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Performance of Primers Containing Polyphosphate-Based Ion-Exchange Pigments for the Protection of Galvanised Steel

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Summary: The environment protection is pressing the replacement of chromate based pre-treatments and anti-corrosive pigments with environmental compatible coating systems, in particular in the coil industry, and many studies are being connected to this field.

A relatively new class of inhibitive pigments is the ion-exchange pigments. Commercial available ion exchange pigment based on calcium-exchanged silica gel are applied in wide range of coatings technology. The inhibition mechanism is related to the ion-exchange reaction and the deposition of a protective layer, but the mechanism is not yet completely known.

The aim of the present study is an electrochemical evaluation of corrosion protection performance of environmental friendly coating systems, whose primer is consisting of polyphosphate and ion-exchanger based anticorrosive pigments.

The results proved that the use of electrochemical techniques like electrochemical impedance spectroscopy is important in order to characterize and understand the corrosion protection mechanism and efficiency of organic coatings containing active pigments, as ion exchange pigments. Moreover it was shown that in the coatings the pigments have a significant inhibitive effect and they act as cathodic inhibitors.

Keywords: inhibitive pigments, organic coatings, electrochemical impedance spectroscopy, polyphosphate

Introduction

Nowadays the environment protection and the decrease of pollution are key subjects in different fields of research and development. The replacement of chromate based pre-treatments and anti-corrosive pigments with environmental compatible coating systems is also very important in the coil industry and many studies are being connected to this field [1]. The longest established low

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toxicity anti-corrosive pigments are zinc phosphate, $Zn_3(PO_4)_2.2H_2O$ (in Europe) and barium metaborate (in the USA).

A relatively new class of inhibitive pigments are the ion-exchange pigments [2,3,4]. They are inorganic oxides with comparatively high surface area loaded with ionic corrosion inhibitors by ion-exchange with surface hydroxyl groups. The ion-exchangers are chosen for their acid and basic properties to provide cation- or anion exchangers, thus usually silica is used as a cation and alumina for anion support. The corrosion protection behaviour of pigments is controlled by the rate of ion-release process of exchanger [5,6,7]. The ion-exchange release mechanism allows efficient use of a comparatively low loading of inhibitive pigments.

The other advantage of this approach is to allow the use of otherwise highly soluble inhibitors. With the knowledge of kinetics of ion-release process within the primer it is possible to control the accessibility of inhibitors, and therefore to control its diffusion onto the metal surface.

Commercially available ion exchange pigment is Shieldex® [3] based on calcium-exchanged silica gel applied in the coatings technology. The inhibition mechanism is related to the ion-exchange reaction. Upon exposure of paint films to the aggressive environment, due to water uptake, exchange of calcium to hydrogen ions and release of calcium ions are taking place. Dissolution of polysilicate anions is also supposed [8,9]. The diffusion and deposition of both dissolved species onto the metal surface result in a formation of protective layer. Deposition of these species within pores of the coating is also presumed to improve its barrier function.

Polyphosphates form the base of third generation anticorrosive pigments. Polyphosphates are cathodic inhibitors, and protect most metals by precipitation mechanism; i.e., they form almost insoluble complexes with calcium, magnesium ions. The most important polyphosphates are tripolyphosphate and hexametaphosphate. Polyphosphates has low toxicity but they are alga nutrients. Due to their hydrolysis in acidic and alkaline conditions, they can easily transform to orthophosphates.

The aim of the present study was an electrochemical evaluation of corrosion protection performance of environmental friendly coating systems, whose primer was consisting of polyphosphate and ion-exchanger based anticorrosive pigments. The corrosion protection properties and mechanism of primers have been studied by electrochemical impedance spectroscopy.

Experimental

The studied materials were steel sheets with hot dipped zinc alloy coating (Zn + 1.5 ± 0.5 % Al) with thickness of 11 µm followed with fluotitanate pretreatment.

Sheets of galvanized steel were covered by coil coating technology with a 5 µm thick polyester primers cured with isocyanate containing inhibitive pigments (PVC 30 wt%) of:

CAPP – Calcium-Aluminium-polyphosphosilicahydrate: samples PC

ZAPP – Zinc-Aluminium-polyphosphatehydrate; samples PZ

The results of elemental analysis of inhibitive pigments are reported in Table 1.

Table 1. Elemental analysis of the main components of the inhibitive pigments

CAPP	31% CaO 28% SiO_2 26% P_2O_5 7% Al_2O_3	ZAPP	48% P_2O_5 30% ZnO 12% Al_2O_3

The shape and the dimension of the pigments is very different as it is possible to see in figure 1: smaller in size and more regular for ZAPP (average dimension 2 µm), bigger and less regular for CAPP (dimensions 5-15 µm).

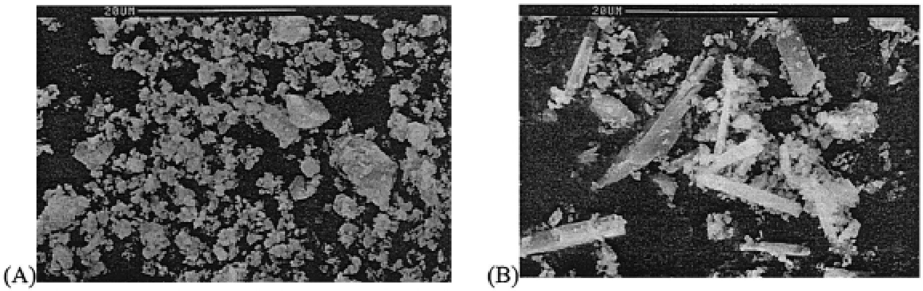


Figure 1. Morphology of pigments ZAPP (A) and CAPP (B).

Polarisation curves were performed using a PAR 273 potentiostat at 0.5 mV/s of scan rate and the impedance measurements were performed using PAR 273 potentiostat and Solartron 1255 frequency response analyzer in the frequency range of 100 kHz – 1 mHz with a sine amplitude of 10 mV. The electrochemical cell was a three-electrode cell with an Ag/AgCl reference electrode

[+207 mV vs. SHE] and platinum counter electrode. All of the experiments were performed in 0.3 % Na_2SO_4 solution at room temperature. The studied surface area was 25 cm^2.

The morphology of the deposits was observed by Scanning Electron Microscopy and the chemical composition was evaluated by EDXS Analysis. In order to improve the chemical information, the zinc surface after exposure in the solution containing the pigments was analyzed by FTIR measurements (Nicolet DXL in reflectance).

Results and discussion

In order to characterize the effect of inhibitive pigments on anticorrosion performance of coatings, initially we studied galvanized steel samples covered with only primer without topcoat. In this case, the degradation process of coatings takes place in a relatively short time. By the use of electrochemical impedance spectroscopy technique, the complex electrochemical behaviour of coating system can be studied, e.g., the dielectric properties of coating, the corrosion properties of underlying substrate.

The impedance spectra of primer-coated substrate in 0.3 % Na_2SO_4 solution can be characterized mainly by three time constants. It means that in the Nyquist plot three different semicircles are visible. The high frequency one is related to the properties of the coating because the values of the impedance are independent on the applied potential and from the capacitance value just after immersion it is possible to calculate a value of the dielectric constant which is close to the theoretical one for the polymer matrix. The intermediate frequency loop is related to the electrochemical reaction on the metal surface because it is potential dependent and the value of the time constant is almost the same of the time constant of bare zinc corroding in the same solution. The cathodic reaction is the oxygen reduction and therefore it is possible to consider the low frequency tail caused by the diffusion process of oxygen molecule, which is the slowest, rate-determining process of corrosion. The proposed circuit, according with literature [10] is shown in figure 2. The high frequency elements describing the coating properties are the non-ideal coating capacitance (Q_{coat}), which is mathematically described by constant phase element (CPE) and the coating resistance (R_{por}) that is the ionic resistance through the coatings (through defects or pores and through the intact coating). The lower frequency part of impedance spectra is related to the corrosion process taking place on the metal surface: Q_{dl} is a non ideal capacitance of double layer and R_{ct} charge transfer resistance is related to the faradic reaction. Further, the lowest frequencies of impedance spectra is determined by the diffusion which can be modeled, for finite diffusion path, as a resistance in parallel with a constant phase element (R_{diff} and Q_{diff}) [11].

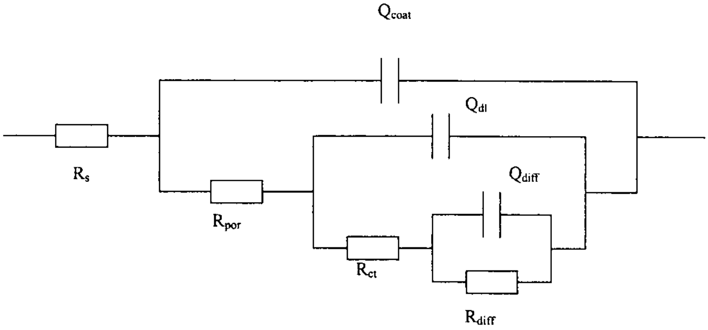


Figure 2. Equivalent electrical circuit for impedance spectra of primer coated metals.

Although the impedance spectra of corroding system is more complex, and likewise the complete electrochemical behaviour of the system contains more processes (for example zinc dissolution can involve two steps [12]), inclusion of further elements to the model is not required partly because these elements can be determine only with high relative error and for this reason its values are hardly uncertain, partly because neglecting these element from the model, the values of others elements are not significantly modified.

Figure 3 shows the change of evaluated parameters in time for the studied materials.

The coating capacitance (Q_{coat}) is increasing in time in both cases (PC and PZ), and the coating resistance (R_{por}) which is influenced by the presence of defects and conductivity through the pores, is decreasing in time. These changes refer to the pore formation and deterioration of primer due to the interaction with corrosive electrolyte. The general trend is the same, but clear differences are evident comparing the two kind of samples: the coating capacitance growth is higher in the case of PC samples. In this case the increase of Q_{coat} cannot be simply related to water uptake caused by diffusion of water molecules in the polymeric matrix, but there is also an important contribution due to the interaction of the electrolyte with the pigments which are soluble and can cause a further water uptake [13], even because the water can occupy the space becoming free by the pigment dissolution. It means that the coating capacitance change are due to two different phenomena: the water diffusion in the coating changing the average dielectric constant of the coating and the pigment solubilisation interacting with the polymeric matrix of the coating.

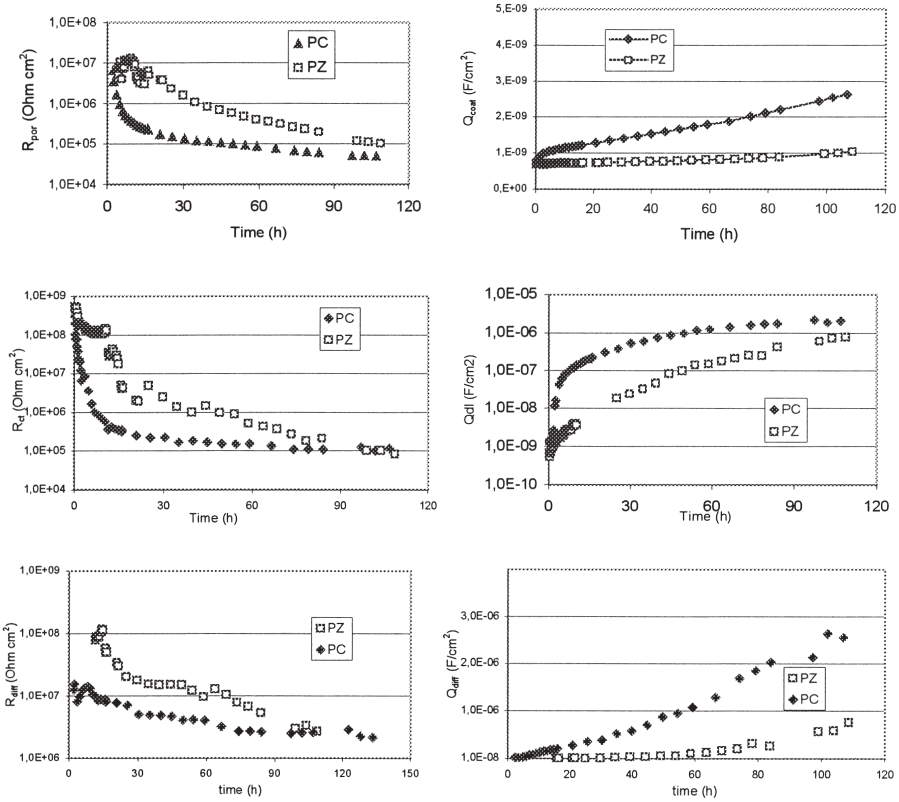


Figure 3. Coating resistance (R_{por}), coating capacitance (Q_{coat}), charge transfer resistance (R_{ct}), non-ideal double layer capacitance (Q_{dl}), diffusion resistance (R_{diff}) and diffusion capacitance (Q_{diff}) vs. the immersion time of polyester based primers pigmented with CAPP (PC) and ZAPP (PZ).

Also the coating resistance R_{por} is decreasing faster in the case of samples containing CAPP (PC), probably because the solubilisation of the pigments favours the ions penetration, but after about 120 hours the values become very similar. In accordance, the corrosion rate is increasing, which appears in the decrease of both charge transfer resistance (R_{ct}) of metal dissolution and diffusion resistance (R_{diff}). Also in this case, after an initial period in which the samples containing CAPP show a higher reactivity, after 5 days of immersion the values of R_{ct} and Q_{dl} are very similar. The only parameter which is becoming more and more different with the immersion time is the value of Q_{diff}. It is important to remember that we suppose that the species controlled by diffusion is oxygen. But with impedance we are measuring only the impedance of charged species and therefore R_{diff} is not the resistance to diffusion of oxygen, but the resistance to diffusion of ions. If the diffusion control is due to the presence of corrosion products it is well known that corrosion products can block the oxygen diffusion more that the ions diffusion. For this reason is more useful to look to the values of Q_{diff}, which are related to the presence of corrosion products inducing a capacitative contribution to the impedance. The values of Q_{diff} indicate that the diffusion processes are reduced in the case of the PC samples. This difference is probably due to the presence of more corrosion products under the coating in the case of PC primer acting as a partial oxygen barrier. This phenomenon is not so evident for the sample PZ because of the lower corrosion rate.

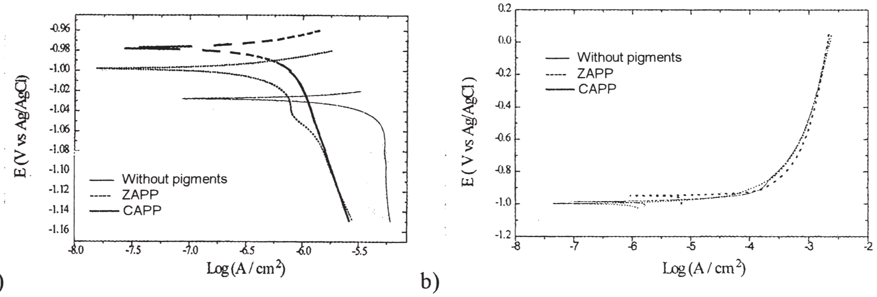
The deterioration process of primer is faster in the case of PC, which is pigmented with polyphosphate, calcium, silicon and aluminium (CAPP). The reason probably can be traced back to the difference in stability constants and solubility of Ca-polyphosphate and Zn-polyphosphate. The lower solubility of Zn-polyphosphates is well-kown in the literature [14]. This property can cause a lower dissolution rate of the pigments and also a higher tendency to re-precipitation on the metal surface.

In order to verify the accuracy of the proposed equivalent circuit model, and to get deeper knowledge on the anticorrosive mechanism of pigments, the polarization effect was studied after 2 weeks of immersion time. The primer-coated panels was polarized at first cathodically at –1100 mV vs. [Ag/AgCl], and then anodically at –800 mV.

During the cathodic polarization (which is lower of the free corrosion potential of the samples in the testing solution which is about –1000 mV) the low frequency resistance (R_{diff}) is decreasing, while the opposite occurs during the anodic polarization, which indicates, that the corrosion is controlled by the cathodic half-reaction (oxygen depolarization). On the contrary the values of R_{ct} do not change so much with the polarisation potential and the values remain lower than R_{diff} which therefore controls the total reaction.

After the cathodic polarization, the open circuit potential shifted to anodic direction in both cases (PZ and PC). Due to the polyphosphate, zinc and calcium ions are cathodic inhibitors; the enhanced adsorption should have contributed to the shift towards the cathodic direction. Thus the reason for anodic shift of corrosion potential and increase of polarization resistance seems to be the hydrolysis of polyphosphate to orthophosphate, which is anodic inhibitor and have good passivation effect. The hydrolysis of polyphosphate is probably activated by the increase of local pH near the metal/polymer interface due to the enhanced OH^- formation during oxygen depolarization reaction.

In order to have a confirmation of the cathodic inhibition effect of the studied pigments, some polarization curves in the same solution (0.3% of Na_2SO_4) saturated with the pigments were performed on bare zinc samples. The cathodic (figure 4a) and anodic (figure 4b) behavior is a clear indication of the cathodic inhibition, while ZAPP and CAPP pigments seems to have very similar electrochemical effect.



a) b)

Figure 4. Cathodic (a) and anodic (b) behaviour of zinc in 0.3% Na_2SO_4 solution saturated with ZAPP and CAPP pigments.

Different is, on the contrary, the appearance of the zinc surface after the cathodic polarization: only on the sample immerse in the ZAPP solution it was possible to note a chemical conversion layer deposited on the surface (figure 5), looking like flat small crystal, while in the case of sample immersed in the CAPP solution it was impossible to note any difference in comparison with the zinc surface before immersion.

Also the EDXS measurements confirmed in the case of samples immersed in containing ZAPP solution the presence of P and Al (and a higher presence of oxygen) on the zinc surface while the sample immersed in the CAPP solution showed EDXS spectra equivalent to the spectra of new zinc surfaces.

In order to obtain more information on the chemical nature of the deposit in the ZAPP solution, a FTIR analysis was carried out and the results are in figure 6. The presence of peaks characteristic of phosphorous-organic compounds bonds (between 1000 and 1400 cm^{-1})are visible together with peaks which it is possible to relate to carbon-hydrogen bonds.

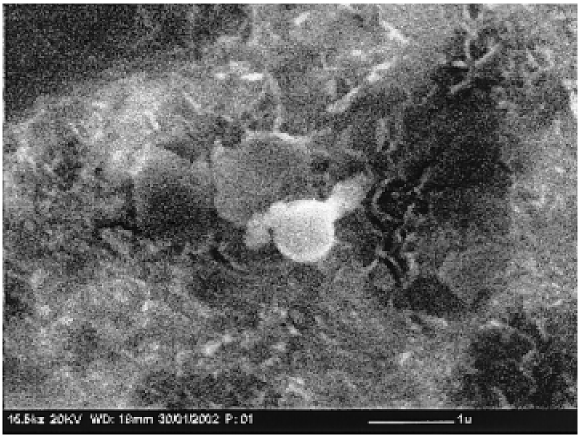


Figure 5. Zinc surface morphology after cathodic polarisation in containing ZAPP solution.

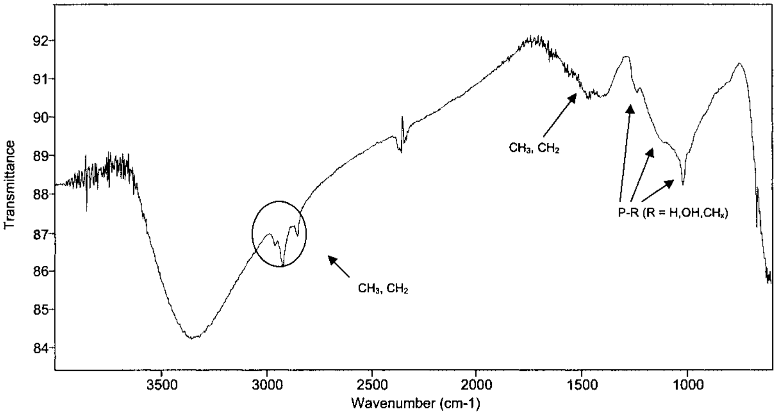


Figure 6. FTIR spectrum of Zn surface after cathodic polarization in the containing ZAPP solution.

From this characterization we can conclude that the ZAPP pigment is able to protect acting as a cathodic inhibitor by the deposition of a layer on zinc in alkaline conditions. The higher solubility of the CAPP pigments cause a faster primer degradation, moreover the deposition of a protective layer for this pigments is not proved, even if a cathodic inhibition activity was measured.

Conclusions

The use of electrochemical techniques, like electrochemical impedance spectroscopy, is useful in order to characterize and understand the corrosion protection mechanism and efficiency of organic coatings containing active pigments as ion exchange pigments.

For the studied materials it is possible to summarize the main results in the following points: In the primers the pigments have a significant inhibitive effect and they act as cathodic inhibitors. The pigment action results in a layer deposition on the metal surface reducing the corrosion rate. The higher solubility of CAPP causes a faster degradation of the corrosion protection properties of the primers containing this pigment in comparison with the primers containing the pigment ZAPP. Moreover the formation of a protective layer on the metal surface of the CAPP pigments was not proved.

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