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Introducing rice husk after utilizing new technology as anticorrosive pigments in organic coatings

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ABSTRACT

The aim of this study is to introduce rice husk after simple chemical modification as new eco-friendly anticorrosive pigments. Uncontrolled burning of rice husk is often considered the most disposal method in Egypt; this seasonal and highly localized massive burning generates excessive air pollution. The usage of this waste as anticorrosive pigments will decrease the danger of environment pollutions. The new anticorrosive pigments based on rice husk as core comprising 80–85% of new pigment covered with thin shell of ferrites that comprises about 15–20% were prepared using new technique called "core-shell". The different ferrites/rice husk pigments were characterized using different analytical and spectro-photometric techniques, such as X-ray fluorescence (XRF), Energy dispersive X-ray (EDAX) and transmission electron microscopy (TEM). These core-shell pigments were then incorporated in solvent-based paint formulations based on epoxy resin. The physico-mechanical properties of dry films were tested. The corrosion properties using immersion test in 3.5% NaCl and electrochemical impedance spectroscopy (EIS) for 28 days were determined.

1. Introduction

The use of by-product and waste materials play a very important role in solving present ecological problems. Rice husk is one of the most important agro-wastes, which is produced in millions of tons per year as a waste by-product in agricultural and industrial processes. Rice husk are shells produced during the de-husking of rice that one ton of rice can produce about 200 kg of husk, which on combustion produces about 40 kg of ash [1,2]. Rice husk constitutes about fifth of the 300 million metric tons of rice that are produced annually in the world. Rice plant is one of the plants that absorbs silica from the soil and assimilates it into its structure during the growth, with high percentage of silica concentrated in its husk that is more than 80–85%. Since rice husk is considered as one of the most important agro-wastes and is rich in silica, many studies have been done to use it in many different fields due to its high silica content which is a good advantage, especially in anticorrosive coating industry [3–5].

In anticorrosive paint industry, silica is considered as highly known and efficient material in corrosion protection and in enhancing coating properties such as abrasion and scratch resistance and being high chemically durable in different media [6].

With the development of the chemical preparation techniques, core-shell technique comes in the front of the most developed methods to reuse by-products and waste materials.

Core-shell structured particles are now attracting more and more investigation interest, since these particles are constructed of cores and shells having different chemical composition [7]. The properties of core-shell particles in general, are different from both of the pure core and the shell materials. The usage of this technique in utilization of waste material is done by using the waste material as the core comprising about 80–90% of the new composite. This is done by precipitating a thin shell of active material on the core surface which comprises 10–20% only to prepare novel compounds with new properties which gathers the properties of both the core and the shell materials at the same time. In coatings industry, the pigments are considered as one of the most important components that are used for different purposes such as decoration and protection. Generally, inhibitive pigments are introduced into organic coatings as the main material for corrosion inhibition.

Ferrite pigments with spinel structure have been studied for decades; they have the general formula MFe_2O_4, where M is a divalent metallic ion [8]. They possess high hardness, coverage power, insolubility and coloration. They usually lead to high thermal stability; high quality and are chemically and mechanically stable pigments [9,10]. The proper choice of the cations present in the oxide lattice can resolve the non-toxicity of the final compound [11].

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In this work core-shell technique was used as a method for utilization of rice husk as pigment, by using it as source of silica precipitating on its surface a layer of ferrite pigments which is well known anticorrosive pigments. The prepared core-shell pigments contain only (10–20%) of ferrite pigments as shell material precipitated on (80–90%) rice husk as core. These pigments were tested as anticorrosive pigments in paints. The modification of rice husk was done by precipitating thin layer of (Zn, Mn and Zn·Mn) ferrites on its surface. Ferrite pigments (Fe) are known as efficient anticorrosive pigments and they are present in the shell which is in direct contact with the surrounding materials. The anticorrosive performance of the new ferrites/rice husk (Fe/RH) core-shell pigments was measured to prove their efficiency as anticorrosive pigments in the different epoxy-based paint formulations. The results showed that core-shell pigments based on rice husk are highly efficient in their anticorrosive performance.

2. Experimental

2.1. Materials

- *Zinc, manganese and ferric nitrates* are powders of high purity and were obtained from Win-lab, Sigma-Aldrich, ALPHA CHEMIKA, respectively.
- *Rice husk* is a by-product obtained from rice plant in Egypt. The obtained rice husk was ground to the finest form as preparatory step to outfit the preparation of the new pigments [12].

Rice husk and prepared core-shell ferrites/rice husk (Fe/RH) photos are represented in Fig. 1.

2.2. Preparation of core-shell ferrites/rice husk

Zn, Mn and/or Zn·Mn nitrates were mixed with Fe nitrate in situ in the presence of ground rice husk at 100 °C for 1 h; in this step oxy-hydroxy iron compounds are formed. The formed paste was then heated up to 400 °C, after this temperature the iron oxides are formed. Then, grinding of the paste was done. At last, calcinations of the powder took place at 1000 °C, and in this last step the ferrites were formed on the surface of rice husk. A flow chart of the preparation process is presented in Fig. 2. From the preparation process it can be deduced that the burning then calcinations process is essentially for the formation of ferrites that are precipitated on the rice husk surface and there was not initial burning step to the rice husk before the ferrite precipitation.

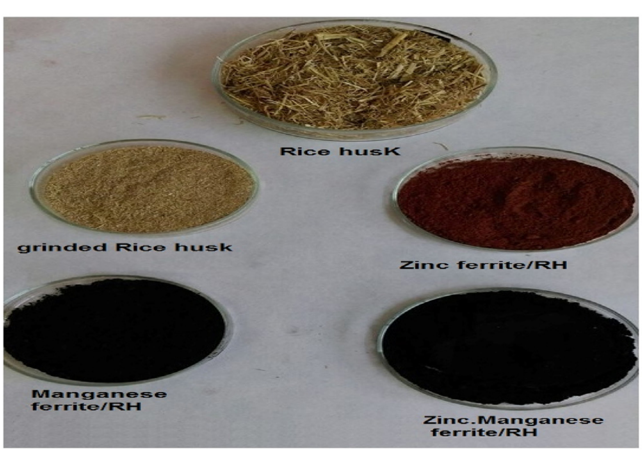

Fig. 1. Rice husk (RH) and ferrite/rice husk (Fe/RH) core-shell prepared pigments.

2.3. Methods of instrumental analysis

2.3.1. X-ray fluorescence

The different concentrations of each element in the prepared pigments were determined using an Axios, sequential WDX-ray fluorescence (XRF) spectrometer, PANalytical 2005, USA.

2.3.2. Transmission electron microscopy (TEM) analysis

Various pigments were examined using JEOL JEM 2100 (Japan) technique with micro-analyzer electron probe to determine the particle shapes and sizes of the prepared pigments.

2.3.3. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDAX) analysis

Energy-dispersive X-ray analysis technique and scanning electron microscopy (JEOL JX 2840) micro-analyzer electron probe (Japan) was used in this work to estimate the particle shapes and elements deposited on silica surface

2.4. Anti-corrosive paint formulations of ferrite/rice husk core-shell pigments

The prepared core-shell ferrites/rice husk pigments were incorporated in paint formulations beside paint formulation free of rice husk as blank for comparison. Paint film thicknesses range from 120 to 150 μm. All paint formulations were based on epoxy resin, and the formulations were divided into three groups with different pigment loadings from 30 to 50% of the total solids.

2.5. Mechanical properties of paint films containing the prepared pigments

A variety of physical and mechanical evaluations of the paint films were carried out. Relevant methods of sample preparation and evaluations include;

- Determination of the resistance of paints against impact (ASTM D5638-00, 2007)
- Determination of paint resistance against cupping in Erichsen apparatus (ASTM D 5638-00, 2007)
- Determination of paint hardness (ASTM D 6577-00, 2007)

2.6. Corrosion studies

The corrosion behavior of coating containing different prepared pigments was evaluated using two methods as following;

2.6.1. Immersion in salt solution 3.5% NaCl (ASTM D 870)

After 28 days of exposure, the coated steel panels were evaluated for the;

- Degree of rusting (ASTM D 6294-98, 2007),
- Degree of blistering on painted steel surfaces according to (ASTM D 714-07, 2007),
- Determining the degree of coating adhesion by means of a cross-cut test (ASTM D 3359-97, 2007).

2.6.2. Electrochemical impedance spectroscopy (EIS)

The corrosion protective performance of coatings was investigated using EIS (SP-150), which is obtained from biologic science instruments, (France). EIS is one of the most powerful techniques used for the investigation and prediction of corrosion protective performance of coatings. The impedance spectra for different Nyquist plots were analyzed by fitting the experimental data to a simple equivalent circuit mode [Cf/Rf/(Cdl + Rct)] for steel, which is protected with coatings containing the prepared pigments (Fig. 3).