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Influence of Egyptian nanoilmenite/amorphous silica composite particles on the electrochemical and mechanical properties of cold galvanizing formulation coatings

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ABSTRACT

In the present work, Egyptian ilmenite nanoparticles (FeTiO₃ NPs) were obtained with the average diameters of 20 nm by a direct solid-phase milling process and synthesized amorphous silica powder grains were processed to prepare a novel fabricated Egyptian nanoilmenite/amorphous silica composite (ENI/AS) particles. Flaky-like nature of ENI/AS and the spherical shape of Zn-dust particles were emphasized by scanning electron microscopic (SEM) micrographs. The nano features of ENI/AS particles were confirmed by transmission electron microscope (TEM) investigation. Various alkyd-based cold galvanizing coating formulations were modified using different uniformly dispersing amounts of the processed ENI/AS particles as a modifier to form some nanocomposite coatings. The electrochemical behavior of nanocomposite modified coated steel films in oil-wells formation water solution have been studied by both potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The mechanical properties of the coated films were studied through some coating tests as cross-cut adhesion, bend and impact to assert their application efficiency. Scanning electron microscope (SEM) technique was utilized to survey the protective film formed on the carbon steel surface by these modified coatings in formation water solution. The results of this study reinforced remarkable corrosion protection properties of ENI/AS modified cold galvanizing coating.

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1. Introduction

Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nm [1]. The solid phase can be amorphous, semi-crystalline grain or a combination. The solid phase can also be organic, inorganic, or a combination. In general, functional organic coatings are applied onto various metallic substrates to avoid the detrimental effect of corrosion. The orientation of the pigments in the coating must be parallel to the surface, and they should be highly compatible with the matrix resin to provide a good barrier effect. The reinforced properties are the result of the much greater surface to volume ratio of the nano-sized pigment which is often characterized by very high aspect ratios [2].

Investigation on preparation of epoxy-clay nanocomposite coating by Bagherzadeh et al. [3] indicated that the incorporation of

nanoclay particles into organic coatings enhances the anti-corrosive properties of coating. Alkyd-based coatings are well known for good corrosion protection, high gloss and the ease of application [4]. Min Zhi Rong et al. [5] found that the friction behavior of epoxy-TiO₂ nanocomposites under sliding environment was rather sensitive to the dispersion states of the nanoparticles and when the micro structural homogeneity of the nanocomposites was enhanced, their wear resistance could be improved significantly. The modification of nanocomposites consisting of organic polymers and TiO₂ or amorphous SiO₂ nanoparticles enhanced the recognized properties of these nanocomposites such as anti-corrosion properties, mechanical implementation and thermal characteristics [6–8].

The incorporation of nanoferrite (Fe₂O₃) particles in soya alkyd coating enhanced corrosion resistance and physico-mechanical properties [9]. Modification of alkyd coatings with aluminum oxide (Al₂O₃) nano-sized pigment improved anti-corrosion properties, UV resistance and mechanical properties [10,11]. It has been

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illustrated that application of ZnO nanoparticles improves the anti-corrosion behavior of alkyd based coatings [12].

Ilmenite is a non-toxic pigment contains titanium-iron oxide mineral with the idealized formula (FeTiO_3). It is a weak magnetic black solid. From the commercial perspective, ilmenite is the most important ore of titanium dioxide pigment. Cold galvanizing coating is an organic single-component coating in which gives the same cathodic protection as hot-dip galvanizing, but it is applied as paint. This type of coatings requires no mixing with other chemicals to make it cure. Cold galvanizing coating acts as an active coupling to the steel parent metal to form an electrolytic bond. It is called a duplex system in which offers a cathodic protection and a passive layer (as paint). Zinc-rich paints (ZRPs) have been utilized for a long time to protect steel adequately in aggressive atmospheres mainly in marine and industrial environments against corrosion. Two essential protection mechanisms work in ZRPs [13]: (1) the galvanic activity stage, which relies on the electrical contact among the zinc particles themselves in the coating and in addition amongst them and the steel substrate; (2) the barrier-like behavior stage, which is strengthened by the concentration and nature of zinc corrosion products leading to the promotion of the stable formation of dielectric surface films. These coatings are extraordinary in that they provide the protection to the steel surface even with voids, scratches, pinholes and other small defects in the coating system. Kalendova et al. [14] studied the behaviors of organic Zn-rich coatings were modified by utilizing lamellar zinc pigments rather than the spherical ones. In comparison with the spherical zinc pigments, the lamellar zinc pigments display a higher surface area/weight ratio which generates more effective electrical contact and lower current density in the protection mechanism of the Zn-rich coatings [15].

The anti-corrosion behavior of fabricated nano-composite coating based on nanoilmenite particles and amorphous silica grains was investigated in the term of cold galvanizing technology [16].

The present work aims to prepare Egyptian nanoilmenite/amorphous silica composite particles and evaluate their electrochemical and mechanical properties when added with different loading levels to some novel cold galvanizing coating formulations. These coatings were applied on the carbon steel surface and evaluated through a series of electrochemical corrosion measurements and some coating performance tests. Also, to study the surface morphology of these modified cold galvanizing coated films against uncoated blank carbon steel in formation water solution by using SEM technique.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

Soya bean short alkyd resin 40% and Benton were conducted from Chemical Partners Company. Zn-dust pigment was acquired from WL Company for Paints and Chemicals. White sand, potassium and sodium feldspars, calcium carbonate, boron, zinc, aluminum and zirconium oxides were obtained from ARKAN Company for Industry and Mining. BYK-066 N (polysiloxanes), was obtained from BYK-Chemie USA Inc. Xylene, ethylene glycol, n-butyl glycol were gained from El-Mohandes Company for Chemicals and Trading and used in technical grades.

2.1.2. Egyptian ilmenite ore (FeTiO_3 , iron titanium oxide pigment)

A great deposit of Egypt occurs in Wadi Abu Ghalaga in the South Eastern Desert. The area covers the eastern portion of Hamata Sheet, 30 km of Red Sea and 100 km South Marsa Alam. Ilmenite was anatomized by Thermo ARL ADVANT XP-385 XRF model and its physicochemical characteristics are depicted in Tables 1 and 2.

2.1.3. Preparation of the carbon steel samples and its composition

The carbon steel samples used in the present study were divided into specimens with dimensions of $1 \text{ cm} \times 1 \text{ cm} \times 0.8 \text{ mm}$ for SEM and the electrochemical investigations. The working specimens were used for coating tests with dimensions $15 \text{ cm} \times 10 \text{ cm} \times 0.8 \text{ mm}$. The specimens were mechanically prepared with emery paper up to 80 (medium grade). Then, the samples were washed by acetone and double distilled water before immersion in the test solution and its chemical composition is listed in Table 3.

2.1.4. Test solution

The utilized test solution in this work was the connected formation water during crude oil production handed over from Qarun Petroleum Company (QPC), Egypt. The chemical composition of this water has been illustrated using ionic chromatography as depicted in Table 4. The specific gravity of this water was 1.109, pH (6.23), The salinity as NaCl (151,581 ppm,wt), The total alkalinity (350 ppm,wt) and the total hardness (19.321).

2.2. Methods and techniques

2.2.1. Preparation of Egyptian nanoilmenite particles [FeTiO_3 (NPs)]

Nanoilmenite particles were prepared by a solid-phase milling method. The planetary ball mill PM 200-RETSCHE-short grinding times was utilized to grind $20 \mu\text{m}$ size of ilmenite powder for 12 h in an automatic grinding chamber with two grinding stations to get the highest degree of ilmenite fineness in the range of 20 nm size.

2.2.2. Synthesis of amorphous silica composite particles

Amorphous silica particles were fabricated by mixing 70.3% by weight of Egyptian white sand (source of SiO_2), 3% potassium feldspar (source of K_2O), 1.14% sodium feldspar (source of Na_2O), 6.9% calcium carbonate (source of CaO), 0.5% boron oxide (B_2O_3), 0.3% zinc oxide (ZnO), 17.36% aluminum oxide (Al_2O_3) and 0.5% zirconium oxide (ZrO_2) after grinding process to reach $0\text{--}75 \mu\text{m}$ size powder range for 20 min in a collection column. Heat treatment (fusion) for the powder mixture at 1350°C in ITALO oven was carried out until a molten liquid was composed then, water quenching operation at temperature 30°C was made [16,17]. The final product was ground to $0\text{--}20 \mu\text{m}$ size powder range with specific gravity of 2.78 g/cm^3 and Mohs scale of hardness equal 7.9. XRF analysis of the obtained amorphous silica composite particles was listed in Table 5.

2.2.3. Preparation of Egyptian nanoilmenite/amorphous silica composite (ENI/AS) particles

ENI/AS particles were prepared by mixing 20 g of nanoilmenite and 80 g of synthesized amorphous silica composite particles as 20:80 by ratios in a container for 20 min homogeneously. The mixture formed was added gradually to 40 g ethylene glycol and 10 g BYK-066 N (polysiloxanes with ingredients as 2,6-dimethyl 4-heptanone and 2-butoxyethanol dissolved in diisobutyl ketone) and stirring by using ultrasonic devices for 45 min was made till a suspension with homogeneous appearance be formed to establish the Egyptian nanoilmenite/amorphous silica composite paste. Then, the suspension was dried at 70°C for 24 h. After milling, the product is made up of fined black powder [16,18,19].

2.3. Transmission electron microscope (TEM) characterization of Egyptian nanoilmenite/amorphous silica composite (ENI/AS) particles

Transmission electron microscope of the ENI/AS particles was conducted at an accelerated voltage of 200 kV electron microscopes (JEM 2100 La B6 Japan). In the TEM, the solid samples was dispersed

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