline containing vinyl coatings containing in 0.1 N HCl and 3 wt. % NaCl by open circuit potential and impedance measurements. The open circuit potential showed that the coatings with polyaniline maintain the potential in the noble range whereas the coatings without polyaniline exhibit potentials in the active range. EIS studies revealed that the sulphonate doped polyaniline is able to protect the steel in acid and in neutral media even after 100 days of exposure [17]. We recently investigated corrosion prevention performance of paint containing polyaniline-hydrochloride as pigment by potentiodynamic polarization studies and observed that 2 wt% polyaniline-hydrochloride based paint is more effective than paints containing lower loading of PANI-HCl for corrosion prevention of low

carbon steel in 0.1 N HCl solution and 3.5 wt% NaCl [18]. To extend our work, the corrosion performance of PANI-HCl based paint coatings is evaluated using electrochemical techniques, alternating immersion testing and salt spray and reported in this work.

## 2. EXPERIMENTAL

**2.1 Materials:** Aniline (AR grade supplied by Loba Chemicals, Colaba, Mumbai-400 005, India) was double distilled prior to use. Chemicals - hydrochloric acid, ammonium persulphate and ammonia solution (AR grade supplied by Loba Chemicals, Colaba, Mumbai-400 005, India) were used without further purification. Ingredients - Xylene, titanium dioxide ( $TiO_2$ ) and dioctyl phthalate (DOP) (R grade supplied by Loba Chemicals, Colaba, Mumbai- 400 005, India) were used as received. Standard epoxy resin (GY 250 supplied by Huntsman Advanced Materials (India) Pvt Ltd. Andheri (East), Mumbai- 400 093, India) was used as received. Low carbon steel samples (AISI 1015) were purchased from local supplier.

### 2.2 Conducting polyaniline based paints preparation and its application

Conducting Polyaniline was synthesized from aniline in aqueous HCl solution using ammonium persulphate as catalyst by following the method of Chaing and MacDiarmid [19]. Conducting polyaniline based paints were prepared by following a similar technique developed by P.C. Deb and his co-workers [5] and elaborated below. The ingredients listed in the Table 1 were added after filtering to the solution of epoxy resin and the mixture was ball milled for 16 hrs (Drive motor : Crompton Make - 2 HP, 1440 rpm 415 V, 50 Hz, FLP foot mounted motor along with gearbox U 287, 25:1 Shanthy Make : Ball Mill supplied by Indo German Industries, Daman, India). The purpose of adding  $TiO_2$  and Dioctylphthalate (DOP) in epoxy resin is to improve viscosity and elastic properties of paints. Xylene was used as a solvent for paint formulation. The paints were filtered through fine cotton and applied on the low carbon steel samples. The paint thickness on steel sample was maintained at  $120 \pm 5 \mu m$ .

**Table 1.** Conducting polyaniline based paint ingredients

Ingredients	Wt %
Epoxy Resin (GY 250)	100 gm
PANI-HCl ( 1 N HCl )	0.1 gm to 3.5 gm
$TiO_2$	10 gm
DOP	10 gm
Xylene	10 gm

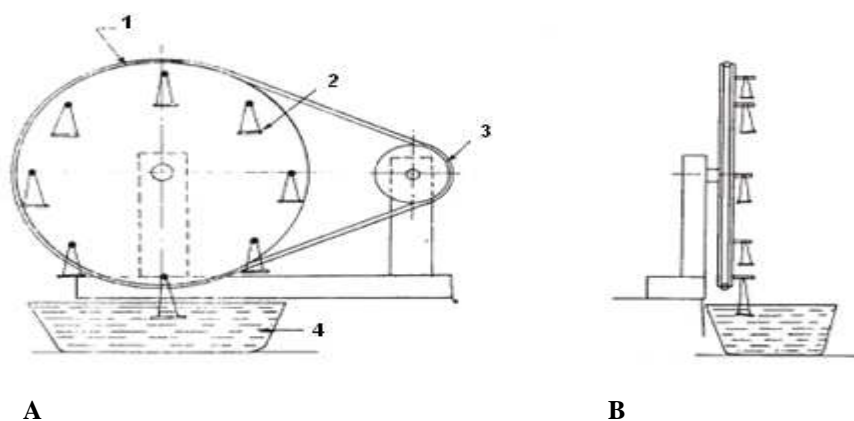
### 2.3 Characterization

The UV- Visible absorption study of chemically synthesized conducting polyaniline powder in DMSO was carried out ex situ in the wave length range 200- 1200 nm using micro processor controlled double beam UV-vis spectrophotometer (Model V 520, Jasco, Japan ). The morphology of conducting polyanilinebased paint on low carbon steel was studied by using scanningelectron microscopy (JEOL JSM 6360A).

## 2.4 Corrosion studies

**2.4.1 Impedance Measurements:** A corrosion cell having three electrode geometry of paint coated sample as working electrode ( $8 \text{ cm}^2$ ), stainless steel as counter electrode and saturated calomel electrode (SCE) as a reference electrode was used. The cell was coupled with Gamry Reference system 600 (Wilmington, USA) for impedance measurements.

**2.4.2 Alternating Immersion Testing:** In order to access the performance of the paint coated samples under atmospheric corrosion, the painted samples were tested for alternating immersion test. An arrangement for carrying out an alternate immersion testing in our laboratory is shown in the figure 1. Diameter of the wheel is 300 mm. The paint coated samples were suspended from the spokes of the wheel by a thread so that there is no metallic contact between the two. The speed of rotation of wheel was kept constant - 0.2 rpm so that each rotation was completed within 5 minutes. During each rotation, the sample gets partially immersed in 3.5 wt% NaCl aqueous solution and exposed to atmosphere. The potential was measured immediately after its immersion in the medium against SCE. The potential measurements were taken after regular interval of 24 hours up to 4 days.

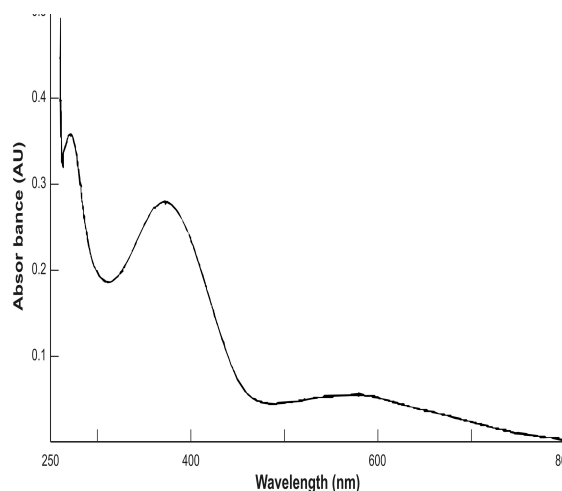


**Figure 1:** Alternating immersion test set up showing A) front view and B) side view.  
1. Rotating wheel, 2. Painted sample, 3. Motor Pulley, 4. Solution of 3.5 wt% NaCl + H<sub>2</sub>O.

**2.4.3 Salt Spray Testing:** The salt spray testing of paint coated low carbon steel samples were carried out as per ASTM B117-09 standards. The exposure period during salt spray test was 288 hrs.

## 3. RESULTS AND DISCUSSION

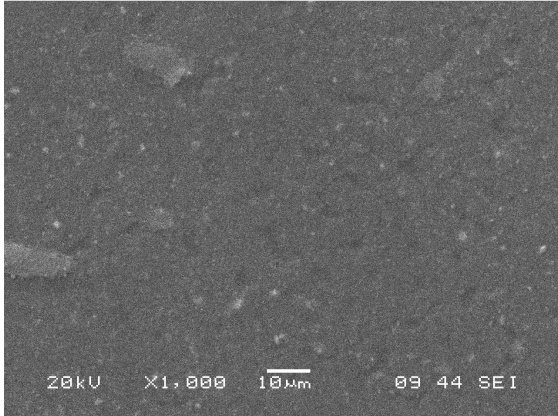
**3.1 Chemically synthesized conducting polyaniline powder:** The optical absorption spectrum of the chemically synthesized conducting polyaniline powder in DMSO is shown in the figure 2.



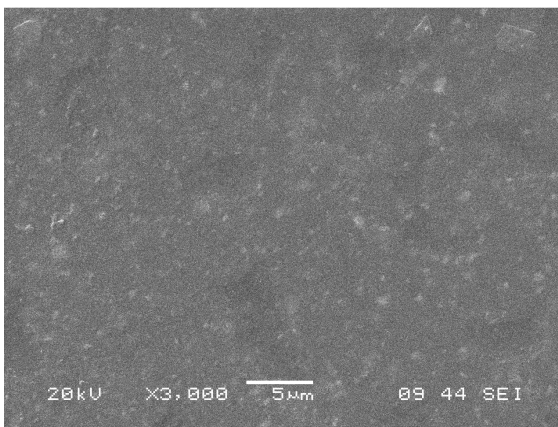
**Figure 2.** UV Analysis of the conducting polyaniline powder in DMSO

This spectrum shows the characteristics peak at 327 nm and a weak broad peak at 580 nm. The first one corresponds to the  $\pi - \pi^*$  transition and  $n - \pi^*$  transition. The second one at 580 nm can be assigned to the excitation transition which is rather weak in these polymers [20].

**3.2 Paint Application:** Scanning electron photo micro graphs of 2.0 wt % PANI-HCl coated steel at 1000 X and 3000 X magnifications are shown in the figures 3 and 4.



**Figure 3.** SEM image of 2.0 wt % PANI-HCl coated steel sample at 1000X



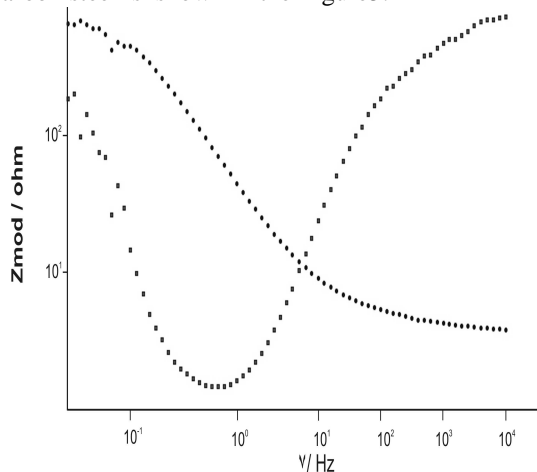
**Figure 4.** SEM image of 2.0wt % PANI-HCl coated steel sample at 3000X

The SEM photomicrographs reveal the entire coverage and uniformity in conducting polyaniline based paint coating on steel substrate.

### 3.3 Corrosion studies

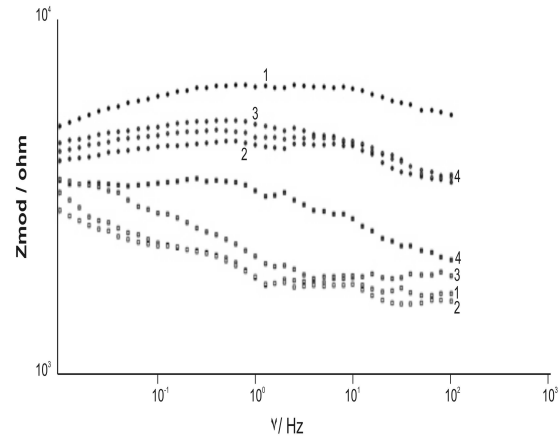
#### 3.3.1 Electrochemical Impedance Spectroscopy:

Electrochemical Impedance Spectroscopy studies on unpainted low carbon steel and polyaniline based painted low carbon steel samples were carried out in 3.5 wt % NaCl and reported here in terms of Bode plots. The impedance behaviour of unpainted low carbon steel is shown in the figure 5.

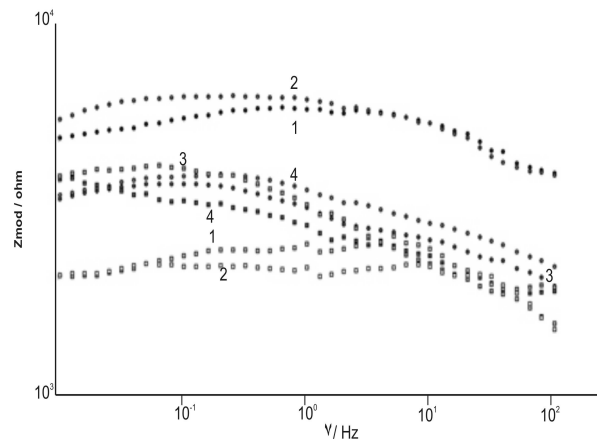


**Fig.5.** Bode plot of unpainted bare low carbon steel in 3.5 wt % NaCl.

The impedance behaviour of conducting polyaniline based painted low carbon steel samples is shown in the figures 6 and 7.

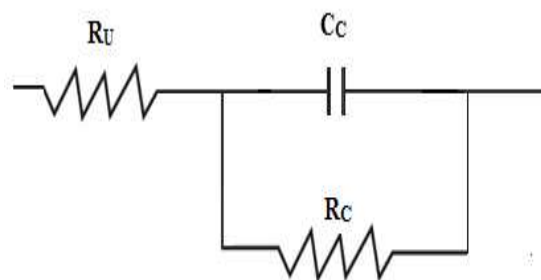


**Fig.6.** Bodeplots of conducting polyaniline based paint coated low carbon steel samples in 3.5 wt % NaCl (1 - 1 wt % PANI, 2- 3 wt % PANI, 3- 0.5 wt % PANI, 4- 0.1 wt % PANI).



**Fig. 7.** Bodeplots of conducting polyaniline based paint coated low carbon steel samples in 3.5 wt % NaCl (1 - 1.5 wt % PANI, 2- 2 wt % PANI, 3- 2.5 wt % PANI, 4- 3.5 wt % PANI).

The Bode plots shown in figure 6 and 7 are modeled by using the equivalent circuit depicted in the figure 8.



**Figure8:** Equivalent circuit used for modeling impedance curve.

It consists of the electrolyte resistance ( $R_u$ ), the coating resistance ( $R_c$ ) and the coating capacitance ( $C_c$ ). The impedance parameters were obtained by using Gamry software and recorded in the Table2.

**Table 2: Impedance Values**

Wt % of conducting polyaniline	$R_c$ Ohm $cm^2$	$R_u$ Ohm $cm^2$	$C_c$ $\mu F$
0.1	89.98	27.96	0.052
0.5	98.11	2.07	0.048
1.0	100.22	12.06	0.032
1.5	109.06	25.06	0.027
2.0	112.03	21.12	0.020
2.5	104.097	11.37	0.045
3.0	101.14	0.298	0.689
3.5	98.38	0.189	0.646

It can be seen that the capacitance values of coating ( $C_c$ ) are decreased from 0.052  $\mu F$  to 0.020  $\mu F$  with increasing weight percentage of polyaniline and again increased to 0.646  $\mu F$  for 3.5 wt% of polyaniline. The coating resistance ( $R_c$ ) is found to increase with weight percentage of polyaniline in paint upto 2 wt % and then subsequently decreased. The high coating resistance and low capacitance values confirm the more protective nature of conducting 2 wt%

polyaniline PANI based paint coating on low carbon steel.

**3.3.2 Alternating immersion testing:** The results of alternating immersion testing in 3.5 wt % NaCl are recorded in Table 3.

**Table 3: Alternating immersion test results**

Wt % PANI	Initial Potential, V	Potential, V after 24 hours	Potential, V after 48 hours	Potential, V after 72 hours	Potential, V after 96 hours
0.1	0.0	0.0	-0.34	-0.40	-0.48
0.5	0.0	0.0	-0.33	-0.35	-0.46
1.0	0.0	0.0	-0.30	-0.34	-0.44
1.5	0.0	0.0	-0.28	-0.32	-0.42
2.0	0.0	0.0	-0.24	-0.30	-0.40
2.5	0.0	0.0	-0.30	-0.34	-0.42
3.0	0.0	0.0	-0.32	-0.36	-0.44
3.5	0.0	0.0	-0.34	-0.40	-0.46

Alternating immersion results reveal that the conducting polyaniline based paint coatings protect low carbon steel against drying and wetting cycles. There was no change in potential up to 24 hours indicating the coating was protective. After 48 hours, potential was found to increase. However, even after 96 hours, there is no significant change in

potential was noted. Therefore, it can be argued that this paint formulation protect low carbon steel against drying and wetting cycles in atmosphere.

**3.3.3 Salt Spray testing :** Results of painted samples exposed to salt spray are given in the Table 4.

**Table4:Salt spray exposure of HCl-PANI containing paint**

1 N HCl-PANI Paint									
Exposure time (hrs)	Wt. % PANI-HCl % of area corroded								
	0.0 (without PANI-HCl)	0.1 %	0.5%	1.0 %	1.5 %	2.0 %	2.5%	3.0%	3.5%
24	No defects observed	----	----	----	----	----	----	----	----
48	No defects observed	----	----	----	----	----	----	----	----
72	spot	----	----	----	----	----	----	----	----
96	Blister	----	----	----	----	----	----	Spot	Spot
120	Red Rust observed	Spot	Spot	spot	spot	----	----	Spot	Spot
144	5	Blister	Blister	spot	spot	----	----	Blister	Blister
168	15	Blister	Blister	Blister	Spot	----	----	Blister	Blister
192	25	15	15	10	Blister	----	Spot	Blister	10
216	50	35	40	25	Blister	----	Spot	2	25
240	65	50	60	40	10	----	Blister	10	45
264	85	75	75	50	25	----	Blister	25	55
288	95	85	80	60	40	Spot	2	40	70

As noted in the Table 3, up to 72 hrs no defects were observed in all painted samples. After 72 hrs of exposure, black spots were observed in the samples painted with paint without PANI-HCl. The black spots were observed on the samples after 96 hrs for the paint containing 3.0 and 3.5 wt % of PANI-HCl, whereas the black spots were observed on the samples containing 0.1, 0.5, 1.0 and 1.5 wt % of PANI-HCl after 120 hrs. The black spots on the samples painted with 2.5 and 2.0 wt % of PANI-HCl were observed after 192 and 288 hrs respectively.

The blistering was observed in the samples painted with paint without PANI-HCl after 96 hrs and the blistering was observed after 144 hrs for the samples painted with paint containing 0.1, 0.5, 3.0

and 3.5 wt % of PANI-HCl, whereas blistering was observed after 192 and 240 hrs in case of samples painted with paint containing 1.5 and 2.5 wt % of PANI-HCl. No blistering was observed in the sample painted with paint containing 2.0 wt % of PANI-HCl even after 288 hrs.

The samples painted with paint without PANI-HCl revealed 5 % area corroded after 144 hrs, 50 % area corroded after 216 hrs and 95 % area corroded after 288 hrs. The samples painted with a paint containing 0.1, 0.5, 1.0 and 3.5 wt % PANI-HCl showed 15 to 10 % area corroded after 192 hrs. After 288 hrs, the samples painted with PANI-HCl showed 2 to 85 % area corroded whereas the sample painted with paint containing 2.0 wt % PANI-HCl only black

spot was seen. Therefore, it can be said that salt spray results support electrochemical impedance investigations and are in well agreement with the previous reports [5, 8 and 18].

#### **4. CONCLUSIONS**

Low carbon steels can be corrosion protected by conducting polyaniline based paint and a paint containing 2wt% conducting polyaniline offers significant corrosion protection in chloride medium. In addition, this paint formulation protects low carbon steel against drying and wetting cycles in atmosphere. The salt spray results confirm excellent corrosion protection properties of conducting polyaniline based paints containing 2wt % PANI-HCl.

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