## Nanomer<sup>®</sup> coatings containing flake-type zinc-manganese metal phosphate particles as corrosion protection additives for mild steel

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## ABSTRACT

Zinc phosphates and metal phosphates are commonly known to show interesting protection effect on steel against corrosion. The fundamental mechanism behind of the protection effect is still under discussion in literature. Barrier properties against diffusion, passivation of the steel surface, shielding and anti-cathodic disbonding abilitiy were reported in the past. In this study, we report the formation crystalline, anisotropic flake-type shaped zinc phosphates and mixed zinc-manganese phosphates as new corrosion protection pigments and their protection effect on mild steel. The corrosion protection ability was investigated by means of polarization and electrochemical impedance spectroscopy in dependence on the particles morphology and the molar ratio of zinc to manganese. Furthermore the particles were tried as active fillers in polymer matrix based Nanomer<sup>®</sup> coatings.

*Keywords*: zinc phosphate, corrosion protection, mild steel, polymer coating, nanocomposite

### **1 INTRODUCTION**

Galvanization, cathodic protection, or the deposition of a protective organic or inorganic coatings are common approaches to protect mild steel against corrosion. The latter is extensively studied because it enables to select appropriate matrix materials, fillers and other additives in order to provide tailormade solutions for practical applications. Zinc phosphate pigments as an alternative for toxic ingredients used in the past showed a positive effect at protecting steel against corrosion but its protection ability was limited and difficult to demonstrate using accelerated corrosion tests as it as a low solubility in water [1, 2, 3]. For this reason the present work had two approaches to achieve a higher solubility: synthesizing particles with a flake-type morphology having a higher surface to volume ratio than corresponding spheres and introducing manganese as a second metal into zinc phosphate. In order to evaluate the protective behaviour of the different metal phosphate particles, they were dispersed in various testing electrolytes that could be used to immerse mild steel samples.

## 2 EXPERIMENTAL PART

#### 2.1 Metal phosphate particles

All chemicals were ordered from Sigma Aldrich. Zinc phosphate, Manganese phosphate and mixed zinc-manganese phosphate particles were obtained through a precipitation route, as previously described using water as solvent [4].

### 2.2 Coating preparation

Epoxy resin BECKOPOX®EP307 (EP307) and phenolic resin PHENODUR®PR722/53BG/B (PR722) were both from Cytec Surface Specialties Germany GmbH & Co KG; solvent Methylpropylacetate (MPA)) from Sigma Aldrich, surface additive Byk 310 (BYK) from BYK-Chemie GmbH. Coating materials are based on an epoxy-phenolic resin matrix with a wt.-% ratio of 80:20 EP307:PR722. To obtain of a processable solution the resulting matrix was diluted with MPA under magnetic stirring. In this diluted matrix the metal phosphate fillers were added under magnetic stirring in order to prepare a homogeneous composite coating dispersion.

For preparation of coating layers mild steel substrates 10 cm x 10 cm x 1 mm (ST 1203) coated by manual spraying and curing in laying position in a temperature program up to 200  $^{\circ}$ C.

### 2.3 Experimental methods

The morphology of the particles were determined by scanning electron microscope (SEM) using a Quanta 400 F (FEI). The corrosion protection properties of the particles alone were demonstrated optically and by electrochemical testing using a SP-240 potentiostat-galvanostat equipped with impedance spectroscopy (Biologic). A steel ST1203 plate (surface exposed: disc of 14 mm diameter), a Pt coiled wire (23 cm<sup>2</sup>) and an Ag/AgCl 3M NaCl electrode were used as working, counter and reference electrodes respectively. A solution of 3.5 % NaCl in H<sub>2</sub>O (pH 6.3) and solutions of 0.5M NaCl in H<sub>2</sub>O containing various concentrations of H<sub>2</sub>SO<sub>4</sub> to control the pH were used as standard electrolytes. The electrolytes containing sulphuric acid had a pH of 3.8 and 2.7 for concentration of H<sub>2</sub>SO<sub>4</sub> of 0.1 mM and 1 mM respectively.

## 3 RESULTS AND DISCUSSION 3.1 Morphology of metal phosphate particles

All the synthesized metal phosphate particles present a flake-like morphology as shown in figures 1-3. The zinc manganese phosphate (ZMP) flakes with molar ratio Zn:Mn 0.3:0.7 are much thinner and smaller than the zinc phosphate (ZP). The manganese phosphate particles (MP) also show a broad size distribution like the ZP but the fraction of the smaller particles seem to approach a needle type shape. The flake-like morphology was desired as a high aspect ratio is expected to lead to an improved reactivity of the particles when a corrosive electrolyte gets in contact. This would lead to an increased solubility from the edges of the particles. When incorporated in a coating matrix, the particles can be oriented more or less parallel to the surface of the metal, thus increasing the barrier properties by roof-tile arrangement which leads to prolonged diffusion pathways for corrosive substances.



Figure 1: SEM micrograpch of zinc phosphate flakes after washing and centrifugation.



Figure 2: SEM micrograpch of zinc-manganese phosphate after washing and centrifugation.



Figure 3: SEM micrograpch of manganese phosphate after washing and centrifugation.

X-ray diffraction analysis confirmed the formation of different metal phosphate varieties with respect to the crystal structure. The zinc phosphate exhibited the hopeite structure. The mixed phosphate was identified as gamma zinc manganese phosphate and the manganese phosphate showed the hureaulite structure.

# **3.2** Exposure of mild steel to electrolytes containing metal phosphate flake particles

In order to obtain first results on the protection ability of the different zinc and zinc manganese phophates synthesised the metal phosphate powders were added to standard electrolytes to mimic the behaviour of pigments dispersed in paints and at the same time to allow them to directly interact with the mild steel surface. Steel substrate plates were immersed in the obtained dispersions. Their appearance after 24 h of immersion is shown in figure 4.



Figure 4: Steel plates (ST 1203) immersed for 24 h in 3 different electrolytes (pH 6.3, 3.8, and 2.7) containing no particles, 1% zinc phosphate (+ZP), 1% zinc-manganese phosphate (+ZMP), or 1% manganese phosphate (+MP).

All the plates immersed in the electrolytes not containing metal phosphate extracts showed large signs of corrosion after 24 h immersion. The corrosion process was different depending on the pH of each solution. Already after 2 h at pH 6.3, red rust formation was observed; however when the medium becomes more acidic, iron oxides are dissolved again. It became visible that iron ions were formed and bubbles due to water splitting were built at the steel surface. The steel plates immersed in the electrolyte containing manganese phosphate dispersion did also show some traces of corrosion in all the electrolytes. Both the zinc phosphate and the zinc manganese phosphate extracts are inhibiting the corrosion of steel plates. After 24 h, when compared to the electrolytes not containing any metal phosphate, the ones containing manganese phosphate extracts did show only a very limited effect on protecting steel against corrosion. On the other hand, electrolytes containing zinc phosphate or zinc-manganese phosphate did still show a protective effect and this effect was more pronounced in acidic electrolytes. This can be explained because of the higher solubility of the phosphates in acidic solutions as was already discussed by Bethencourt et al. [5]. The concentration of the protective phosphate species in the dispersion is thus expected to be higher. Finally, the dispersion containing zinc manganese phosphate was providing the best corrosion protection effect at pH 6.3 whereas in the acidic range the best protective behaviour was obtained with the zinc phosphate flake dispersion.

#### **3.3** Electrochemical investigations

Electrochemical impedance spectroscopy measurements were also performed on steel plates immersed in the electrolytes dispersions containing zinc phosphate and those containing zinc-manganese phosphate to evaluate the resistance of the metal plates after 18 h immersion. The resistance values given below were all obtained through fitting of the impedance spectra over a maximal range of frequencies. When compared to the steel plate resistance in the solutions not containing metal phosphate, it is possible to calculate the inhibition power of each of the dispersions (% IP) according to the following equation:

$$\% IP = \frac{R - R'}{R'}$$

Where R is the resistance in the tested electrolyte and  $R^0$  is the resistance in the electrolyte not containing metal phosphate. The calculated resistance and inhibition power values after 18h of immersion in the different electrolytes are shown in table 1.

As expected from the visual observation made before, both the metal plates immersed zinc phosphate and the zinc-manganese phosphate containing electrolytes present an increased total resistance over the metal plate immersed in the electrolytes not containing extracts. The protective effect of the metal phosphates is more easily seen after calculation of their corrosion inhibiting power.

	w/o metal phosphate	+ ZP R/Ω (%IP)	+ ZMP R/Ω (%IP)
pH 6.3	2405	3730 (55)	3420 (42)
рН 3.8	2820	5070 (80)	4310 (53)
рН 2.7	1970	4610 (134)	4730 (140)

Table 1: Resistance  $(R, \Omega)$  of steel plates immersed in solutions containing metal phosphate dispersions and inhibition power (% IP) of the different metal phosphates.

As observed before, the lower the pH, the higher the inhibiting power of the metal phosphate dispersions as a higher concentration of metal phosphate is expected to be dissolved in the electrolytes. At pH 6.3 and 3.8 and after 18 h of immersion, the inhibition power of the zinc phosphate dispersion is higher than the one of the zincmanganese phosphate. Surprisingly these data do not correspond to observation made after 24 h of immersion (Figure 4) where less signs of corrosion were observed on the steel plate immersed in the ZMP containing electrolytes. Different reactions seem to take place to protect the steel from corrosion and they seem to have different kinetics. The zinc-manganese phosphate protective effect seems to show slower kinetics and thus takes longer to be fully reacted. At pH 2.7, as expected the protection ability of the two dispersions (ZP or ZMP containing electrolytes) is further improved and both extracts present a similar inhibition power after 18 h immersion.

In addition polarization of the metal plates was performed to examine their behaviour when their potential is shifted to anodic or cathodic values. The polarization curves obtained are presented in Figure 5 and Figure 6.



Figure 5: Polarization curves of steel plates immersed for 18 h in electrolytes (pH 3.8) containing no particles, 1% zinc phosphate (+ZP), 1% zinc-manganese phosphate (+ZMP), or 1% manganese phosphate (+MP). At pH 3.8, when compared to the electrolyte free of phosphates, all the metal phosphate containing electrolytes present an ennoblement of the steel plate corrosion potential is observed. In the case of the steel plate immersed in the electrolyte containing zinc phosphate a displacement of the anodic branch of the polarization curve is also observed, it corresponds to an anodic inhibition related to the presence of zinc or phosphate ions. Surprisingly this phenomenon is not observed for the steel plate in the electrolyte containing zinc-manganese phosphate.



Figure 6: Polarization curves of steel plates immersed for 18 h in electrolytes (pH 2.7) containing no particles, 1% zinc phosphate (+ZP), 1% zinc-manganese phosphate (+ZMP), or 1% manganese phosphate (+MP).

At pH 2.7, the corrosion protection effect on the steel in each of the metal phosphate containing electrolytes is observed by a large lowering of the corrosion current and for all cases a displacement more or less pronounced of the anodic branch. This displacement is the most pronounced for the steel immersed in the zinc phosphate containing electrolyte highlighting again the protective effect of the zinc and phosphate ions that, in an acidic electrolyte, are expected to be at a higher concentration in solution.

Additionally the different particles were dispersed in an epoxy based Nanomer<sup>®</sup> matrix and applied on mild steel by spray coating and subsequent thermal curing. The dry film thickness achieved was  $25 \,\mu\text{m} \pm 5 \,\mu\text{m}$ . After introduction of an artificial scribe the samples were placed in the neutral salt spray test in order to get a first impression on the macroscopic corrosion behaviour. The results after 300 h exposure are shown in figure 7. Subsurface migration and pitting corrosion are clearly visible on the unfilled Nanomer<sup>®</sup> matrix. The addition of 2 wt.-% ZP flakes in the same matrix leads to a reduced subsurface migration near the artificial scribe. The same tendency is observed for the coatings containing 2 wt.-% MP where it seems that the situation is even improved compared to ZP. Nevertheless the artificial scribe releases red rust and it is obvious that further investigation would be needed to reach optimised conditions. It will be of special interest to perform a mechanistic study on how the different phosphate flakes act in protecting the steel at the micro scale.



Figure 7: Nanomer<sup>®</sup> coatings on mild steel (ST1203) containing no phosphate (w/o ZP), 2 wt.-% zinc phosphate (ZP), or 2 wt.-% manganese phosphate (MP) after 300 h neutral salt spray test.

#### 4 CONCLUSIONS

Zinc phosphate and zinc-manganese phosphate pigments of anisotropic shape showed to have a corrosion inhibiting effect on mild steel plates when the plates were directly immersed in an electrolyte containing a dispersion of 1% of the metal phosphate flakes. Furthermore, this effect is linked to the acidity of the corrosive media. This is expected to be related to the concentration of ions zinc, manganese and phosphate dissolved in the electrolyte since at lower pH, the phosphate particles are more prone to dissolve. The nature of the metal phosphate is not the only parameter that as an effect on the particles ability to protect from corrosion. Here we showed that the flake-type shape of the synthesized particles plays an important role in addition. Particles shaped as flakes present a high surface to volume ratio rending them more active against corrosion. Careful control of their dispersion in a polymer based Nanomer matrix led to an improved protective barrier effect. A mechanistic and microscpic study on the protective effect exhibited directly at the coating / steel interface will be the aim of future investigations.

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