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Evaluating Novel Inhibitor Pigment Blends using Electrochemical Scanning Techniques (EIS, SVET and SKP)

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Abstract
One of the main applications coming to the fore for scanning vibrating electrode technique (SVET) and scanning Kelvin probe (SKP) systems is ability to look at inhibitor combinations, which could be used to replace chromates in coil-coated galvanized steels. The results are very promising using the SVET system and results with the SKP system also show results to be comparable with the SVET system. Electrochemical impedance spectroscopy (EIS) is also used to understand the mechanism of inhibition by mixture of pigments. The more promising pigment combination involves mixture of phosphates and calcium ion-exchange pigments for inhibition of corrosion on organic-coated galvanized steel. This paper presents 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. 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. The data confirm the anticorrosion efficiency of the pigment blend dispersed in organic coating on galvanized steel.

Keywords: inhibitors, EIS, SVET, SKP, pigments, chromates, molybdates, phosphates, calcium ion-exchange silica

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INTRODUCTION

Organic coatings play an important role in the protection of metallic constructions against corrosion. The efficiency of their protection depends on the following properties: The composition of the coating, character of the metal substrate, surface pretreatment and the application procedure [1–3]. Organic coating composition consists of four basic constituents: a binder, pigments, fillers, additives (plasticizers, curing agents and organic modifiers) and solvents or diluents.

Therefore, their properties depend strongly on the makeup of these constituents, the procedures and precautions taken during application and also curing of the final solid film. The corrosion protection provided by organic coatings is determined by the barrier action of the layer or the inhibition of corrosion reactions at the steel/coating interface. Ideally, a coating forms a physical barrier between metal substrate and the corrosive environment. In real conditions, however, all organic coatings are permeable to ions, water and oxygen [4, 5].

Active anticorrosion pigments (inhibiting or sacrificial) are often incorporated into the first polymer layer (the primer) to provide additional protection through an inhibitive or electrochemical mechanism when water and corrosive agents reach the metal surface.

The protective action of the polymer coating can take place simultaneously by the physicochemical or barrier, adhesion and electrochemical mechanisms. However, only one of the mechanisms may prevail at a certain stage. The multicomponent interactions between coating, steel and environment make

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under-paint corrosion a very complicated phenomenon. In general, under-paint corrosion starts at places where the paint is damaged. The corrosion proceeds with corrosion of metal or with paint delamination followed by corrosion of the substrate. The causes of organic coating delamination at the corrosion front, as reported by different investigators [6], can be physical, anodic, cathodic, mechanical, or a combination. A number of general models, proposed in the literature to describe the mechanism of propagation of under-paint (or underfilm) corrosion are discussed [7, 8]. The two basic models are anodic undermining and cathodic delamination, which give an insight into the most important causes of corrosion propagation. In practical applications, it is quite difficult to determine specific aspects of the coating, the substrate, the pretreatment and the environment, responsible for the actual degradation mechanism. The physico-chemical phenomena responsible are often highly interrelated.

Pigments

Pigments are essentially dry powders which are insoluble in the paint medium and which consequently need to be dispersed in it by a "grinding" technique. They range from naturally occurring minerals to man-made organic and inorganic compounds and may be subdivided broadly into priming pigments, color pigments, extenders and metal powders [9, 10]. Pigments may be added to a coating for two reasons [6, 10]. They provide color to the coating system, which is important for aesthetic purposes. Pigments may be used to improve the corrosion protection properties of a coating.

These pigments may dissolve slowly in the coating and may provide protection by covering corrosion-sensitive sites under the coating and sites of coating defects, by sacrificially corroding themselves, thus protecting the substrate metal, or by creating an absorbed inorganic film on the metal surface, or by passivating the surface.

Passivating pigments reconstruct and stabilize the oxide film on the exposed metal substrate. Commonly, chromates with limited water solubility are used as passivating pigments (zinc chromate, strontium chromate). In aqueous solutions, they may cause anodic passivation of a metal surface with a very stable chromium- and oxygen-containing passive layer [11].

Coil-Coated Galvanized Steel

Coil-coated, galvanized steel is widely used in the construction industry as a material for roof and wall cladding [12]. It typically comprises zinc or zinc/aluminum alloy-coated steel strip, which is further protected with an inhibitor-containing organic primer and an organic topcoat. Strontium chromate is often used as the corrosion inhibitor in the primer coating, though concern over the toxicity of hexavalent chromium has prompted research into possible alternatives.

Chromate Inhibitors

There is a generally held belief that chromate is an effective corrosion inhibitor for steel, zinc, aluminum, and many other metals [11–16]. In general, chromates are effective in aerated and deaerated solutions and in acid, neutral and alkaline environments. They are one of the most versatile inhibitors. Chromates are oxidizing inhibitors and assist in the development of a thin oxide coating on the surface of the metal, a major cation of which is the substrate metal. It can be observed as a so-called "passivation plateau" on an anodic polarization curve which was recorded on chromatized metallic samples, similarly as in case of stainless steel [11]. Under these conditions, the corrosion potential of the sample is moved to positive direction if compared with the control experiment without inhibitor. However, the same minimal level of inhibitor concentration in corrosion solution exists and the effect of metal passivation cannot be detected at lower levels of concentrations. Nevertheless, the inhibition action of chromates is observed very often even at lower concentrations in corrosion solution. At this situation, the chromates behave as cathodic-type inhibitors.

The conventional theory of operation of inhibitive chromate pigments in paint coatings is that water permeating through a primer leaches out soluble chromate ions from the pigment. These ions passivate the metal surface and consequently the surface is protected and the corrosion process is controlled. However, the solubility of most of the chromate pigments is very low and the

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three-dimensional network of a paint film reduces the effective solubility of pigments even more [17–19].

Thus, in summary chromate ions diffuse to the metal/polymer interface, together with penetration of the environment into the chromate primer. At local places of mechanical damage, the inhibition of corrosion takes place and the anodic reaction slows down. The effectiveness of chromate is overshadowed; however, by its toxicity, and pollution consideration frequently prevent the use of chromates as universal inhibitors [20, 21].

Phosphate Inhibitors
Phosphate pigments are used as a nontoxic alternative to chromate pigments. They have been shown to provide corrosion-inhibiting properties when incorporated into primer coats and paints for iron and steel [22–24]. Regarding the mechanism of inhibition of zinc phosphate-containing primer, it has been suggested that it slowly phosphates the metal surface thus rendering it passive. Reference [23] suggests that tribasic zinc phosphate may be converted into a more soluble form by reaction with atmospheric acids or by ion exchange with carboxyl groups present in the polymer. Highly insoluble pigments such as zinc phosphate rely on hydrolysis or reaction with acid contaminants to release the anticorrosive species. This process is essentially fortuitous and likely to be slow, although hydroxide from the cathodic corrosion reaction may aid hydrolysis [25]. Reference [26] concluded that the major limitation of zinc phosphate as an inhibitive pigment is its poor solubility. They found the solubility of zinc chromate and zinc phosphate pigments in 0.5 M NaCl solution increased on both sides of the neutral range and were far more pronounced in the acidic range.

Therefore, for zinc phosphate-containing primer on steel, it is expected that an iron phosphate layer is deposited onto the substrate at a coating defect exposed to a corrosive environment.

Molybdate Inhibitors
Molybdate inhibitors are classified as non-oxidizing, anodic inhibitors for iron and steel [27]. They are not used by themselves but are combined with phosphates and these have been used as inhibitive pigments and possible alternatives to strontium chromate.

Calcium Ion-Exchange Silica
Ion-exchange pigments were also developed as nontoxic alternatives to the chromate pigments [28, 29]. They consist of a silicate carrier or amorphous silica gel to which calcium ions are bound. They act by exchanging their calcium ions for hydrogen ions in the paint film. In this way, acidic chemical substances are neutralized. They can also bind to chloride, sodium and sulphate ions, which are passing from the corrosion environment to the metal surface across the paint film. The Ca/SiO_2 complex can interact with the paint film constituents also. The release of anticorrosion species (Ca^{2+} and SiO_2) follows the ion-exchange process. The calcium ions and polysilicate ions then precipitate onto the metal oxide surface creating a protective film. For conventional pigments, the corrosion rate is very low at the start of exposure but after a time, as the inhibitor is depleted and as the film becomes more porous, the corrosion rate rises markedly. For Ca/silica, measured corrosion rate is initially slightly higher and quickly falls off and continues at a low rate. This initial period can be considered as the "induction time" – the time taken for calcium to be released and for the protective layer to be formed. Once the layer is formed, corrosion essentially stops [30]. It was established that the modified silicate pigment is an effective inhibitor of iron corrosion in slightly acidic and neutral solutions. It appears to act through the formation of Ca^{2+} and polysilicate ions in the solution. The polysilicate anions adsorb on the iron surface and inhibit oxygen reduction, hydrogen evolution and iron dissolution [31]. The anticorrosive and adhesion-promoting properties of these pigments in coil coating applications on pretreated galvanized steel look very promising [29].

The objective of this work was to study the inhibition of galvanized steel corrosion by phosphate and ion-exchange pigments which can be used in coil-coated cladding instead of chromates.

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EXPERIMENTAL
Electrochemical Impedance Spectroscopy

The corrosion behavior of coated galvanized steel was investigated using electrochemical impedance spectroscopy (EIS). The measurements were carried out in artificial acid rain solution [32] using a three-electrode electrochemical cell with a sample testing area of 3.14 cm^2 and with a platinum electrode and a saturated calomel (SCE) as auxiliary and reference electrodes respectively. The impedance measurements were carried out close to the corrosion potential using an EG&G potentiostat Model 263A and a Solartron frequency response analyzer 1250 in the 10 kHz to 5 MHz frequency range. The signal amplitude was 30 mV. Measurements were carried out using Zplot2 software and impedance spectra were interpreted with Zview 2 [33]. Artificial defects were introduced by making a 1 cm long and 100 µm wide scratch on the epoxy composition-coated sample with a sharp scalpel blade.
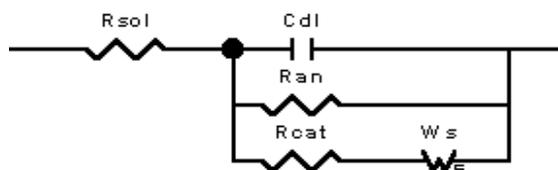

Fig. 1: *Electrical Equivalent Circuit That Was Used to Model Impedance Spectra of Galvanized Steel with Damaged Epoxy Coatings.*

The coating binder in these experiments was a two-pack clear epoxy composition produced by H. Marcel Guest Ltd., Manchester (U.K.). The coatings were applied onto acetone degreased galvanized steel in two layers using a drawbar; firstly, the inhibitor-containing primer (30 µm) dry film thickness and then secondly, the topcoat (100 µm). The size of the galvanized steel was 8×15 cm with a hot-dip zinc coating thickness of 15 µm. Four different systems were used – two containing zinc molybdate-phosphate and calcium-containing silica gel in blends of 3/3 vol.% (E8) and 7/11 vol.% (E7), one containing strontium chromate at 1.5 vol.% (E17) and a TiO$_2$ formulation at 6 vol.% (E7) were used as a control sample. The pigments were separately introduced into the

epoxy binder and mixed for 24 h at 20 ^{o}C and post cured in an oven for 6 h at 60 ^{o}C.

As can be seen from Figure 3, the lowest solution resistance has been found for epoxy coating pigmented with E7, which is not an inhibiting pigment but acts as a control sample. The solution resistance decreases steadily over time and stabilizes. Samples E8 initially starts at a value of 6800 Ω and E16 starts at a value of 6000 Ω but steadily decreases to the same value over time.
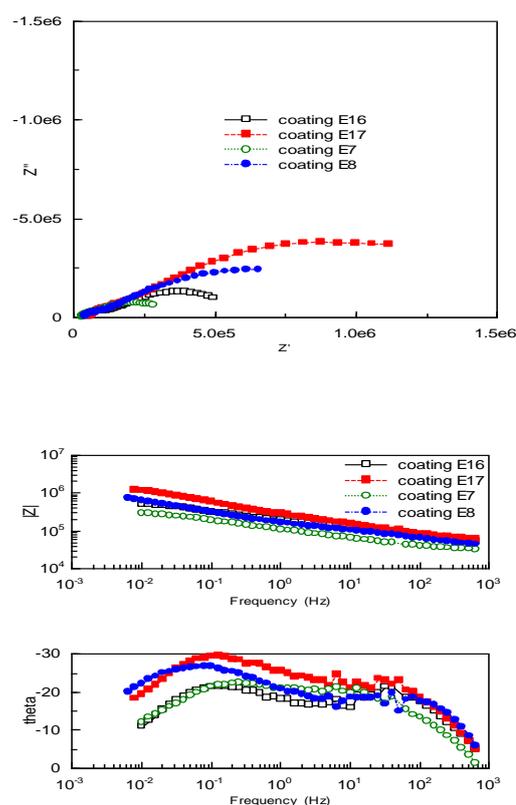

Fig. 2: *Impedance Spectra of Galvanized Steel with Artificially Damaged Epoxy Coatings after 3-Days Exposure in Artificial Acid Rainwater Solution.*

E17 (strontium chromate 1.5 vol.%) has the highest solution resistance and after 3 days, the solution resistance value lies between E8 and E16. All the samples were exposed to artificial acid rainwater solution and the solution resistance varied as concentration of ions varied. With more corrosion, more ions are produced which lowers the solution resistance but only in the small solution volume (20 mL) in this case.
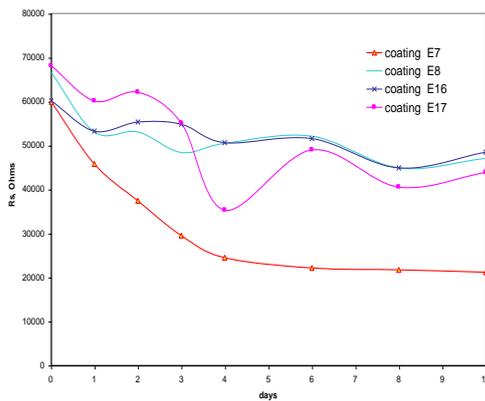
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***Fig. 3:** Time Dependencies of Solution Resistance for Galvanized Steel with Damaged Epoxy Coatings.*

Solution resistance dependencies correlate with the capacitance data (Figure 4). E7 (TiO$_2$ 6 vol.%) has the highest capacitance value, which rises sharply and continues to rise to a final value of 2×10^{-7} again; this is the control sample. Sample E8 starts at a lower value and then rises rapidly, thereafter steadying but always well below the values for the control. Sample E16 is similar to E8 and in turn they are same as for E17 (strontium chromate 1.5 vol.%). Capacitance for the three-pigmented coatings stays at a much lower level and does not exceed 7.5×10^{-8} F.
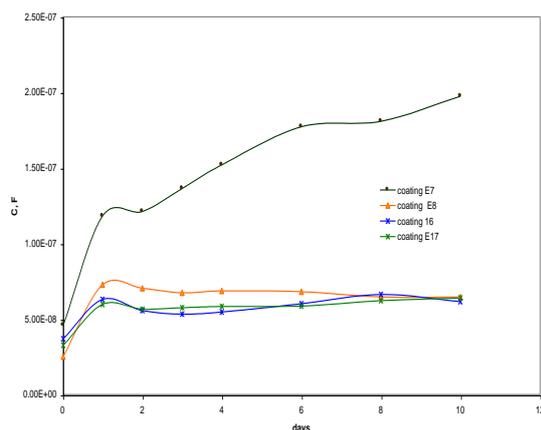

***Fig. 4:** Time Dependencies of Double-Layer Capacitance for Galvanized Steel with Damaged Epoxy Coatings in Artificial Acid Rainwater Solution.*

An addition of both chromate and novel inhibitor blend pigments to epoxy primer

increases the charge transfer resistance of the cathodic reaction (Figure 5). The R$_{cat}$ for uninhibited coatings E7 (TiO$_2$ 6 vol.%) stays in the range of 18000–24000 Ω during exposure in artificial acid rainwater solution but it rises for pigmented samples. The resistance for the epoxy coating E16 is even higher (rising to the level of 55000 Ω) than for chromate-containing E17 (strontium chromate 1.5 vol.%), which does not exceed 45000 Ω.
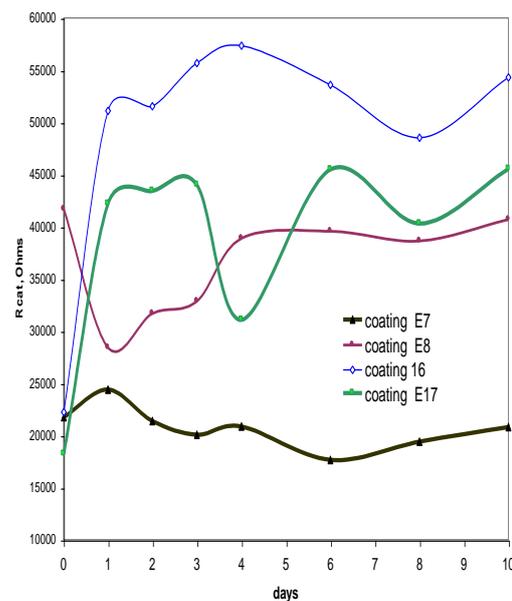

***Fig. 5:** Time Dependencies of Charge Transfer Resistance for Cathodic Reaction on Galvanized Steel with Damaged Epoxy Coatings in Artificial Acid Rainwater Solution.*

The charge transfer resistance R$_{an}$ for coatings E16 and E8 do not exceed the range of 6×10^5–1×10^6 Ω and for chromate-containing coatings E17 (strontium chromate 1.5 vol.%) it was found to be in the range of 1.2×10^6–1.4×10^6 Ω (Figure 6). Thus, it can be stated that E7 (TiO$_2$ 6 vol.%) is worst as compared to the other formulations and E16 is best on the cathodic process, while E7 (strontium chromate 1.5 vol.%) and E8 are similar in behavior. Therefore, E17 (strontium chromate 1.5 vol.%) is best as can be seen from charge transfer resistance for the anodic reaction. Samples E8 and E16 are similar and E7 (TiO$_2$ 6 vol.%) is the worst.
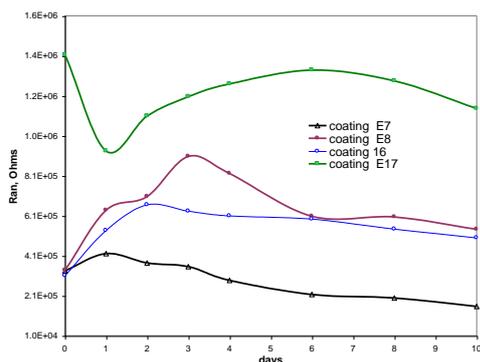
Fig. 6: *Time Dependencies of Charge Transfer Resistance for Anodic Reaction on Galvanized Steel with Damaged Epoxy Coatings in Acid Rain Solution.*

Scanning Vibrating Electrode Technique

A scanning vibrating electrode (Uniscan Instruments SKP100E system in scanning vibrating mode) was used to study localized corrosion on galvanized steel with artificially damaged epoxy coatings in artificial rain solution [34, 35]. These experiments were carried out using a 500 μm diameter microdisc electrode, vibrated in a plane perpendicular to the sample surface at amplitude via an electrometer and lock-in amplifier. The mean distance between the microtip electrode and the sample surface was 100 um. All experiments were carried out at the free corrosion potential. In this case, the coatings had two layers: firstly a pigmented epoxy primer and secondly a topcoat of unpigmented epoxy. The total dry film thickness was about 130 μm (30 μm primer; 100 μm topcoat) with a sample area of 30 cm. The scanning area (1.4 cm^2) included a drilled defect of 1.5 mm in diameter and intact coating close to it.

Scanning Kelvin Probe Technique

The Uniscan Instruments SKP100E system was used in scanning Kelvin probe mode. The scanning Kelvin probe (SKP) is a noncontact, non-destructive instrument designed to measure the surface work function difference between conducting, coated, or semi-conducting materials and a metallic probe [36]. The technique operates using a vibrating capacitance probe, and through a swept backing potential, the work function difference is measured between the scanning probe reference tip and sample surface. The work function can be directly correlated to the surface condition. A unique aspect of the SKP is its ability to make measurements in a humid or gaseous environment. The samples used were as prepared for the SVET system. These experiments were carried out using a 500 μm diameter microdisc electrode made of tungsten wire, vibrated in a plane perpendicular to the sample surface at amplitude via an electrometer and lock-in amplifier. The mean distance between the microtip electrode and the sample surface was 50 μm. All experiments were carried out at the free corrosion potential.

RESULTS AND DISCUSSION

Electrochemical impedance spectroscopy (EIS) has been used in this work to estimate the anticorrosion effectiveness of the 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 [32], experimental impedance spectra usually consist of two semicircles. The capacitive loop at the 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 (Figure 1) 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 Ws 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.

An addition of both chromate and blend pigments to the epoxy primer increases the charge transfer resistance of the cathodic reaction (Figure 5). The R_{cat} for uninhibited coatings stay in the range of 18000–24000 Ω during the exposure in acid rain solution but it rises for the pigmented samples.

The resistance for the epoxy coating E16 is even higher (rises to the level of 55000 Ω) than for chromate-containing one, which does not exceed 45000 Ω. The coating E16 contains an increased concentration of the pigment combination and thus may provide more calcium and phosphate ions into the cathodic area. These ions then can interact with each other and with zinc ions derived from corrosion dissolution of the zinc coating forming an 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 (Figure 6). The charge transfer resistance R_{an} for coatings E16 and E8 does not exceed the range of $6*10^5$–$1*10^6$ Ω and for chromate-containing coatings E17 it was found in the range of $1.2*10^6$–$1.4*10^6$ Ω. 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 as compared to non-pigmented one and does not exceed 7.5e–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 the defect.

The scanning vibrating electrode technique (SVET) has been developed [34, 35] 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.
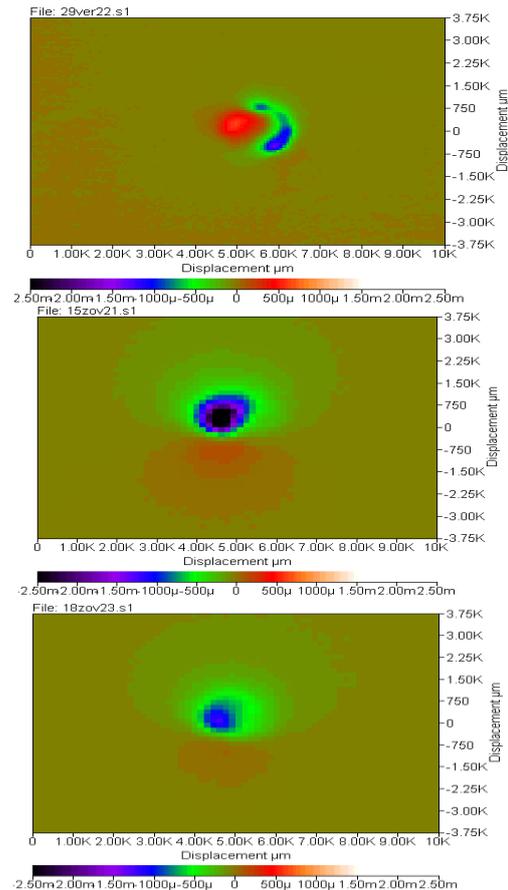

Fig. 7: *SVET Maps of Local Solution Potentials for Galvanized Steel with Coating E7 (a), E16 (b) and E17(c) after 60 h Exposure in Acid Rain Solution.*

The measured distributions of potentials around the holes are given as 2-dimensional maps for each coating formulation. Relatively light areas on the maps represent local anodic sites, whereas the darker areas correspond 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 the center of the hole (Figure 7(a)). 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 center 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 center of the defect (Figure 7(c)). There are

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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 the 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 significant move of the total base 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 cannot move into bulk solution anymore and create a positive potential gradient. The deposited film reduces oxygen reduction in the center of scratch.

In order to make a quantitative assessment of corrosion activity, the total anodic (Figure 8) and cathodic potentials (Figure 9) measured at every point were summed separately for each map. The results indicate that the cathodic currents for chromate-free and chromate-pigmented coatings are equivalent and after 70 h 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.
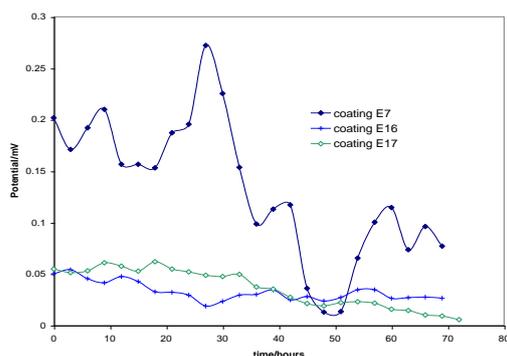

Fig. 8: The Total Cathodic Activity on Galvanized Steel Samples with Damaged Epoxy Coating (Hole Defect) in Artificial Acid Rain Solution.

The summed anodic current also decreases during exposure for all coating compositions. After 70 h, the lowest anodic current was recorded for the sample with chromate-containing coating and the highest for the TiO_2

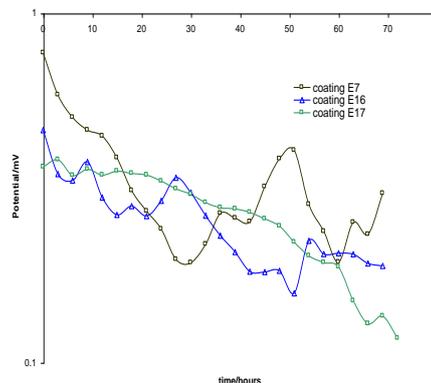sample. The pigment sample was intermediate but closer to the chromate.

Fig. 9: The Total Anodic Activity on Galvanized Steel Samples with Damaged Epoxy Coating (Hole Defect) in Acid Rain Solution.

The SKP data (Figure 10 (a)) show a 2D area map of the hole defect. The SKP data (Figure 10 (b), (c)) show comparison of results for the different inhibitors in comparison to a control sample. E coating (epoxy) and E7 (TiO_2 6 vol.%) have more positive potentials in the center of the defect. Here, the corrosion activity is developing and no significant inhibition occurs except some inhibition due to zinc ions deposited onto the cathodic surface and formation of zinc hydroxide. E16 has more negative potentials than clear epoxy and E7. This shows that there is some cathodic control of the corrosion reaction within the defect area for the E16 case. This control can be caused by deposition of protective film of calcium and zinc phosphates. Corrosion is also developing faster for coatings without inhibiting pigments. E16 has more negative potentials away from the defect as well. E17 has relatively (if compared with the potentials for E17 away from the hole) low potentials inside of hole (potential peak). Absolute values of potential for E17 are more positive than for E16.

It is known that chromate passivates steel, zinc and galvanized steel and moves their corrosion potential toward positive values. So, corrosion of galvanized steel under coatings E17 (especially hole area) is under anodic control. It can also be observed that barrier properties

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of chromate-containing coatings are less strong than those for E16 case.

Higher solubility of strontium chromate can also influence the barrier properties of E17 and corrosion potential outside of the hole. The instrument is able to detect the changes in potential due to the inhibition action of the added components. E17 (strontium chromate 1.5 vol.%) has a great effect on the delamination rate as it acts like anodic inhibitor making the potential more positive, therefore, decreasing the full width of the lines (delamination). E16 and E18 have some effect but E17 (strontium chromate 1.5 vol.%) is superior.
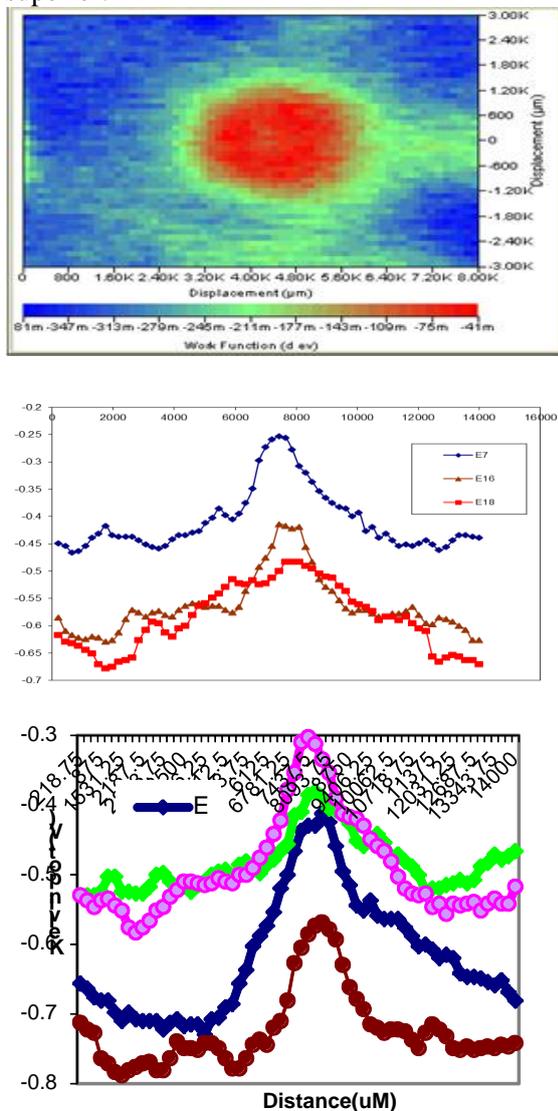

Fig. 10: *(a) 2D Area Map for Hole Defect (b), (c) SKP Line Scan Data for Hole Defect (0.5 mm Diameter) after 432 h Exposure E (Clear Epoxy), E7 (TiO$_2$), E16, E17 (Strontium Chromate 1.5%) and E18.*

CONCLUSIONS

The combinations of zinc phosphate and calcium ion-exchanged silica have a significant anticorrosion effect for galvanized steel in acid rain solution as compared to these pigments used separately. The pigment blend is more effective in protection of galvanized steel than mild steel. Zinc ions, which are released due to corrosion processes, play an important role in the inhibitive synergism of pigments. Their interaction with calcium, phosphate and silicate ions leads to the creation of an absorbed surface film with high barrier properties.

The SVET has been successfully applied to measure the activity of artificial defects (drilled hole) through the organic layer into the substrate. Previous work carried out used a platinum wire probe [34, 35]; in the current study, a microdisc electrode is used and has been shown to give better resolution and stability of results [37]. Quantitatively summing the anodic and cathodic values for different samples, it was shown that phosphate/calcium-containing pigments were viable and comparable to chromates in suppressing the electrochemical activity. EIS analysis confirmed at the defect site the pigment blend is more effective as a cathodic inhibitor and that chromate is a better anodic inhibitor.

The results for the SKP have been obtained using a tungsten wire probe, which has been shown to be less height dependent and to give better resolution [37]. Previously, probes used different designs and different metals [36]. The SKP was able to measure the increase in delamination of an industrial coating. The decrease in delamination was clearly detected by the system, with the added pigment combinations.

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