



Formulation and evaluation of $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nanopaint

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ABSTRACT

Purpose: In this project, the formulation of $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nanopaint was discussed.

Design/methodology/approach: The paint was formulated in alkyd resin using ball milling process. Intermolecular bonding between $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ and the alkyd resin was studied by Fourier transform infrared spectroscopy. The water contact angle was measured and it is found to be hydrophilic in nature. The prepared $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nanopaint disclosed good corrosion-resistant behaviour in acid treatment test. The inhibition efficiency was calculated to ensure the anticorrosive behaviour of paints.

Findings: The recorded results reveal that, $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nanopaint has moderate solid content and mechanically low irregularities compared with bare steel. Corrosion resistance is high in nanoformulated paints and therefore it has high inhibition efficiency. The contact angle reveals the film is hydrophilic in nature which enhance the spreading rate of paints.

Research limitations/implications: The method is not limited to $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nanopaint but is also suitable for the preparation of other nanomaterial-based paint.

Originality/value: In this project, iron oxide and titanium oxide act as the corrosion inhibiting pigment.

Keywords: Nanoformulated paints; Corrosion; Acid treatment; Inhibition efficiency

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Iron oxide is the inorganic compound with the formula Fe_2O_3 and TiO_2 , which has anticorrosion property for steel. These nanoparticles were incorporated into paints to enhance the photocatalytic behaviour hence reducing the volatile organic compounds. Ag doped TiO_2 shown the best retention of photo activity. Irradiation of the coatings

resulted in an increase in wettability [1]. Monoclinic structure of metal oxide nanoparticle was synthesized by aqueous precipitation method [2]. Corrosion resistance of 316 austenitic stainless steel specimens was tested in the sulphuric acid test and phosphoric acid. The polarization curve was shifted into active side [3,4]. The anticorrosive rubber coating has chemical resistance property and also used in chemical, marine and water born industries [5,6].

MoSi₂/SiC coated mild steel was tested in various acids such as HCl, H₂SO₄ and HNO₃ in different acid concentration and corrosion rate, inhibition efficiency and weight loss are predicted and corrosion behavior was studied by Response Surface Methodology [7]. The epoxy paint containing the Ti⁴⁺-Zn mixed metal oxide was exhibited higher corrosion efficiency [8]. The antifouling coating of mild steel has impact, wear and corrosion resistance and their interaction to increase the lifetime of the paint [9,10]. TiO₂ paint surface was resistive to the growth of the bacteria by agar dilution method [11]. Polymeric coating for steel was essential to reduce salt water corrosion. A corrosion rate reduction of about 77% was realized for coated surfaces compared to uncoated steel surface [12]. The inhibition efficiency of the GO nanopaint coating was about 88.70% suggesting the potential utility of the GO nanopaint in acidic resistant coating [13]. The properties for nanoformulated paints were analyzed by Glossiness, Solid Content and Hiding power of nanoformulated paints are higher when compared to commercial paints. Corrosion behaviour is low in nanoformulated paints and therefore it has high inhibition efficiency [14]. In this project, Iron oxide and titanium oxide act as the corrosion inhibiting pigment.

2. Materials and methods

2.1. Synthesis of metal oxide nanoparticles

The iron oxide and titanium oxide were purchased in Applied Nanotech, Inc. at Austin.

2.2. Synthesis of mixed metal oxide nanoparticles

Iron oxide and titanium oxide was mixed with equal ratio of 1:1 and added with 100 ml of distilled water. The mixed TiO₂.Fe₂O₃ metal oxide solvent was taken in round bottom flask and heated at 80°C in reflux condenser for 2 h. The solvent was filtered and dried, resulting in the formation of TiO₂.Fe₂O₃ metal oxide particle.

2.3. Synthesis of TiO₂.Fe₂O₃ paints

The 50-60% of pigment was added with 30% of alkyd resin and 10% of thinner. All the components of the paint were placed in a tungsten carbide bowl and milled using tungsten carbide balls. The ball-to-powder weight ratio was maintained with a milling speed of approximately 300 rpm, which was maintained for 5 h. The TiO₂.Fe₂O₃ nanopaint was formulated.

2.4. Solid content measurement

The solid content of the paint is the ratio of total weight of mass of dried paint residue to mass of wet paint. The quantity of solid present in the paint was determined by drying 1 g of paint in a clean, dry watch glass. Based on the initial and final weight measurements, the solid content of TiO₂.Fe₂O₃ paint was evaluated using the following equation (1).

$$\% \text{ of non - volatile content} = \frac{\text{Mass of dried paint residue}}{\text{Mass of wet paint}} * 100 \quad (1)$$

2.5. Instrumentation

The ball milling process for preparation of TiO₂.Fe₂O₃ paint was carried out using a Pulversitte 6.0 HEBM. The phase purity and crystallize size of the TiO₂.Fe₂O₃ nanoparticle were determined by a Rigaku X-ray diffractometer (XRD) operated at 40 KeV and 40 mA with Cu K α radiation. Fourier transform-infrared (FT-IR) spectra of the samples were recorded using an Alpha-T spectrometer (Bruker Optics GmbH, Ettlingen, Germany). The surface morphology studies of the paint coating were performed on scanning electron microscope (Carl Zeiss MA15/EVO 18). The wettability of the paint coated sample was analyzed by goniometer (Data physics instrument, Germany). This test is useful for characterizing the wettability of surfaces.

2.6. Acid immersion method (or) weight loss method

In acid medium, mild steel was easily corroded. Using acid immersion method, the corrosion inhibition of TiO₂.Fe₂O₃ nanopaint (in acidic environment such as HCl, H₂SO₄ and HNO₃) was calculated. For this project, the TiO₂.Fe₂O₃ nanopaint was coated on mild steel substrates using hand brushing method. Both the bare and the painted mild steel substrates were immersed in 0.1 N HCl, 0.1 N H₂SO₄ and 0.1 N HNO₃ for 24 h at room temperature. Then, the substrates were removed from the beakers and immersed in distilled water to remove the acidic impurities and dried at room temperature. The weight of each substrate before and after the reaction was measured and used to calculate the corrosion inhibition of the coating.

3. Results and discussion

3.1. XRD analysis

The crystalline nature of the nanoparticles is confirmed through XRD. The TiO₂.Fe₂O₃ oxide shows diffracted peaks

at $2\theta=24^\circ, 25^\circ, 33^\circ, 35^\circ, 41^\circ, 54^\circ, 62^\circ, 63^\circ, 68^\circ$ were assigned to (111), (110), (104), (200), (202), (211), (210), (002), (002) respectively (Fig. 1). The Lattice plane which indicates the presence of both TiO_2 and Fe_2O_3 nanoparticles. This is well accordance with the JCPDS file no. 21-1272, 87-1164).

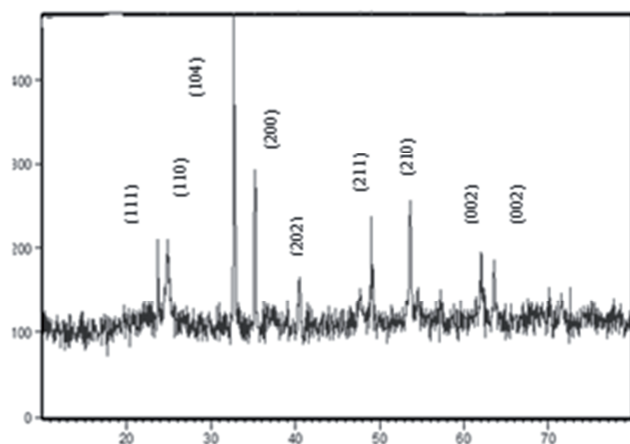


Fig. 1. XRD Analysis of $\text{TiO}_2.\text{Fe}_2\text{O}_3$ nanoparticle

3.2. FESEM analysis

The surface morphology of the prepared nanoparticle is shown in Figure 2. It reveals that, there is agglomeration of nanoparticles of TiO_2 and Fe_2O_3 nanoparticles. It was clear that the particles obtained were in nano size ranging in the diameter from 150-200 nm.

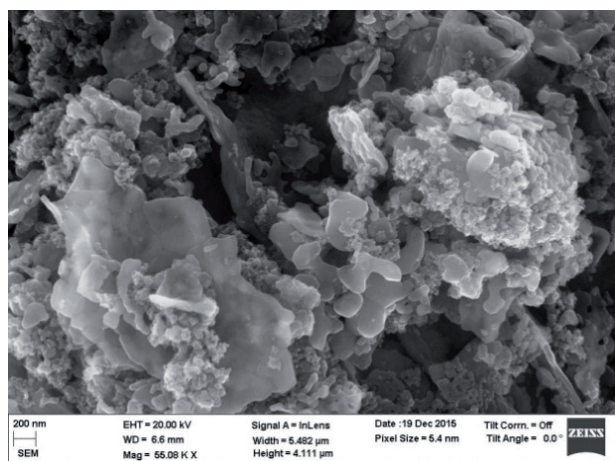


Fig. 2. Analysis of FESEM of $\text{TiO}_2.\text{Fe}_2\text{O}_3$

3.3. Spectroscopic investigation

The bonding interactions between the alkyd resin and $\text{TiO}_2.\text{Fe}_2\text{O}_3$ paint were determined by Fourier transforms

infrared (FTIR) spectroscopy. Figure 3 shows the FT-IR spectra of the $\text{TiO}_2.\text{Fe}_2\text{O}_3$ incorporated alkyd resin. The FT-IR spectra of alkyd resin shows the presence of C–O–C groups (1254 cm^{-1}), a carboxylic group (1724 cm^{-1}), C–H vibrations ($2800\text{--}3000\text{ cm}^{-1}$) respectively. Titanium oxide and Iron oxide are present at 738 cm^{-1} and 479 cm^{-1} respectively.

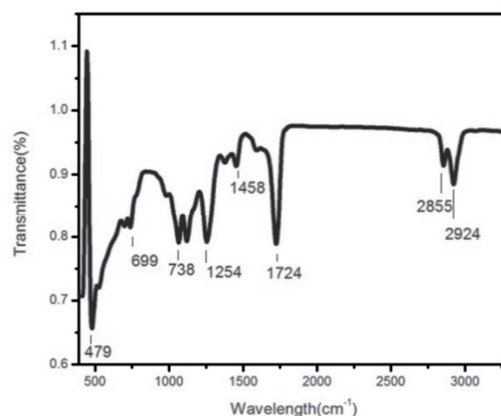


Fig. 3. Fourier transforms infrared spectra of the alkyd resin and $\text{TiO}_2.\text{Fe}_2\text{O}_3$ nanopaint

3.4. Properties of $\text{TiO}_2.\text{Fe}_2\text{O}_3$ paint

Characterization such as solid content, surface roughness and contact angle were identified for the $\text{TiO}_2.\text{Fe}_2\text{O}_3$ nanopaint in order to ensure its quality. Paint can be classified into high and low solid paint depending on the percentage of solid content in the paint. High solid paints have low emission of volatile organic compounds. The solid content of the $\text{TiO}_2.\text{Fe}_2\text{O}_3$ nanopaint was calculated as 55% using Eq. (1). In contact angle measurement, $\text{TiO}_2.\text{Fe}_2\text{O}_3$ paints has contact angle of 65.45° . The $\text{TiO}_2.\text{Fe}_2\text{O}_3$ coatings were hydrophilic in nature since the contact angle is less than 90° . A low advancing contact angle value ($<45^\circ$) is indicative of wetting and angles of 10 to 20° are indicative of excellent wetting. Water can be used as a test liquid (Fig. 4) to establish whether a surface is hydrophilic (angle $<45^\circ$), hydrophobic (angle $>90^\circ$), or somewhere in between (angle of 45 to 90°). The hydrophilic nature of paint substrate lowers the contact angle and allows the paint to spread and penetrate surfaces. This is proved that $\text{TiO}_2.\text{Fe}_2\text{O}_3$ is hydrophilic in nature.

The roughness measurement was done using Surface Roughness Tester and the roughness value of coated and uncoated steel was listed in Table 1. P1, P2 and P3 denotes different places picked in the steel plates in Uncoated and Coated steel.



Fig. 4. Contact angle measurement using water for $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ paint steel

Table 1.
Various roughnesses values for bare and paint coated substrate

Sample	Roughness, μm			Average roughness, μm
	P1	P2	P3	R_a
Uncoated Steel	2.214	1.701	1.961	1.958
$\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$	0.363	0.778	0.376	0.505

3.5. Corrosion in acidic medium

The $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nanopaint was inspected for their applications in corrosion resistant coatings (in acidic medium) using the weight-loss method (2). The bare steel and $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ paint coated substrate was immersed in an acidic solution (0.1 N HCl, 0.1 N H_2SO_4 and 0.1 N HNO_3) for 24 h. However, there is no formation of rust have been observed in the $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ paint coated substrate, suggesting the stability of the as prepared paint in the acidic environment. Quantitatively, the corrosion inhibition efficiency of the $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nanopaint coating was calculated by the weight loss method from the equation (2):

$$\text{Inhibition Efficiency \%} = [(W_{\text{uncoated}} - W_{\text{coated}}) / W_{\text{uncoated}}] * 100 \quad (2)$$

where, W_{uncoated} is the weight loss of the bare substrate, and W_{coated} is the weight loss of the substrate coated with the $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nanopaint. The corrosion-inhibition efficiency of the $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nanopaint coating was about 99.40%, 99.54% and 99.52% suggesting the potential utility of the $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nanopaint as acidic resistant coating.

Table 2 represent the weight loss values recorded for bare and $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ paint coated steel. The inhibition efficiency is tabulated in Table 3.

Table 2.
Representing weight loss values of bare and $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ paint coated steel

Painted Specimen		Weight of the Steel Plate before dipping W_1 , g	Weight of the Steel Plate after dipping W_2 , g	Weight Loss $W=W_1-W_2$, g
Bare	HCl	7.3072	7.1050	0.2022
	H_2SO_4	7.2330	6.7036	0.5294
	HNO_3	7.2317	6.7660	0.4657
$\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ coated steel	HCl	7.3014	7.3002	0.0012
	H_2SO_4	7.3112	7.3088	0.0024
	HNO_3	7.3040	7.3018	0.0022

Table 3.
Inhibition efficiency for $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ paint coated steel

Materials	HCl	H_2SO_4	HNO_3
Bare			
W_{uncoated} , g	0.2022	0.5294	0.4657
$\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$			
W_{coated} , g	0.0012	0.0024	0.0022
Inhibition Efficiency, %	99.40	99.54	99.52

4. Conclusions

We have formulated a cost efficient nanopaint, which possess multifunctional property. The method is not limited to $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nanopaint but is also suitable for the preparation of other nanomaterial-based paint. The recorded results reveal that, $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nanopaint has moderate solid content and mechanically low irregularities compared with bare steel. Corrosion resistance is high in nanoformulated paints and therefore it has high inhibition efficiency. The contact angle reveals the film is hydrophilic in nature which enhance the spreading rate of paints.

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