



# The effect of polyaniline phosphate on mechanical and corrosive properties of protective organic coatings containing high amounts of zinc metal particles

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## ABSTRACT

The objective of this paper is to reduce the zinc metal content in organic coatings while preserving their high anticorrosive efficiency. The two goals can be achieved by using conductive polymers as components of the protective coating. Polyaniline phosphate (PANI-H<sub>3</sub>PO<sub>4</sub>) was investigated as the conductive polymer and was also used in surface treatment of steatite talc Mg<sub>3</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub>. Both PANI-H<sub>3</sub>PO<sub>4</sub> and Mg<sub>3</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub>/PANI-H<sub>3</sub>PO<sub>4</sub> were specified using physico-chemical parameters. An epoxy ester resin was used as binder for the organic coatings investigated. Organic coatings were prepared by combining zinc metal with PANI-H<sub>3</sub>PO<sub>4</sub> or Mg<sub>3</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub>/PANI-H<sub>3</sub>PO<sub>4</sub>. The mechanical resistance of the prepared films was evaluated using the results of mechanical tests. The anticorrosive efficiency of the prepared films was evaluated using the results of direct corrosion tests.

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## 1. Introduction

Zinc metal has already been used in anticorrosive coatings for many years as the so-called “sacrificed electrode” [1–3]. Corrosion products formed in cathodic protection block the pores present in the film and, accordingly, reduce its conductivity, resulting in the electrochemical mechanism being replaced by the barrier mechanism [4]. An active protection is required since the function of electrochemical cathodic protection takes place upon mechanical damage to the coating [2,5,6]. The maximum anticorrosive protection is achieved when the condition PVC=CPVC has been adhered to in preparation of the coating [7]. However, a high volume concentration of zinc metal has a negative effect on both the mechanical properties of the organic coating and its adhesive capacity [5]. When a zinc powder is combined with conductive polymers, the volume concentration of the zinc metal is reduced while a high anticorrosive efficiency is preserved [8]. Conductive polymers have been the centre of attention in the last several years. Polyaniline, which can be prepared in five different forms, constitutes a very important representative of conductive polymers. Its individual forms differ in the extent of oxidation or the extent of

protonation and also in chemical structure, stability, colour and electrical characteristics [9–11]. The anion present in the polyaniline structure offsets the positive charges present in the chain. The anion present depends on the protonating acid employed [12]. Both the type and concentration of the acid substantially affect the conductivity of the polyaniline conductive form (emeraldine salt) [13,14]. Chemical synthesis [15], chemical stability [16–18], electrical conductivity [19–22] and anticorrosive applications [10,23–25] of the above pigment have been investigated. Oxidative polymerisation represents a possible approach to polyaniline preparation. In the event that foreign particles are present during the aniline oxidation process, a thin film of a conductive polyaniline is formed on their surface. The thickness of the resulting film is about 100 nm [25–27]. The above process has been used to modify a series of conductive and non-conductive materials. Stability of the modified object in acidic media is an indispensable condition [25]. Anticorrosive applications of particles with surfaces modified by a thin polyaniline layer have been studied in a number of papers [26,28].

## 2. Experimental

### 2.1. Preparation of PANI-H<sub>3</sub>PO<sub>4</sub> by precipitation polymerisation

To prepare PANI-H<sub>3</sub>PO<sub>4</sub>, aniline is oxidised by potassium peroxodisulphate in an acidic medium. The (exothermic) reaction takes place in air at ambient temperature.

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250 ml of 0.2 M aniline (Merck) was dissolved in 0.8 M phosphoric acid and 250 ml of 0.25 M potassium peroxodisulphate (Merck) was dissolved in distilled water. The two solutions were mixed and the resulting liquid was stirred mechanically for 60 min. During the polymerisation the originally colourless reaction mixture first became blue and finally assumed the green colour of PANI-H<sub>3</sub>PO<sub>4</sub>. The reaction mixture was then left overnight.

The resulting PANI-H<sub>3</sub>PO<sub>4</sub> precipitate was filtered off using a Buchner funnel, and the product was washed with dilute phosphoric acid and with acetone. The resulting PANI-H<sub>3</sub>PO<sub>4</sub> powder was dried for 24 h in air and subsequently in an oven at 60 °C.

## 2.2. Preparation of the Mg<sub>3</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub>/PANI-H<sub>3</sub>PO<sub>4</sub> pigment by precipitation polymerisation

Surface-treated pigment was prepared in air at ambient temperature.

The only difference compared with PANI-H<sub>3</sub>PO<sub>4</sub> preparation as described above was that the talc Mg<sub>3</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub> (20 g) was added to the (mixed) solution of 0.2 M aniline in 0.8 M phosphoric acid.

## 2.3. Specification of the pigments employed

Morphology of the zinc metal, PANI-H<sub>3</sub>PO<sub>4</sub> and Mg<sub>3</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub>/PANI-H<sub>3</sub>PO<sub>4</sub> particles was determined by electron microscopy (JEOL – JSM 5600 LV, Japan). The resulting micrographs used to follow the shape and the surface structures are shown in Fig. 1. 10% suspensions of the pigments in redistilled water were then prepared and values of pH and conductivity were followed for 21 days. The critical volume concentration of the pigments was calculated from the density determined using Autopycnometer Micromeritics 1320 and oil absorption was determined according to the Czech State Standard (CSN) 67 0531 using the “pestle–mortar” method.

## 2.4. Formulation and preparation of organic coatings

As a convenient binder, the epoxy-ester resin was used. Organic coatings were prepared by combining zinc metal with PANI-H<sub>3</sub>PO<sub>4</sub> and Mg<sub>3</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub>/PANI-H<sub>3</sub>PO<sub>4</sub>, using the pigment volume concentrations (PVC) 0.1%, 0.5%, 1%, 3%, 5%, 10% and zinc metal volume concentration (PVC/CPVC) equal to 0.67. To compare the results obtained with conductive polymers an organic coating containing only zinc metal (at PVC/CPVC=0.67) was prepared. Organic coatings were dispersed using a Disolver-type equipment at 4000 rpm for 40 min. An epoxy ester resin was used as binder for the organic coatings investigated.

Commercial name, manufacturer:	WorléeDur D 46, Worlée-Chemie GmbH, Germany
Composition:	WorléeDur D 46 is a short oil epoxy ester based on conjugated drying fatty acids
Technical data:	Content of epoxy resin approx. 60% Oil content approx. 40% Acid value, DIN EN ISO 3682 max. 4 Delivery form 60% in xylene Density 0.98 g cm <sup>-3</sup> (20 °C)

## 2.5. Mechanical properties of the coatings

The test techniques measure the variables associated with the degradation of organic coatings. The physical–mechanical quantities indicate the flexibility, the elasticity and the strength of the paint film. These tests provide a basis for studying the mechanism of action of protective organic coatings. The physico-mechanical evaluation was carried out after application on steel panels – size

**Table 1**  
Characteristics of the pigments employed.

Pigment	Particle morphology	CPVC (%)	pH [21]	Conductivity [21] (mS/cm)
Mg <sub>3</sub> (Si <sub>4</sub> O <sub>10</sub> )(OH) <sub>2</sub>	Lamellar	45.1	8.9	0.1
Mg <sub>3</sub> (Si <sub>4</sub> O <sub>10</sub> )(OH) <sub>2</sub> /PANI-H <sub>3</sub> PO <sub>4</sub>	Lamellar	32.7	4.4	1.9
PANI-H <sub>3</sub> PO <sub>4</sub>	Isometric	61.7	1.5	15.7

152 mm × 75 mm × 0.8 mm (Standard low-carbon steel panels S-36, Q-Lab Corporation). The dry film thickness (DFT) was measured using a magnetic gauge in accordance with ISO 2808.

The mechanical properties of the coating systems were evaluated according to standards.

### 2.5.1. The surface hardness of the paints by a pendulum apparatus

The hardness of the paint film was determined by means of a Persoz pendulum. The results are indicated as percentages related to the hardness of glass standard.

### 2.5.2. The degree of the adhesion of the coatings by a lattice method (ISO 2409)

Determination was made by means of a special cutting blade with cutting edges 2 mm apart and involved the degree of adhesion of the created 2 mm × 2 mm squares to a base substrate.

### 2.5.3. Impact resistance (ISO 6272)

The test revealed the height of the free fall of a weight (1000 g) at which the paint film still resists damage. The test was performed on the reverse of the panel with a coating.

### 2.5.4. The resistance of the coating against cupping in an Erichsen cupping tester (ISO 1520)

The objective of this test is to identify the resistance of the paint film against on-going deformation of a coated steel panel with a pressed-in 20 mm steel ball. The result of the test gives the so-called cupping in mm during which the first disturbance of the coating occurred.

### 2.5.5. The resistance of the coating during bending on a cylindrical spindle (ISO 1519)

The result of this test indicates the diameter of the spindle (in mm) on which the cohesion of the paint film became disturbed.

## 2.6. Corrosion test procedures

Accelerated corrosion tests are based on the intensification of the effects of natural forces that have a decisive influence on the protective properties of the paints, their degradation, and primarily on the extent of corrosion under the paint film on a protected base. The accelerated corrosion tests were carried out in three types of corrosion atmosphere: a corrosion test with water steam condensation, a corrosion test in an SO<sub>2</sub> atmosphere with water steam condensation, and a corrosion test in a NaCl atmosphere with water steam condensation. The first test paints were applied on the steel panels – size 152 mm × 102 mm × 0.8 mm (Standard low-carbon steel panels S-46, Q-Lab Corporation) by an applicator with a 250-µm slit. The second layer was put on steel plates using a 200-µm applicator after drying the first coat. The dry film thickness (DFT) was measured using a magnetic gauge in accordance with ISO 2808. To test the anticorrosive efficiency, a test cut (about 7 cm) was made at the bottom of all paints.

The degree of blistering on the surface of the coatings (ASTM D 714-78), the degree of corrosion at the test scribe (ASTM D

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