# Vliv tvaru zinkových částic na korozní vlastnosti organických povlaků obsahujících vodivý polymer

# Effect of zinc particle shape on the anticorrosion properties of organic coatings containing zinc and a conductive polymer

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**Summary**

The aim of this work was to prepare organic coatings containing a conductive polymer and either spherical or lamellar zinc particles and to evaluate their mechanical and corrosion resistance. Polyaniline phosphate was used as the conductive polymer. This substance was prepared by oxidative polymerisation of aniline in 1 M phosphoric acid using ammonium peroxodisulphate as the oxidant. The oil number and density were determined for the pigment and the critical pigment volume concentration was calculated by using the data. Once the basic characteristics of the pigment had been established, the organic coatings were formulated. The organic coatings contained polyaniline phosphate at pigment volume concentrations 1%, 5% and 10%, to which zinc – spherical in one concentration series and lamellar in another series – had been added in amounts such that the total pigment volume concentration was constant and equal to the critical pigment volume concentration. The organic coatings were subjected to mechanical and corrosion tests. Mechanical tests included the impact test, bending test, cupping test and adhesion test. Corrosion was assessed in an accelerated cyclic test in salt spray atmosphere.

**Key words**: spherical zinc, lamellar zinc, conductive polymer, polyaniline, coating

## Introduction

Zinc powder is used as an anticorrosion pigment in paints, in which it constitutes what is called a sacrificed electrode [1, 2]. Spherical zinc particles are typically used in corrosion protection applications, although lamellar particles are sometimes also used. Lamellar particles exhibit a lower tendency to settle and are capable of sorbing larger amounts of the binder than the spherical particles, which implies that they are able to attain a lower pigment volume concentration (PVC) in the paint [3]. As another asset, the lamellar pigment extends the travelling path of the liquid medium diffusing from the surface to the substrate; reflect ultraviolet radiation, thereby protecting the binder from degradation; and, also importantly, plays the role of reinforcement improving appreciably the paint film's mechanical properties [4].

Zinc coatings protect the steel substrate cathodically only during the first phase of the corrosive action. Slowly, the pores in the coating are sealed by the zinc corrosion products such as zinc oxides, zinc hydroxide and basic zinc carbonates, whereby the coating becomes impermeable for the incoming components of the corrosive medium. Hence, the zinc particles are soon coated with zinc corrosion products, electric conductivity decreases and this type of protection ceases to exist: cathodic protection transforms to barrier protection. The neutralisation and filtration mechanisms also play a role in addition to the barrier mechanism [5].

So it can be reasonably assumed that the long-term protective effect of a non-damaged zinc coating is based on the filtration effect. As the aggressive electrolyte penetrates through the paint layer, zinc corrodes spontaneously and takes up oxygen (playing the role of the depolariser) as well as the agents stimulating ion corrosion ($H^+$, $Cl^-$, $SO_4^{2-}$). Ultimately, only the non-aggressive aqueous solution can reach the steel surface. The emerging corrosion products also enhance the barrier effect in the coating and facilitate neutralisation of the electrolyte penetrating through the film from the outside [6-9].

## Experimental part

### *Polyaniline phosphate synthesis*

The polyaniline phosphate (PANI-$H_3PO_4$), was prepared by oxidative polymerisation in dilute phosphoric acid by using ammonium peroxodisulphate as the oxidant. The synthesis is depicted in **Fig. 1**.

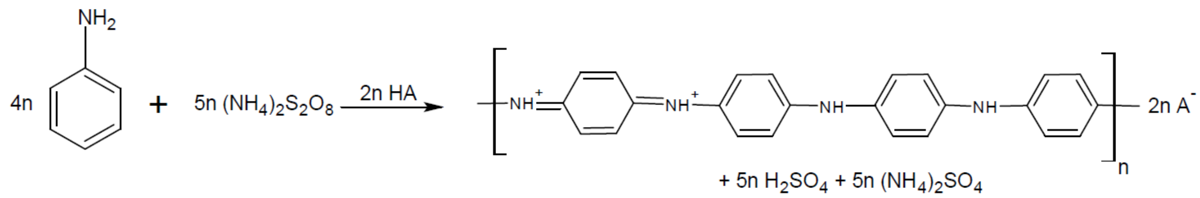



Figure 1. Synthesis of the polyaniline phosphate.

### *Pigment parameter determination*

Pigment density was determined by using a Micromeritics AutoPycnometer 1320. Oil absorption was measured by the "pestle – mortar" method based on Czech Standard CSN 67 0531. The data were used to calculate the critical pigment volume concentration (CPVC). Microphotographs of the pigment particles were obtained on a JEOL–JSM 5600 LV electron microscope (Japan) and used to deduce the pigment particle shape. The mean particle size ($d_{50}$) was determined on a Mastersizer 2000 (Malvern Instruments Ltd., UK).

### *Formulation and preparation of the organic coatings*

In the present study, two series of organic coatings was prepared by using polyaniline phosphate at volume concentrations 1%, 5% and 10% and by completing the total pigment volume concentration to the critical level (critical pigment volume concentration, CPVC) with spherical zinc (series 1) or with lamellar zinc (series 2). A Dissolver type system was used at 4000 rpm/40 minutes to prepare the paints. Once prepared, the paints were applied to steel panels (standard S-36 low-carbon steel panels, Q-Lab Corporation) and the dry film thickness (DFT) was measured with a magnetic gauge as per ISO 2808. An artificial vertical cut was made through the paint films for the accelerated corrosion tests. The cut was 80 mm long and 0.5 mm deep and was made in accordance with EN ISO 12944–6 by using a cutting tool complying with ISO 2409 (tool for single cuts).

### *Mechanical properties of the paints*

The paints were subjected to tests providing information on the paint film elasticity and strength. Surface hardness of the paint films was also measured, viz. with a Persoz pendulum system in accordance with ISO 1522. Adhesion of the films to the substrate was assessed on cutting a lattice into the films as per ISO 2409, by using a special cutting blade with cutting edges 2 mm apart. The impact strength of the paint films applied to steel panels was determined by letting a 1000 g weight fall onto the panels from different heights and recording the largest height (in mm) at which the film integrity remained undisturbed (ISO 6272). The paint film resistance to cupping was evaluated by measurement on an Erichsen cupping tester. The result is the steel ball indentation depth (in mm) at which the film integrity remained undisturbed, as specified in ISO 1520. The test aimed at evaluating the paint film resistance to bending consists in bending the painted panels over mandrels of different diameter and recording the largest diameter (in mm) at which the paint film integrity is disturbed, as specified in ISO 1519.

***Corrosion test procedures***

The organic coatings were applied to steel panels and subjected to an accelerated cyclic corrosion test in a neutral salt spray atmosphere (ISO 9227). The exposure of the samples in a testing chamber was performed in 12-h cycles divided into three parts: 6 h of exposure to a mist of 5 %-solution of NaCl at a temperature of 35 °C; 2 h of exposure at a temperature of 23 °C; and 4 h of humidity condensation at a temperature of 40 °C. The samples were evaluated after 720 h of exposure. The corrosion effects after completion of the test were evaluated as specified in the above ISO standards. Blistering on the paint film surface and in the test cut was assessed by comparing with the photographs of standards included in the ASTM D 1654–92 standards. Corrosion on the metal plane was evaluated (after stripping the paint film down) by comparison with the photographs of standards included in the ASTM D 610-85 standard. Corrosion in the test cut was evaluated by measuring the distance to which corrosion propagated from the cut to its sides.

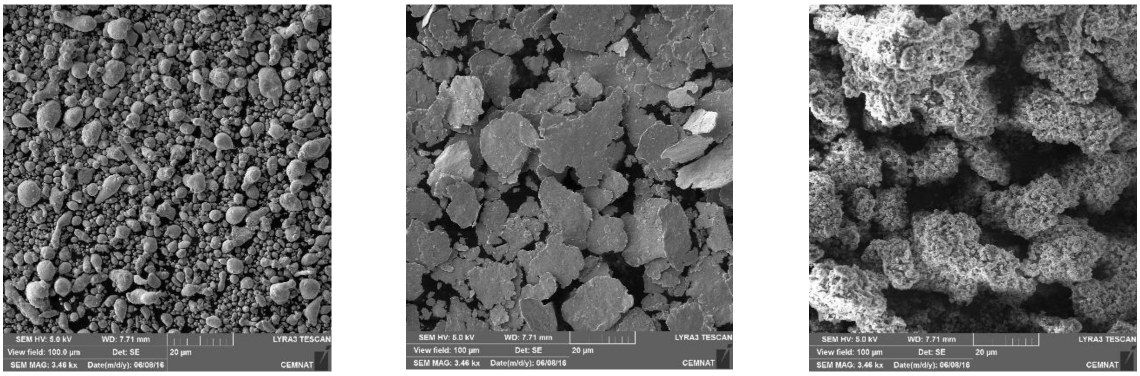
## Results and discussion

***Pigment specification***

The pigments' densities and oil numbers were determined and the data were used to calculate the critical pigment volume concentrations. Accurate knowledge of this parameter is imperative for obtaining correct formulations. The mean particle sizes were measured and were found nearly identical for spherical zinc and PANI-$H_3PO_4$, while the lamellar zinc particles were nearly twice as large. The pigment particle shapes were evaluated from microphotographs (Fig. 2) taken on an electron microscope.

Table 1. Characteristics of the pigments

| Pigment | Density [g/cm$^{-3}$] | Oil absorption [g/100g] | CPVC [%] | Particle size [μm] |
|---|---|---|---|---|
| spherical zinc | 7,14 | 6,4 | 67 | 5,8 ± 0,1 |
| lamellar zinc | 6,55 | 23,3 | 38 | 13,0 ± 0,1 |
| PANI-$H_3PO_4$ | 1,54 | 50,2 | 55 | 6,8 ± 0,1 |



a) b) c)

Figure 2. Scanning electron micrographs: a) spherical zinc; b) lamellar zinc; c) PANI-$H_3PO_4$

***Mechanical properties of the organic coatings***

Mechanical properties of the organic coatings were evaluated by using 4 tests (Tables 1 and 2). The data demonstrate that the organic coatings with lamellar zinc particles attained a mechanical resistance level nearly twice as high as the coatings pigmented with spherical zinc. This can be explained so that the lamellar particles laminate, i.e. reinforce, the binder, their elasticity can play a role even at a low binder content, thereby imparting a mechanical resistance to the coating. Spherical zinc lacks this ability due to its spherical particle shape. Furthermore, the data demonstrate that the coatings' mechanical resistance increases with increasing PANI-$H_3PO_4$ volume concentration. In other words, the use of PANI-$H_3PO_4$ as a pigment in zinc coatings was beneficial in all the formulations. This pigment (PANI-$H_3PO_4$) was used here to increase the organic coatings' adhesion and resilience. This effect is contributed to by the anions derived from phosphoric acid, which make up for the positive charge at the chain of this conductive polymer and improve coating adhesion to the substrate metal.

Table 1: Mechanical test results for organic coatings containing PANI–$H_3PO_4$ and spherical zinc (DFT = 110 ± 10 μm)

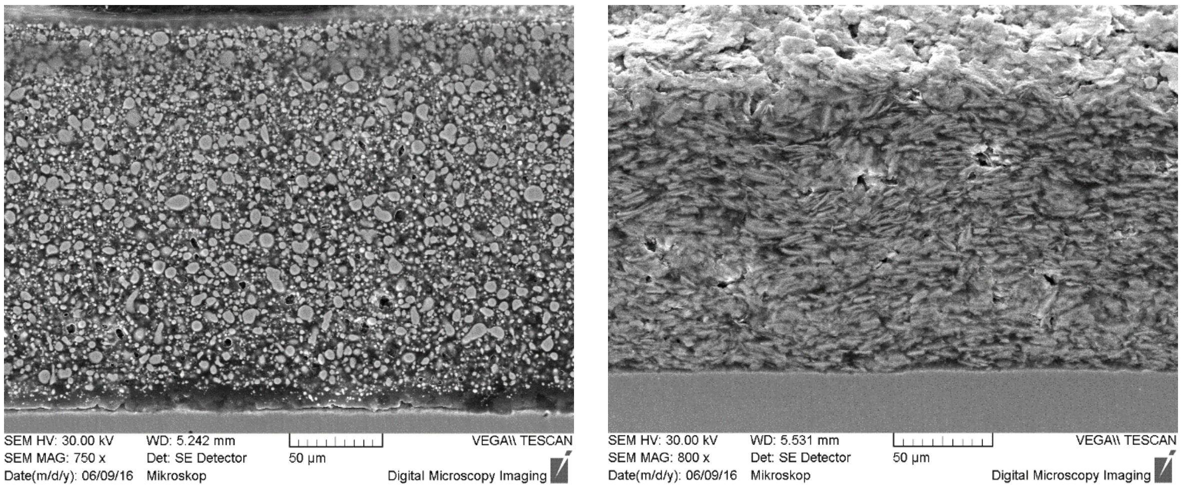
| **$PVC_{PANI-H3PO4}$ [%]** | **Cupping test [mm]** | **Impact test [cm]** | **Adhesion test [dg]** | **Bend test [mm]** |
|---|---|---|---|---|
| **0** | 4,0 | 30 | 1 | 10 |
| **1** | 4,1 | 30 | 1 | 8 |
| **5** | 4,4 | 35 | 1 | 6 |
| **10** | 4,5 | 35 | 1 | 6 |

Table 2: Mechanical test results for organic coatings containing PANI–$H_3PO_4$ and lamellar zinc (DFT = 120 ± 10 μm)

| **$PVC_{PANI-H3PO4}$ [%]** | **Cupping test [mm]** | **Impact test [cm]** | **Adhesion test [dg]** | **Bend test [mm]** |
|---|---|---|---|---|
| **0** | 4.9 | 45 | 0 | 8 |
| **1** | 5,7 | 45 | 0 | 6 |
| **5** | 6,2 | 50 | 0 | 6 |
| **10** | 6,5 | 50 | 0 | < 4 |

***Corrosion properties of the organic coatings***

The results of the accelerated corrosion test, which was terminated after 720 hours, are listed in Tables 3 and 4. The tables show that the corrosion resistance was lower for the coatings with spherical zinc particles than for coatings with lamellar zinc particles. The superiority of the latter is due to the larger surface area of the lamellar particles, facilitating contact between the pigment particles. Owing to this contact, electric conductivity of the paint film with lamellar zinc particles is higher than that of the paint film with spherical zinc particles, in which the zinc particle contact area is very small. Moreover, owing to their shape, the lamellar particles in the coating are able to make up an efficient physical barrier against the penetrating corrosive medium (barrier protection mechanism). This fact can also be seen in the microphotographs of sections of organic coatings containing either spherical or lamellar zinc particles (Fig. 3).




Organic coating pigmented with spherical zinc (PVC = CPVC)

Organic coating pigmented with lamellar zinc (PVC = CPVC)

Fig. 3. Microphotographs of sections of organic coatings containing either spherical or lamellar zinc particles.

PANI-$H_3PO_4$ had a beneficial effect by increasing the organic coatings' corrosion resistance. This conductive polymer was used to improve electric contact between the zinc particles, which is a prerequisite for electrochemical reaction of zinc. Furthermore, use is made of the polyaniline salt's ability to capture electrons and use them to transform to the polyaniline base [10].

Table 3: Corrosion test results for organic coatings containing PANI – $H_3PO_4$ and spherical zinc (DFT = 90 ± 10µm)

| **$PVC_{PANI-H3PO4}$ [%]** | **Blistering** | | **Corrosion** | |
|---|---|---|---|---|
| | **In a cut [dg]** | **Metal base [dg]** | **Metal base [%]** | **In a cut [mm]** |
| **0** | 2D | 2 D | 50 | 2-2,5 |
| **1** | 4 D | 2 MD | 33 | 1-1,5 |
| **5** | 4 D | 4 MD | 16 | 1-1,5 |
| **10** | 4 D | 4 MD | 16 | 1-1,5 |

Table 4: Corrosion test results for organic coatings containing PANI – $H_3PO_4$ and lamellar zinc (DFT = 90 ± 10μm)

| **$PVC_{PANI-H3PO4}$ [%]** | **Blistering** | | **Corrosion** | |
|---|---|---|---|---|
| | **In a cut [dg]** | **Metal base [dg]** | **In a cut [dg]** | **Metal base [dg]** |
| **0** | 2 MD | 2 MD | 33 | 1,5-2 |
| **1** | 4 MD | 4 M | 1 | 0,5-1 |
| **5** | 4 MD | 4 M | 0,3 | 0,5-1 |
| **10** | 4 MD | 4 M | 0,3 | 0,5-1 |

## Conclusion

The results of the mechanical tests and corrosion tests show that organic coatings pigmented with PANI-$H_3PO_4$ and containing lamellar zinc particles can attain higher mechanical and anticorrosion efficiencies than coatings without the conductive polymer or coatings with spherical rather than lamellar zinc particles. The improved mechanical resistance can be explained in terms of the reinforcing ability of the lamellar zinc particles, the improved anticorrosion resistance, in terms of the good electric contact between the zinc particles provided by the larger contact area of the lamellar particles. Moreover, the coatings with lamellar zinc constitute a better physical barrier separating the substrate metal from the corrosive environment. It was confirmed that PANI-$H_3PO_4$ improves both the mechanical properties and the corrosion resistance of the zinc-pigmented organic coatings.

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