

UDC 620.197, 621.181:669.018

Peculiarities of corrosion inhibition by mixture of phosphate and calcium containing pigments

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Several possible alternatives to toxic chromate pigments have been considered for a variety of inhibitive applications. One of the more promising pigment combinations involves mixtures of phosphate and calcium ion-exchange pigments for inhibition of corrosion on organic coated galvanized steel. This paper presents recent work on a detailed study of the mechanisms of action of this mixture which has been established as effective in cut edge and zinc inhibition, but as less effective for inhibition of steel. The use of the blend of inhibitors is shown to result in the development of an adsorbed phosphate film on the metal which plays an important role in the development of anodic and cathodic inhibitive control. Zinc ions also appear to have an important synergistic effect on the film composition and structure increasing its coherence and decreasing its porosity. Traditional and localised electrochemical methods (EIS and SVET) were used in this study of corrosion of coated galvanized steel in artificial acid rain solution. The data confirms the anticorrosion efficiency of the pigment blend dispersed in organic coating on galvanized steel and reveals the peculiarities of their inhibiting action at coating defects.

Key words: Corrosion inhibition, pigments, organic primer, galvanized steel, DC polarization.

PACS numbers: 81.65. kn

1 Introduction

Organic coatings on metal are not totally impenetrable barriers for corrosion environments. During exposure in the environment they lose protective properties as a consequence of the formation of local defects. Inhibiting anticorrosion pigments are usually incorporated into the first layer (the primer) of the organic coating to protect the metal where there is environmental penetration to the metal surface.

The most effective anticorrosion pigments, which promote passivation of steel at coating defects, are chromates. They are mixed inhibitors and protect metal from corrosion in pH range from 4 to 9. They can also function as cathodic inhibitors at low (about 10 ppm) concentrations. Chromates protect metal very well in the slightly acid industrial atmospheres. However, the urgent necessity exists to change the toxic chromate pigments for other ones, which will be less dangerous for the environment.

Non toxic phosphate pigments may be the most probable substitutes for chromates. Phosphates used as pigments typically are highly insoluble and their extracts in corrosion solutions protect steel less

effectively than chromate. However, they have been shown to provide very good inhibiting properties when distributed in a primer coating. Probably the protective action of the pigments in the organic coating is accelerated by increased acidity of environment or by ion exchange with the polymer binder. Calcium ion exchange silica pigment is also recommended for use in organic primers as a replacement of chromate. It inhibits the cathodic reaction and probably may have synergetic effect in combination with other pigments. The objectives of this work were to study the inhibition of galvanized steel corrosion by phosphate and ion-exchanged pigments which might be used in coil-coated cladding instead of chromates.

2 Experimental methods

The studied epoxy coatings were based upon a two-pack clear epoxy composition produced by H.Marcel Guest Ltd (Manchester, UK). The basis of the epoxy composition was an epoxy-diane resin and a polyamide hardener. The epoxy coatings were applied onto acetone degreased galvanized steel in two layers, an inhibitor containing primer (30 µm)

and top-coat (100 μm), using a draw-bar technique. The size of galvanized steel samples was 8x15 cm; the thickness of the zinc coating was about 15 μm . Four different primer formulations were used, namely E7 with TiO_2 , E8 with zinc phosphate/molybdate (Actirox 106) /calcium ion exchange silica (Shieldex CP4) blend (3/3 v%), E16 with zinc phosphate / molybdate / calcium ion exchange silica blend (7/11 v%), E17 with strontium chromate (1.5 v%). The pigments were separately introduced into the epoxy varnish by mixing during 24 hours in ceramic ball mill. The coatings were cured for 24 hours at 20°C and post-cured in an oven for 6 hours at 60°C.

The corrosion behavior of coated galvanized steel was investigated using electrochemical impedance spectroscopy (EIS). The measurements were carried out in artificial acid rain solution [1-3], using a three-electrode electrochemical cell with a sample testing area of 3.14 cm^2 and with a platinum auxiliary electrode as a counter and saturated calomel as reference electrode. The impedance measurements were carried out close to the corrosion potential using an EG&G Potentiostat/Galvanostat Model 263A and a Solartron Frequency Response Analyser 1250 in the 10 kHz to 5 mHz frequency range. The signal amplitude was 30 mV. Measurements were carried out using the software Zplot2 and impedance spectra were interpreted with Zview2. Artificial defects were introduced by making a 1-cm long and 100- μm width scratch on the epoxy composition coated sample with a sharp scalpel.

Corrosion potential and potentiostatic polarization measurements of bare steel and zinc electrodes with a testing area of 4.8 cm^2 were carried out in artificial acid rain solution with and without inhibiting pigments, using EG&G Potentiostat / Galvanostat Model 263A, a saturated calomel reference electrode and a platinum counter electrode.

The pigment extracts were prepared by agitation of 1 g of pigments in 1 L acid rain solution, such that solid material remained after 24 hours, then twice filtering.

A scanning vibrating electrode (Uniscan Instruments SKP100E system in scanning vibrating probe mode) was used to study localized corrosion on galvanized steel with artificially damaged epoxy coatings in artificial rain solution. These experiments were carried out using a 500 μm diameter micro disc electrode. This microelectrode is vibrated in a plane perpendicular to the sample

surface, at an amplitude of 30 μm . and the potential is measured at the upper and lower limits of the amplitude via an electrometer and lock-in-amplifier. The mean distance from the micro tip electrode to sample surface was 100 μm . All experiments were carried out at the free corrosion potential, i.e. no external potential was applied. In this case, the coatings had two layers: firstly a pigmented epoxy primer and secondly a top coat of unpigmented epoxy. The total dry film thickness of the coatings was about 130 μm (30 μm primer: 100 μm top coat) with a sample area of 30 cm^2 . The scanning area (1.4 cm^2) included a drilled defect of 1.5 mm in diameter and intact coating close to it.

3 Results and discussion

It was established, using EIS, that the combination of the environmentally friendly phosphate and calcium containing pigments has a synergetic protective effect in preventing corrosion of galvanized steel [4-7]. Thus, the initial charge transfer resistance is about 10 times higher for galvanized steel in an extract of the pigment mixture in acid rain compared to single solution extracts of the chromate-free pigments. A similar effective inhibition of corrosion at the cut edge was also observed in the pigment mixture [8-11]. Inhibition effectiveness of the pigment blend approaches that of the strontium chromate pigment, widely used' in coil-coated architectural cladding. But a basic reason why the inhibitive pigment blend is more effective on zinc surfaces than on mild steel still is not clear. This investigation was started with the aim to more fully understand the mechanism of corrosion inhibition compared with Chromate in the situations described.

The time dependencies of the open circuit potential for steel and zinc exposed in inhibited acid rain solution appear to show an anodic control of the corrosion. Thus, the corrosion potential of zinc moves into the range -0.74...-0.75 V (SCE), compared with -0.92...-0.95 V (SCE) in the uninhibited solution. The potential of mild steel is also more positive compared with uninhibited acid rain, reaching after 10000 sec a value of -0.26 V. However, the zinc potential remains at -0.75 V while the steel potential decreases after 10000 sec of exposure, approaching the corrosion potential values recorded for steel in uninhibited solution. This shows us that the pigment blend extract does not offer long period protection of mild steel.

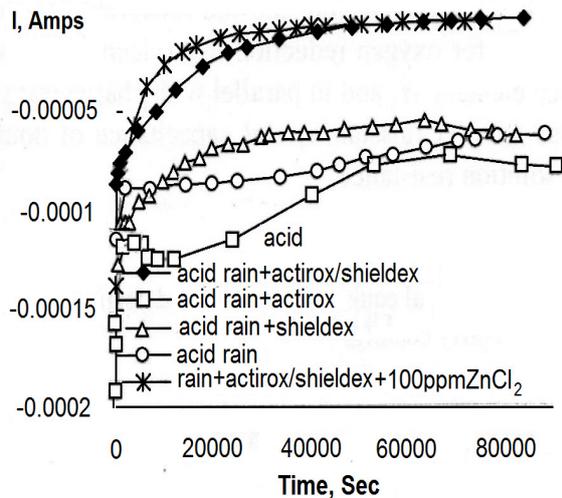


Figure 1 – Time dependencies of current on mild steel samples at cathodic polarization potential of -0.9 V vs SCE

As the sample is galvanized steel, a galvanic couple between zinc and steel will play an important role especially at cut edges. Two reactions are expected here: first, the anodic dissolution of zinc (release of zinc ions) and second, oxygen reduction (generating OH^- ions). The slowing down of both reactions is important from the point of corrosion inhibition. Firstly, the cathodic polarization current for steel exposed to acid rain solution with and without pigments was recorded (fig. 1). It was established that, during cathodic polarization at -0.9V in pigment blend solution, the current decreases rapidly and after 75000 sec approaches to $5.0 \mu\text{A}\cdot\text{cm}^2$ (Fig.1). On contrast, cathodic currents on steel in both single pigment extract and uninhibited corrosion solution are about 10 to 15 times higher. Neither calcium exchange silica nor modified zinc phosphate suppress cathodic activity as effectively as the pigment blend. This shows that a highly protective surface film on cathodic areas of galvanized steel (possibly on uncovered mild steel) was formed in the pigment blend solution. A conclusion can thus be made that the combination of phosphate and calcium containing pigments behaves as a very strong cathodic inhibitor. Further investigation has also shown suppression of the anodic reaction on zinc in the pigment blend solution as well (fig.2). Anodic polarization revealed, that for mild steel anodic inhibition does not persist long because, after about 9000 sec, the anodic current rises rapidly and reaches the level recorded for steel in uninhibited solution. A

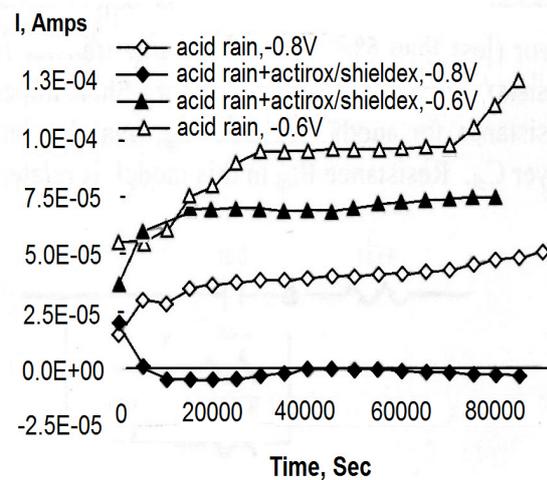


Figure 2 – Time dependencies of current on zinc samples at different anodic polarization potentials

suggestion can be made that the availability zinc ions in solution due to corrosion of galvanized steel could be an important factor in the inhibition by the pigment blend. Probably, there is not sufficient concentration of zinc ions in the case of mild steel corrosion in acid rain solution containing just zinc phosphate and calcium ion exchange silica pigments. Because of single phosphate pigment (Actirox 106) is not so effective for cathodic inhibition as pigment blend (fig. 1). most probably calcium ions, phosphate and zinc ions need to be present in the solution to provide an anticorrosion synergetic effect. It was established (fig. 1) that addition of 100 ppm of zinc chloride to corrosion solution saturated by phosphate and calcium ion exchange silica mixture also is effective at inhibiting the cathodic reaction.

EIS has been used in this work to estimate the anticorrosion effectiveness of chromate-free pigmented epoxy coating with scratched defects on galvanized steel. Measurements of electrochemical impedance have been carried out at open circuit potential after immersion for different times in acid rain solution at 20°C . Because of the high resistivity of the acid rain solution, experimental impedance spectra usually consist of two semicircles. The capacitive loop at high frequencies can be related to geometric electrode effect in solution. However, the second part of the spectra has depressed semicircle and gives information about corrosion processes underneath the organic coating near the defect area. The electrical equivalent circuit (fig.3) was used to

model corrosion behavior of the defective epoxy coatings. The fitting procedure showed relatively very low error (less than 5%). Here the charge transfer resistance for oxygen reduction R_{cat} , (electron transfer resistance) is in series with Warburg-Short impedance element W_s and in parallel with charge transfer resistance for anodic reaction R_{an} (mainly zinc ions transfer resistance) and capacitance of double layer C_{dl} . Resistance R_{sol} in this model is related to solution resistance.

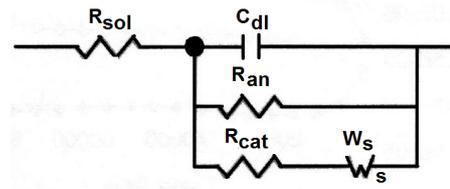


Figure 3 –Electrical equivalent circuit for defective epoxy coatings

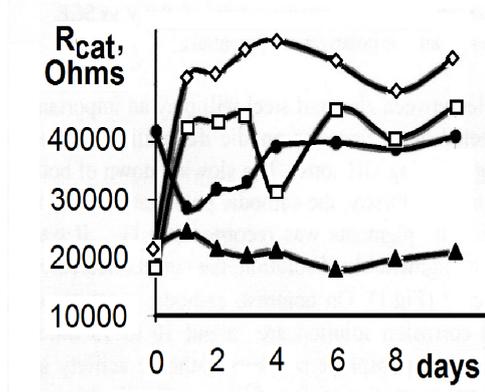


Figure 4 – Time dependencies of charge transfer resistance for cathodic reaction on galvanized steel with damaged epoxy coatings in acid rain solution

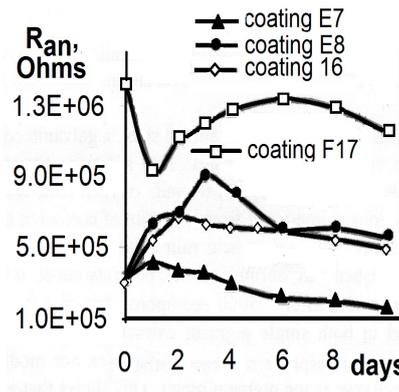


Figure 5 – Time dependencies of charge transfer resistance for anodic reaction on galvanized steel with damaged epoxy coatings in acid rain solution

An addition of both chromate and blend pigments to the epoxy primer increases the charge transfer resistance of the cathodic reaction (Fig.4). The R_{cat} for uninhibited coatings stays in the range of 18000...24000 Ohms during exposure in acid rain solution but it rises for pigmented samples. The resistance for the epoxy coating E16 is even higher (rises to the level of 55000 Ohms) than for chromate containing one which does not exceed 45000 Ohms. The coating E16 contains an increased concentration of the pigment combination and thus may provide more calcium and phosphate ions into cathodic area. These ions then can interact with each other and with zinc ions derived from corrosion dissolution of the zinc coating forming a adherent protective film. This film is presumed to have good barrier properties and to limit diffusion of reactive species to the metallic surface. Thus, the R_{cat} for the pigment blend containing coatings is at least the same or even higher (E16) than strontium chromate containing coatings.

Dissolution of zinc is slowed down by the presence of inhibiting pigment in the organic primer as well. However, it seems that the combination of chromate-free pigments is less effective in anodic

reaction inhibition compared to strontium chromate (Fig.5). The charge transfer resistance R_{an} for coatings E16 and E8 do not exceeds the range of $6 \cdot 10^5$... $1 \cdot 10^6$ Ohms and for chromate containing coatings E17 it was found in the range of $1.2 \cdot 10^6$... $1.4 \cdot 10^6$ Ohms. The double layer capacitance C_{dl} rises rapidly for the control coating sample which confirms increasing corrosion activity in the area of the scratch and also about the increase of active corrosion area underneath the coating along the zinc/epoxy interface. Most likely, this can be related to an increase of cathodic delamination of the epoxy coating. Capacitance for the three pigmented coatings stays at a much lower level compare to non-pigmented one and does not exceeds $7.5 \cdot 10^{-8}$ F. Finally, it can be concluded that the pigment blend is more effective in inhibition of cathodic reaction and chromate pigment is more active in slowing down of anodic reaction on galvanized steel in the area of defect.

Recently the scanning vibration electrode technique (SVET) has been developed [12-14] with the aim of obtaining local current density maps over exposed metallic surface subject to localized

corrosion. The local measurements of currents can help to understand the origin of defects and the influence of inhibitors on the electrochemical activity of these defects.

The measured distributions of potentials around the holes are given as 2-dimensional maps for each coating formulation. Relatively light areas on the map represent local anodic sites, whereas the darker area corresponds to cathodic sites. The map for initial exposure of E7 shows intense corrosion activity at the hole defect with relatively negative (anodic) site along the hole perimeter and positive (cathodic) site in centre of the hole. Thus the SVET data shows clearly that the anodic reaction takes place on the zinc coating cut edge and the cathodic reaction on the bottom of the hole where the zinc coating is removed and the steel is directly exposed to the solution. The cathodic activity in the centre of the hole for the control coating E7 remains quite high during the whole period of exposure. However, in the case of both chromate-free and chromate pigmented coatings, their cathodic activity decreases in the centre of the defect (Fig.6). There are a few possible explanations of this fact. Firstly, the cathodic activity on pigmented samples can spread more widely under the coating due to decrease of total ionic resistance because of paint film contains sparingly soluble inorganic pigments. The SVET technique is less sensitive to current equally distributed around a bigger area of sample. However this will give a significant move of the total basic line level into the cathodic direction for these samples with time, which was not found. Secondly, and most probably OH^- ions, generated in the process of oxygen reduction at the cathode, are strongly involved in other reactions causing deposition of an insoluble product and can not move into bulk solution anymore and create a positive potential gradient. The deposited film reduces oxygen reduction in the centre of scratch.

In order to make a quantitative assessment of corrosion activity, the total anodic and cathodic potentials measured at every data point were summed separately for each map. The results indicate that cathodic currents for chromate-free and chromate pigmented coatings are equivalent and after 70 hours approach zero. But, for the coating without inhibiting pigments the total cathodic current is much higher both at the beginning of exposure and at the end.

The summed anodic current also decreases during exposure for all coating compositions. After 70 hours the lowest anodic current was recorded for the sample with chromate containing coating and the highest for the TiO₂ sample. The pigment blend sample was intermediate but closer to the chromate.

4 Conclusions

1) The combination of zinc phosphate and calcium ion exchanged silica has a significant anti-corrosion effect for galvanized steel in acid rain solution compared to these pigments used separately.

2) It was established, by potentiostatic polarization, that use of the pigment blend leads to a suppression of cathodic activity on steel and anodic activity on zinc. This is probably by protective film development on both surfaces.

3) The SVET method has been applied to study the effectiveness of corrosion prevention in damaged pigmented epoxy coatings on galvanized steel. The technique was able to map and quantify discrete anodic and cathodic sites along the scribe, which were due to the inherent localised corrosion behaviour of zinc. By summing the anodic and cathodic potentials measured using SVET for each scan, a quantitative comparison was made between the chromate and chromate-free inhibitors.

4) The pigments blend is more effective in protection of galvanized steel (a zinc) than mild steel. Zinc ions, which are released due to corrosion processes, play an important role in the inhibitive synergism of the pigments. Their interaction with calcium, phosphate and silicate ions leads to the creation of an absorbed surface film with high barrier properties.

Acknowledgements

We acknowledge with a deep sense of gratitude, the encouragement and inspiration received from our colleagues, working on project 3110/6-F4 "Development of cost-effective technology for production of nanostructured composite coatings chromed-white carbon with improved anticorrosion properties" (IETP). We would also like to thank our friends from Corrosion and protection Centre and Karpenko Physico-Mechanical Institute for their long year scientific cooperation.

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