

## INVESTIGATION OF CORROSION-PROTECTIVE PERFORMANCE OF POLYANILINE COVERED INORGANIC PIGMENTS

M.I. KHAN, \*A.U. CHAUDHRY<sup>1</sup>, S. HASHIM and M.Z. IQBAL<sup>2</sup>

Department of Polymer Engineering, Faculty of Chemical and Natural Resources Engineering,  
Universiti Teknologi Malaysia, 81310 Skudai, Malaysia

<sup>1</sup>Chemical Engineering Program, The Petroleum Institute, Abu Dhabi, P.O. Box 2533, United Arab Emirates

<sup>2</sup>Department of Polymer and Process Engineering, University of Engineering and Technology, Lahore, Pakistan

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In current work, three types of inorganic pigments i.e. iron oxide ( $\text{Fe}_2\text{O}_3$ ), Zinc oxide (ZnO) and Nickel carbonate ( $\text{NiCO}_3$ ) were mixed in equal proportion and surface-modified with inherited electrically conductive polyaniline (phosphate doped polyaniline) by method of in situ polymerization i.e. polymerization of polyaniline in presence of mixed pigments. Ammonium per sulfate was used as an oxidant for polymerization of aniline at low temperature. Fourier Transform Infrared (FTIR) spectroscopy, X-ray Diffraction (XRD) and scanning electron microscopy (SEM) were used to analyze the surface of polyaniline-pigment composites. These characterization techniques revealed that the surface of pigments have been modified by phosphate doped polyaniline. Polyaniline, mixed pigments alone and polyaniline layered mixed pigments were incorporated with solvent based primer of vinyl acrylate and applied on carbon steel panels. Corrosion rate of carbon steel panels obtained after 800 hrs of immersion in 4% sodium chloride. It was least in case of coated samples with coating containing polyaniline modified pigments.

**Keywords:** Polyaniline, Corrosion, Pigments, Corrosion rate.

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### 1. Introduction

The environmental constraints on using chromium (VI) based coatings lead towards development of non-toxic coatings containing electrically conductive polymers for anticorrosion purposes. Among all the conductive polymers, polyaniline from now PANI is very common owing to its, low cost, solubility in common solvents such as *N*-methylpyrrolidinone, xylene, chloroform etc., environmentally stable, good optical properties, very easy and economic preparation and doping dominance [1-9]. PANI can be found in different states which include the conductive (Emeraldine Salt) and nonconductive (Emeraldine Base). It has the ability to become passivate on receiving charge and show nonconductive behavior. In order to improve the physical and mechanical properties of PANI films, it is being used in combination with barrier coatings.

Although the mechanism of corrosion protection

of PANI is still debatable but different theories have been proposed and confirmed. The reported mechanisms are barrier protection, corrosion inhibitions, cathodic and anodic protection [4, 10]. Barrier mechanism deals with the disconnection of metal surface from the corrosive environment such as coatings of surfaces with paints. In case of corrosion inhibitions, the purpose of the applied coating is to slow down the rate of corrosion due to formation of monomolecular layer on the surface. It was reported that this phenomena refers to the adsorption of PANI on the surface endorse the adhesion and hence improved corrosion protection. Anodic protection is technique used for passivating of the materials owing to the formation of oxide layers of PANI which change the electrode potential in passive. The reduction in the cathodic reaction on metal is due to the transfer of the reaction i.e. from metal-electrolyte interface towards electrolyte-polymer interface.

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\* Corresponding author : plastist\_engineer@ymail.com

The use of PANI modified pigments in combination with resin based coatings help to improve the physical properties of PANI [4]. The oxidation and reduction of PANI occurring on the metal surface changes its density and volume, which have an effect on the properties of coatings. Alongwith this, the adhesion and dispersion of PANI are not good [11-12]. These problems can be solved by using stable inorganic pigments surface modified with PANI. The permeability of the PANI can be enhanced by suitable protonation. In most of cases, an acid such as sulphuric acid, phosphoric acid, *p*-dodecylbenzenesulfonic acid, hydrochloric acid etc. is used for doping purpose.

Earlier studies showed that use of PANI-TiO<sub>2</sub> composites has good anticorrosion properties as compared to single use of PANI or TiO<sub>2</sub> in acrylic resin primer. The protection behavior was attributed to the uniform distribution of composite pigments, enhanced conductivity and barrier effect of composite pigments [13]. Similarly, PANI-Fe<sub>2</sub>O<sub>3</sub> composite have been used with acrylic resin applied on mild steel and showed better properties [14]. Kalendová, used four type of pigments i.e. Fe<sub>2</sub>O<sub>3</sub>, FeO(OH), (Mg<sub>3</sub>(OH)<sub>2</sub>·(Si<sub>4</sub>O<sub>10</sub>)) and graphite-C in epoxy coatings. Among all of them, graphite modified with PANI was better, as compared to others due to conductivity of electrons during reduction and oxidation process between iron, PANI and oxygen [15].

A study has been made on corrosion protection of polyaniline modified mixed pigments in equal ratio such as Fe<sub>2</sub>O<sub>3</sub>, ZnO, and NiCO<sub>3</sub>. These pigments were added to solvent based primer of vinyl acrylate primer. The panels of carbon steel were coated with primer and corrosion protective performance was performed by follow ASTM G31.

## 2. Experimental

### 2.1. Materials

Zinc oxide ( 99.7%, BDH Limited Poole, England), Ferric oxide red ( 99.9%, Avondale Laboratories, England), Nickel Carbonate Basic, (Ni content 45% EMORY, Malaysia), ortho-Phosphoric acid 85% (Merck, Germany), Aniline monomer ( 99%, Mallinckrodt, USA), Sodium chloride ( 99%, Merck, Germany), Epoxy paint fineness less than 25 µm and Binder ( Syarikat Sanland Paint industries, Malaysia), Acrylic wall sealer 25% aromatic solvent based ( Nippon Paint, Malaysia), Hydrochloric acid having specific gravity

1.19 (37% QRec, Malaysia), Hexamethylene tetramine (99%, Sigma-Aldrich, Chemie GMBH, Germany), Industrial grade acetone for cleaning purpose only (Kras, Malaysia), Linseed Oil (Eng Lee Seng, Malaysia), Carbon panels were used, data provided by supplier is mentioned in Table 1.

Table1. Characterization of carbon steel.

Element	Percentage
Carbon	0.35
Manganese	1.05
Phosphorus	0.04
Sulphur	0.05
Silicon	0.2

### 2.2. Preparation of Polyaniline and Surface Modified Pigments

Polyaniline-modified pigments were prepared using the method of in situ polymerization mentioned in literature [10]. Three inorganic pigments Fe<sub>2</sub>O<sub>3</sub>, ZnO and NiCO<sub>3</sub> were taken in equal proportion and mixed thoroughly by mortar. An amount of 1 g was taken from the mixed powder and added to 0.2 molar solution of ortho-phosphoric acid solution containing 0.2 moles of aniline. The mixture was stirred using magnetic stirrer for 2h. Pre-cooled 0.25 molar solution of ammonium per sulfate was added drop wise for about 1.5 hours. The reaction was conducted in water bath maintaining temperature 5 °C ±1. After the addition, the stirring was continued for 2 hr. to complete the polymerization. The dark green pigments were filtered, washed with excess of water and dried in air followed by placing in drier at 70 °C. Similarly, PANI was synthesized alone in the absence of mixed inorganic pigments. The acquired pigments were fine grinded first using mortar then blender.

### 2.3. Characterization of Pigments

Infrared spectra in a range of 400-4000 cm<sup>-1</sup> were taken at 60 scans per spectrum using Perkin-Elmer model Fourier Transform Infrared. Samples were prepared in potassium bromide discs at room temperature and background scan was done.

Table 2. Characteristics of pigments.

Type of Pigment	Density $\rho$ (g /cm <sup>3</sup> )	Oil absorption (g per 100 g of pigment)	CPVC (%)
Mixed inorganic pigments alone	10.5	38.5	18.7
PANI alone	1.32	130.4	35.1
PANI-modified Mixed inorganic pigments	3.7	40	38.7

The X-ray diffraction pattern of inorganic mixed pigments alone and after modification with PANI were recorded by Siemens, diffractometer D 5000 using Cu K $\alpha$  radiations in the 2 $\theta$  range 14-90° at a scan rate of 0.050°.

The scanning electron micrographs (SEM) of inorganic mixed pigments alone and after modification with PANI were taken by using JEOL JSM-6390 low vacuum scanning electron microscope (LVSEM). The samples were platinum plated before use and the operating conditions were 2000x magnification and 10 kV.

Critical pigment volume concentration (CPVC) of all pigments was determined through bulk density and linseed oil absorption number.

#### 2.4. Preparation of Coating

The coatings were prepared by using primer of solvent based vinyl acrylate wall sealer with a top coat of epoxy based industrial coating. The characteristics of pigments are mentioned in Table 2. The pigments were grinded finely and mixed with primer using lab attritor for 30 minutes. The loading of pigment included PANI, Mixed inorganic pigments and PANI modified particles were kept 15% by volume with 25 % of Acrylic primer. The main pigments were PANI, PANI modified Mixed inorganic pigments and only Mixed inorganic pigments used. The prepared coatings were kept in air tight jar. The adhesion of coating with substrate was tested by pressure sensitive tape according to ASTM D3359-02. In this method a pressure sensitive tape was applied to coating and then pulled off. The test was found to be passed.

#### 2.5. Preparation of Sample

Carbon steel samples of dimensions 50× 50 × 0.3 mm<sup>3</sup> were polished with emery papers, clean, degreased with industrial grade acetone, dried and

weighed with an accuracy of  $\pm 1$  mg. The samples were stored for two days in desiccators. The panels were dip coated first for 15 sec in acrylic primer and then with an interval of 24 hrs. of dryness, top coated with epoxy based industrial coatings. The epoxy top coats were prepared by mixing four parts of with one part of hardener. The prepared samples were ready for corrosion testing.

#### 2.6 Immersion Testing and Cleaning of Samples for Anticorrosion Properties

The anticorrosion properties of the coatings were studied by immersion test according to ASTM G 31. All panels were placed in special designed apparatus as shown in Fig. 1 for 800 hrs. at 35 °C. The function of this apparatus is to maintain the temperature, air flow and water level constant so that similar conditions can be attained throughout the experiment.

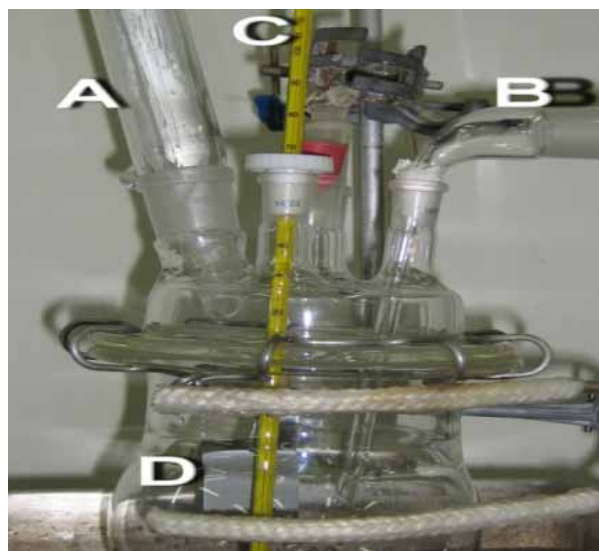


Figure 1. Typical Resin flask for immersion test, A = Condenser, B = Air inlet, C = Thermometer D = Sample hung.

Table 3. Corrosion rate calculation.

Type of pigment incorporated in coating	Weight loss of sample (g)	Corrosion rate (g/m <sup>2</sup> ·min) × 10 <sup>-4</sup>
Mixed inorganic pigments modified with PANI	0.0796	4.37
PANI alone	0.1444	7.9
Mixed inorganic pigments alone	0.1402	7.6
Paint alone	0.1596	8.75

The photographs were taken with an interval of 260 hrs. After completing the period, the samples were taken out cleaned and weighed again. The samples were cleaned in two steps. In the first step coatings were removed by using acetone as a solvent and in second step corrosion products were removed by solution of 3.5 g of hexamethylene tetramine in 500 ml of hydrochloric acid diluted to 1000 ml by distilled water. The samples were dipped for 10 min at room temperature and cleaned with brush. The weight loss method was adopted to evaluate the corrosion rate. The equation for weight loss method is given in equation 1.

$$\text{Corrosion Rate} = \frac{K (\text{constant}) \times \text{Weight loss}}{(\text{Area} \times \text{Time} \times \text{Density})} \quad (1)$$

In equation 1, K is a constant and its value is  $1 \times 10^4 \times \text{Density of substrate (g/m}^2 \cdot \text{h)}$  from ASTM G-31. The density in the constant K cancels out the density in the corrosion rate equation. Time of exposure is represented by T and in this experiment is equal to 800h whereas A is area exposed which is 38 cm<sup>2</sup>. Weight loss of sample after completing test can be seen in Table 2.

### 3. Results and Discussion

The FTIR spectrum in Fig. 2 (a-c) shows the formation of PANI and PANI modified pigments. The typical bands at 1650 and 1538 cm<sup>-1</sup> represented the stretching mode of C=N and C=C of quinoid and benzenoid rings whereas bands at 1296 and 1227 cm<sup>-1</sup> are due to the C—N stretching mode of benzenoid ring. The band at 1140 cm<sup>-1</sup> is due to a plane bending vibration of —NH<sup>+</sup> which is

a indication of positive charge on chain. The spectra for PANI modified pigments showed that it is similar to PANI spectra but with a slight lower wave number i.e. 1648, 1542, 1289, 1235, 1103 cm<sup>-1</sup>. The intercalation peaks are also present at 1053 and 1021 cm<sup>-1</sup> [15-16].

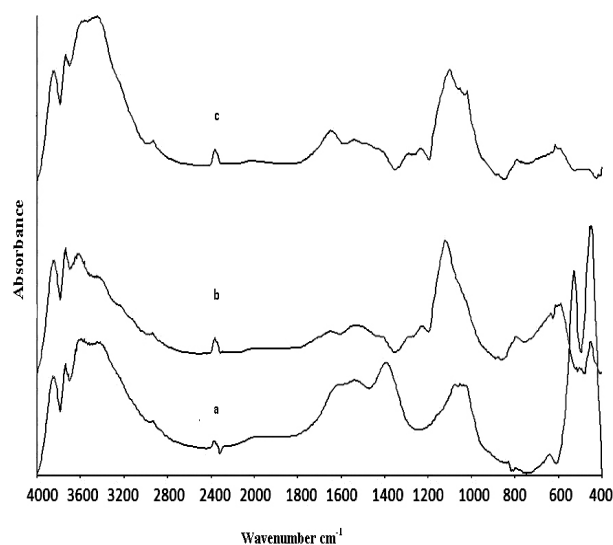


Figure 2. (a-c) FTIR spectra of (a) Mixed inorganic pigments, (b) Polyaniline, (c) Polyaniline modified mixed inorganic pigments

Fig. 3 (a-b) shows X-ray diffraction pattern of mixed inorganic pigments modified with PANI and alone. The peaks are analyzed according to the reference provided by manufacture i.e. ICDD database. In case of mixed inorganic pigments pattern (b) the peaks at  $2\theta = 24^\circ, 33^\circ, 35^\circ, 41^\circ, 49^\circ$  are represented by Fe<sub>2</sub>O<sub>3</sub>, peaks at  $2\theta = 32^\circ, 34^\circ, 36^\circ, 47^\circ$  ZnO, and peaks at  $2\theta = 28^\circ, 38^\circ, 54^\circ$ ,

62°, 67°  $\text{NiCO}_3 \cdot \text{Ni}(\text{OH})_2$ . Similarly, Fig. 3 pattern (a) is represented by mixed inorganic pigments modified by PANI the broader peaks at  $2\theta = 25^\circ$ ,  $26.5^\circ$ ,  $28^\circ$  which represent the some degree of crystallinity and scattering of PANI Chains at interplanar spacings. Also it can be seen that crystallization of PANI is unaffected in case of mixed inorganic pigments modified with PANI. The similar effect was seen by Sathiyarayanan et al. [16].

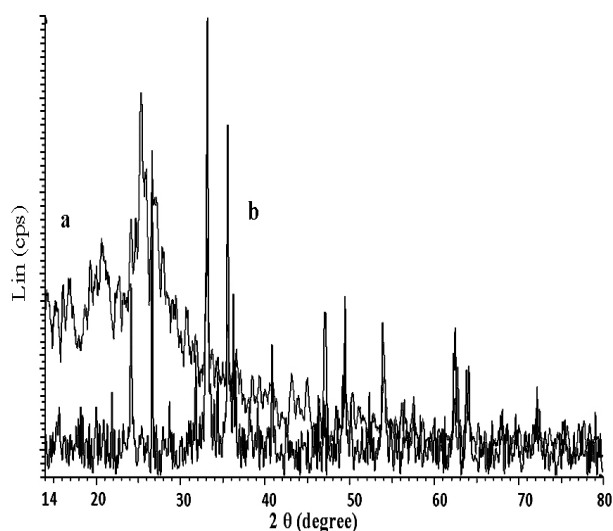
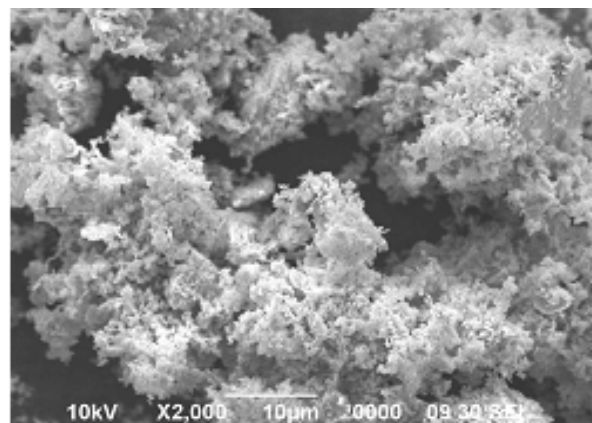


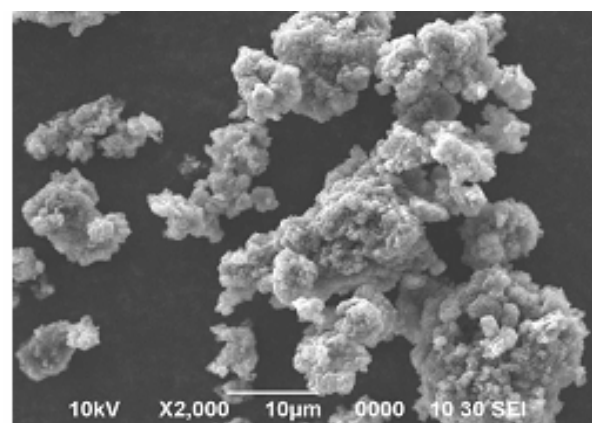
Figure 3. (a-b) X-ray diffraction patterns (a) mixed inorganic pigments modified with PANI (b) Mixed inorganic pigments alone.

Fig. 4 (a-b) shows the morphological assessment of mixed inorganic pigments before and after modification PANI. Dissimilar shapes of particles were observed. It was revealed that the mixed inorganic pigments were covered partially by PANI and overcome the surface imperfections such as holes and fractures alongwith good adhesion and uniform coverage [15, 17]. The mechanism of layering particles with polyaniline was described in literature. Polyaniline formed sub-micrometer film on particles during in situ polymerization. The surface which is required to be coated first enriched with solution of monomer or oxidizing agent and upon adding suitable oxidizing agent or monomer respectively, coating of surface could be achieved. The nature of the developed film depends upon the synthesis conditions [18-19].

The critical pigment volume concentration of pigments was found through linseed oil absorption and density determination as mentioned in Table 1.



(a)



(b)

Figure 4. (a-b) SEM micrographs showing (a) Mixed inorganic pigments (b) Mixed inorganic pigments modify with PANI.

Critical pigment volume concentration of pigments has a significant effect on performance of coatings and pigments. It is a transition point above or below which effect efficiency and properties of coatings and pigments [20].

After taking out samples, no major deterioration on the surface of coating was seen. In Fig. 5 (a-c), the surfaces of the steel panels are shown. As can be seen, the marks of corrosion is more in the case of using paint alone but in case of coating containing PANI modified pigments, the surface of the steel panel has less corrosion marks. This clearly demonstrates the enhancement in corrosion inhibition of coating containing mixed inorganic pigments layered by PANI. This result was also confirmed by the corrosion rates as mentioned in Table 2. The corrosion rate of panels was least in case of coating containing modified particles as compared to all other coatings.

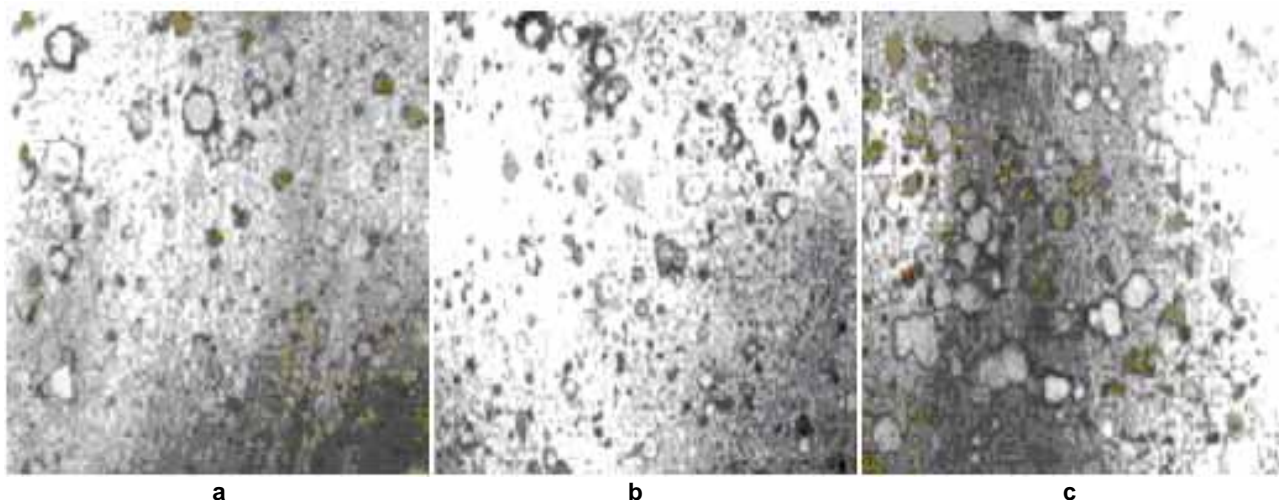


Figure 5. (a-c) After 800 hour's exposure to immersion test of coatings having pigments (a) Mixed inorganic Pigments modified with PANI modified (b) PANI alone (c) Paint alone

This behavior of coating containing mixed particles layered with PANI is probably owing to formation of complex passive layer of PANI which forms due to the charge transfer from the metal. This phenomenon reduces the PANI from conductive to nonconductive state. This layer is responsible for the protection but for a long exposure to corrosive ions, the layer become breakdown [21]. In other case where modified mixed inorganic particles are present, these inorganic pigments have already their own corrosion inhibition effect without modification [22]. These pigments not only facilitate the PANI to reduce effect of change in density during redox process but also improve contact of PANI with substrate surface [4, 23]. Hence the coating containing modified inorganic particles offers better protection than others discussed in this work.

#### 4. Conclusions

The successful synthesis of PANI and mixed inorganic pigments layered with PANI were confirmed by infrared spectroscopy, scanning electron microscope and x-ray diffraction. The pigments were incorporated with acrylic primer and applied on carbon steel. The performance of the coating having PANI modified particles in saline media was better as compared to PANI alone or Mixed inorganic pigments alone.

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