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INHIBITION OF CORROSION BY A MIXTURE OF NONCHROMATE PIGMENTS IN ORGANIC COATINGS ON GALVANIZED STEEL

V. I. Pokhmurs'kyi, I. M. Zin', and S. B. Lyon

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We consider several possible substitutes for toxic chromate pigments. Among the most promising compositions for the corrosion inhibition of galvanized steel with a protective organic coating, we should mention a mixture of phosphate- and calcium-containing pigments. As was shown earlier, such a mixture possesses a high efficiency under conditions of the corrosion of zinc and galvanized steel sheet; however, it is less efficient for the protection of carbon steels. This pigment mixture forms an adsorbed phosphate film on the metal and hinders the course of anodic and cathodic reactions. Zinc ions play an important role for obtaining a synergistic protective effect, increasing the coherence and decreasing the porosity of the deposited film. Traditional and local electrochemical methods (EIS and SVE) were used for studying the corrosion of galvanized steel with coatings in acid rain solution. The data obtained corroborated the high anticorrosive efficiency of a pigment mixture in an organic coating on galvanized steel. In addition, we established some specific features of its inhibiting action near defects in the coating.

Organic coatings on a metal do not form a completely impenetrable barrier for corrosive media. In the course of operation in a corrosive medium, they lose protective properties due to the formation of local defects. It is customary to introduce inhibiting anticorrosive pigments into the first ground coat of an organic coating in order to protect the metal surface at the moment of penetration of the corrosive medium into it.

Chromates are the most efficient anticorrosive pigments, which favor the passivation of steel substrate at the sites of through defects of the coatings [1]. Chromates represent inhibitors of mixed type, which protect the metal against corrosion in a wide range of pH values (from 4 to 9) [2] and can also function as cathodic inhibitors in the case of low concentrations (less than 10 mg/liter). They protect metals well in a subacid industrial atmosphere. However, there is an urgent need to replace toxic chromate pigments by other, less harmful agents for the environment.

Nontoxic phosphate pigments can serve as an alternative for chromates. Phosphate compounds used as anticorrosive pigments are poorly soluble, although their extracts protect steel weaker than chromates. However, when these pigments are dispersed in the mass of an organic binder, they possess satisfactory protective properties [3, 4]. They protect better in subacid media owing to ion exchange with binder molecules. Calcium-containing pigment based on silicon oxide is also recommended for application in anticorrosive prime coats as a substitute for chromates [5]. It inhibits predominantly the cathodic reaction, and its protective properties can improve as a result of combination with other inhibiting compounds.

In the present work, we study the corrosion inhibition of galvanized steel by phosphate and calcium-containing pigments with the purpose of their use on combined metal-polymeric coatings instead of chromates.

Experimental Methods

Preparation of the Specimens of Epoxy Coatings. We manufactured epoxy coatings on the basis of a two-component epoxy composition of the firm H. Marcel Guest Ltd. (Manchester, UK), which contained epoxy-

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Karpenko Physicomechanical Institute, Ukrainian Academy of Sciences, Lviv; Center of Corrosion and Rust Protection of the Manchester University, Manchester M60 1QD, Great Britain. Translated from Fizyko-Khimichna Mekhanika Materialiv, Vol. 40, No. 3, pp. 74 – 80, May – June, 2004. Original article submitted May 12, 2004.

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dianic resin and polyamide curing agent. We applied the organic coatings onto the surface of galvanized steel, degreased with acetone, in two layers [inhibited prime coat (30 μm) and upper layer (100 μm)] using a special applicator. Artificial defects in them of length 1 cm and width 100 μm were made with a scalpel. The size of steel specimens was 8×15 cm, and the thickness of zinc coating was about 15 μm. We used four different compositions of prime coats: A – filled with inert titanium dioxide, B_1 – with modified zinc phosphate (Actirox 106) (3 vol. %) and calcium-containing pigment (Shieldex CP4) (3 vol. %), B_2 – with modified zinc phosphate (7 vol. %) and calcium-containing pigment (11 vol. %), and C – with strontium chromate (2 vol. %). We introduced these pigments into the epoxy composition, grinding it on a ceramic ball mill for 24 h. Finally, the coating was structured for 24 h at 20°C and subjected to additional heat treatment for 6 h at 60°C.

Electrochemical Impedance Spectroscopy. We studied the corrosion of galvanized steel with epoxy coatings by the method of electrochemical impedance spectroscopy (EIS) on a Solartron Frequency Response Analyser 1250 instrument joined with an EG&G Potentiostat/Galvanostat Model 263A under corrosion potential in the frequency range from 5 mHz to 10 kHz. The signal amplitude was 30 mV. Measurements were carried out in artificial subacid rain solution [6]. We used a three-electrode electrochemical cell with an area of the working surface of the specimen of 3.14 cm^2 as well as a platinum auxiliary electrode and a saturated calomel electrode. We controlled the operation of these instruments using the Zplot2 code and processed the impedance spectra by the Zview2 code.

Direct-Current Electrochemical Investigations. Electrochemical investigations of unprotected low-carbon steel and zinc were carried out in subacid rain solution with pigment extracts on an EG&G Model 263A potentiostat. The area of working surface of the specimens was 4.8 cm^2. We prepared the pigment extracts by mixing 1 g of each pigment in 1 liter of corrosive solution for 24 h, whereupon the insoluble fraction was filtered out.

Scanning Vibrating Electrode. This instrument (SKP100E Uniscan Instruments) was used for studying the local corrosion of galvanized steel with artificially damaged epoxy coatings in rain solution. In these experiments, a microdisk electrode 500 μm in diameter was used (Fig. 1). The microelectrode vibrates perpendicularly to the surface of the specimen with an amplitude about 30 μm. Using an electrometer and a synchronous amplifier, we measured the potential difference between the upper and lower positions of the electrode. The average distance from the microelectrode apex to the surface of the specimen was 100 μm. The specimens were not polarized. The total area of the specimen was 30 cm^2, and the scanning area together with a drilled hole of diameter 1.5 mm in the epoxy and zinc coatings was 1.4 cm^2.

Results and Discussion

We have established earlier with the help of EIS that a combination of ecologically safe phosphate and calcium-containing pigments on galvanized steel leads to the synergism of their protective actions [7, 8]. The charge-transfer resistance of galvanized steel in the extract of mixture of both pigments is almost 10 times as high as that in their single extracts. Such a pigment mixture also inhibits edge corrosion efficiently [9]. The inhibiting efficiency of a mixture of nonchromate pigments approaches the efficiency of chromates, which are widely used in combined metal-polymeric coatings for the protection of metal constructions in the atmosphere. However, the principal cause of higher efficiency of this mixture of nonchromate pigments on a zinc surface as compared with a steel surface has not yet been explained. It is necessary to study the mechanism of the corrosion inhibition of zinc and steel by a mixture of inhibiting pigments in comparison with chromates more completely.

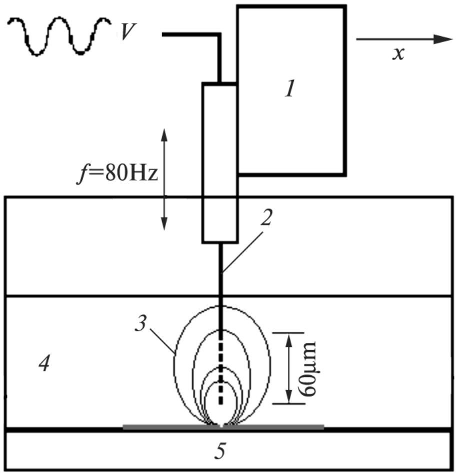


Fig. 1. Schematic diagram of the scanning vibrating electrode: (1) vibrating mechanism, (2) microelectrode, (3) equipotential lines, (4) corrosive solution, (5) specimen with a coating.

Effect of Inhibiting Pigments on the Corrosion Potentials of Steel and Zinc. The time dependences of the corrosion potentials of steel and zinc in the extract of mixture of nonchromate pigments in acid rain solution demonstrate that corrosion is mainly subjected to anodic control. In particular, the corrosion potential of zinc in an inhibited solution is shifted to the range -0.74 to -0.75 V as compared with -0.92 to -0.95 in an uninhibited solution. The potential of low-carbon steel in an inhibited corrosive solution is also more positive than in the reference solution and reaches -0.26 V after 10 ksec. However, the potential of zinc remains stable at the level -0.75 V, but that of steel decreases and approaches its value in an uninhibited solution. Thus, the extract of mixture of nonchromate pigments does not protect carbon steel for long.

Polarization of Steel and Zinc in Pigment Extracts. In view of the fact that the organic layer is applied on galvanized steel in combined coatings, one should expect that the formation of a local galvanic couple between zinc and steel will be an important factor of corrosion failure, especially at crosscut ends and at the sites of through defects. Here, two reactions can take place: the anodic dissolution of zinc (the passage of Zn^{2+} ions into the solution) and oxygen reduction (the generation of OH^- ions). As a result of the retardation of both reactions, corrosion is inhibited. It has been established that, in the course of cathodic polarization under a potential of -0.9 V in the extract of a pigment mixture, the current decreases rapidly and, after 75 ksec, approaches $5.0\ \mu A \cdot cm^2$ (Fig. 2). At the same time, the cathodic currents on steel in the single extracts of phosphate and calcium-containing pigments and in an uninhibited solution are approximately 10–15 times as high. Neither the extract of an ion-exchange-type pigment nor the extract of modified zinc phosphate decreases the cathodic current as efficiently as their mixture. Thus, only in the solution of mixture of nonchromate pigments on the cathode zones of the surface of galvanized steel (probably, on steel substrate that is not covered with zinc), does a protective film with enhanced protective characteristics form. We may conclude that a mixture of phosphate and calcium-containing pigments is a very efficient cathodic inhibitor. Further investigations also established the retardation of the anodic reaction on zinc in the extract of mixture of these pigments (Fig. 3). Anodic polarization showed that the inhibition of the anodic reaction on steel by a pigment mixture is not protracted, and, after 9 ksec of holding in an inhibited medium, the anodic current begins to grow sharply and reaches the level characteristic of steel in an uninhibited solution. We may assume that, as a result of the dissolution of galvanized steel, zinc ions in the solution determine corrosion inhibition by a mixture of nonchromate pigments. For low-carbon steel

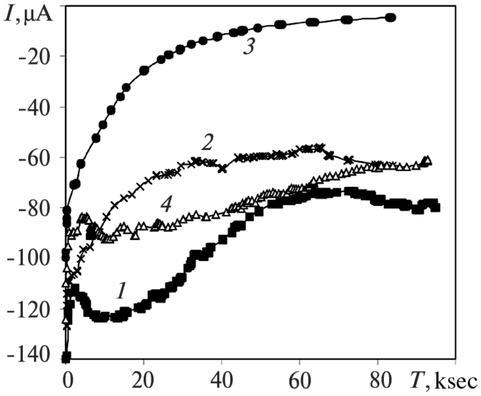


Fig. 2. Current of the cathodic polarization of low-carbon steel under a potential of -0.9 V vs. holding time in pigment extracts: (1) zinc phosphate, (2) calcium-containing pigment, (3) zinc phosphate + calcium-containing pigment, (4) uninhibited solution.

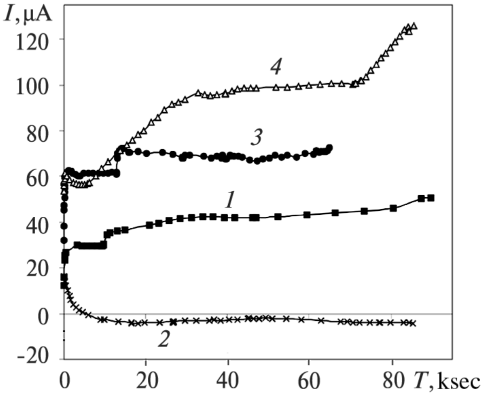


Fig. 3. Current of the anodic polarization of zinc under a potential of -0.8 V (1, 2) and -0.6 V (3, 4) vs. holding time in the extract of zinc phosphate and calcium-containing pigment (2, 3) and in an uninhibited solution (1, 4).

in the extract of a pigment mixture, the concentration of zinc ions is probably insufficient. Since phosphate pigment alone is a not as efficient a cathodic inhibitor as its mixture with calcium-containing pigment (Fig. 2), it is most probable that calcium, phosphate, and zinc ions have to be present in the solution simultaneously in order that the effect of synergism may manifest itself. We have established that, after addition of 100 mg/liter of zinc chloride to a corrosive solution saturated with phosphate and calcium ions, the inhibition of the cathodic reaction also becomes stronger.

Impedance Investigations of Galvanized Steel with Inhibited Epoxy Coatings. We used EIS in order to evaluate the anticorrosive efficiency of an epoxy coating with nonchromate pigments, applied on galvanized steel, in the presence of through defects in the coating. We measured the electrochemical impedance under corrosion potential after different exposures in acid rain solution at 20°C. Its fairly high resistance leads to the appearance of two semicircles in the impedance spectra. For high frequencies, the first of them can be attributed to the pseudocapacitive influence related to the geometry of the electrochemical cell. However, the second (deformed) semicircle gives information on the corrosion of the metal near a through defect in the coating. Calculations with the use of the circuit shown in Fig. 4 give a small relative error (less than 5%). This equivalent elec-

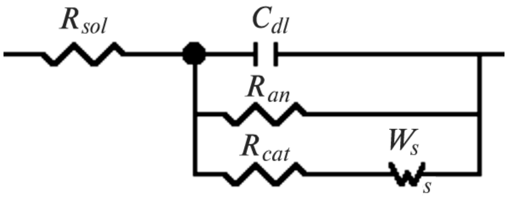
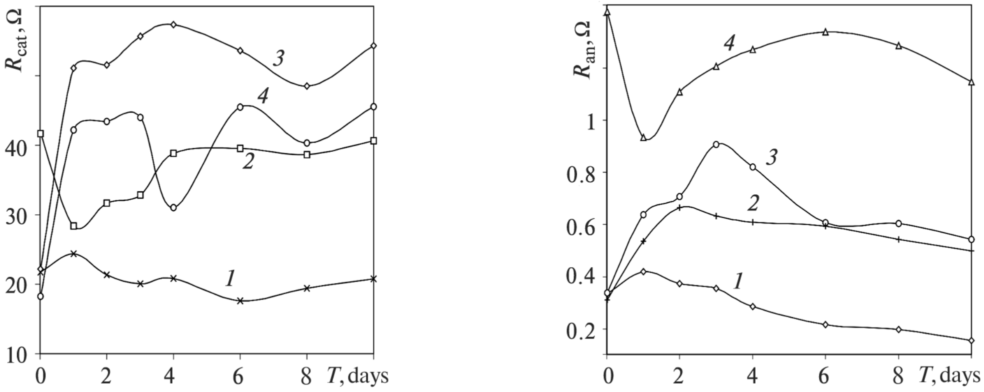


Fig. 4. Equivalent electric circuit for epoxy coatings with a defect.



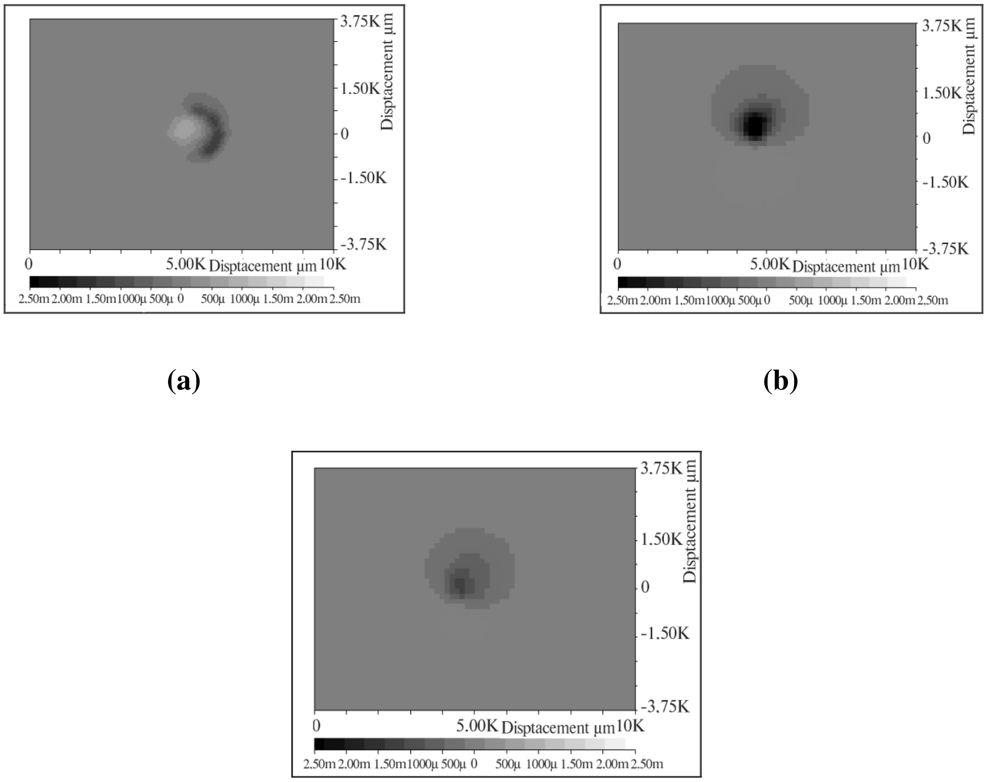
(a) **(b)**

Fig. 5. Time dependences of the charge-transfer resistance of the cathodic (a) and anodic (b) reactions on galvanized steel with an epoxy coating in acid rain solution: (1) uninhibited coating A, (2) coating B_1, (3) coating B_2, (4) coating C.

tric circuit contains the charge-transfer resistance of the cathodic reaction R_{cat} (electron-transfer resistance) connected in series with the Warburg impedance W_s and in parallel with the charge-transfer resistance of the anodic reaction R_{an} (mainly resistance to transfer of zinc ions) and the capacitance of the double charge layer C_{dl}. In this model, R_{sol} is the resistance of the solution.

After addition of both chromate pigment and a mixture of nonchromate pigments to an epoxy prime coat, the charge-transfer resistance of the cathodic reaction grows (Fig. 5a): R_{cat} for an uninhibited coating lies within the range $18-24$ kΩ during the entire time of holding in rain solution but increases significantly for pigmented specimens. This resistance for the epoxy coating B_2 is even greater (reaches 55 kΩ) than for a chromate-containing coating (does not exceed 45 kΩ). The coating B_2 contains more pigment mixture and, hence, increases the quantity of phosphate and calcium ions in the solution near the cathode. These ions can interact between themselves and with Zn^{2+} ions, appearing due to the corrosion dissolution of zinc coatings, and form a protective film with high adhesion to the metal. We may suppose that this film will possess good barrier properties and will retard the diffusion of reactive compounds to the metal surface. This assumption can be corroborated by the values of resistance R_{cat}, which, in the coating with a pigment mixture (B_2), are the same or even higher than in chromate-containing coatings.

In the presence of inhibiting pigments in an epoxy prime coat, zinc dissolution is retarded. However, a mixture of nonchromate pigments inhibits here the anodic reaction less efficiently than strontium chromate (Fig. 5b). The charge-transfer resistance R_{an} for the coatings B_1 and B_2 does not exceed $0.6-1$ MΩ, but it is $1.2-1.4$ MΩ for the chromate-containing coating C. For the reference specimen of coating, the capacitance of the double layer C_{dl} grows rapidly, which is evidence of the enhancement of corrosivity near defects and also of



(a) **(b)**

(c)

Fig. 6. SVE maps of potentials in the solution near the surface of the specimens of galvanized steel with the coatings A (a), B_2 (b), and C (c) after 60 h of holding in rain solution. Local anode zones are lighter, and cathode zones are darker.

the increase in the spread area of underfilm corrosion. Most probably, this can be attributed to the cathodic exfoliation of the epoxy coating. The capacitance of the double layer for pigmented coatings B_1, B_2, and C is significantly lower than that for an uninhibited one and does not exceed 75 mF. Thus, a mixture of nonchromate pigments inhibits the cathodic reaction more efficiently, and chromate pigment retards more strongly the anodic reaction on galvanized steel near defects.

Investigation of Local Corrosion on Galvanized Steel with Epoxy Coatings by the Method of Scanning Electrode. A scanning vibrating electrode (SVE) [10] can be used for obtaining maps of the distribution of currents or potentials in the medium near the surface of corroding metal. This novel method is promising for studying the local corrosion of a metal and the influence of various inhibitors on corrosion as well as for comprehending the specific features of underfilm corrosion near through defects in a polymeric coating [11, 12].

At the beginning of holding, we observe significant corrosion near the defect in specimen A: the anodic reaction is concentrated along the perimeter of the hole, and the cathodic at its center (Fig. 6). Thus, the anodic reaction takes place at the edge of the zinc coating, and the cathodic proceeds on the bottom of the defect, where the zinc coating and corrosive solution contact with steel. The cathodic activity at the center of the defect for the reference coating A remains fairly high during the entire holding time. However, for the coatings inhibited by chromate (C) and nonchromate pigments (B_1 and B_2), this activity at the center decreases gradually (Fig. 6). This feature can be explained in different ways. First, the cathodic reaction on inhibited specimens can spread more under the coating owing to a decrease in its overall ionic resistance in the presence of poorly soluble inorganic pigments. The SVE method is less sensitive to currents distributed uniformly over a greater area of the specimen. However, for such specimens, one should expect a shift of the basic level of current in the cathodic direction with an increase in the holding time, but such a phenomenon was not established. Second, most probably, OH^- ions, which are liberated in the course of oxygen reduction at the cathode, react with other ions with subsequent deposition of insoluble products and, not moving in the solution, do not form a positive potential gradient. This deposited film inhibits the reaction of oxygen reduction at the center of the defect.

To evaluate quantitatively the anticorrosive efficiency of inhibited coatings for each scanning, we separately summed up the pointwise anodic and cathodic potentials. For chromate-containing and chromate-free coatings, they are commensurable and tend to zero after 70 h. At the same time, for coatings without inhibiting pigments, the total cathodic current is significantly greater at both the beginning and end of exposure. The total anodic current decreases during exposure for all coatings. After 70 h, the smallest anodic current corresponds to the specimen with a chromate-containing epoxy coating, and the greatest to the reference specimen with inert TiO_2 pigment. The anodic currents for the specimen of coating with a mixture of nonchromate pigments are intermediate between the uninhibited and chromate-containing specimens, but nearer to the latter.

CONCLUSIONS

Zinc phosphate together with an ion-exchange-type calcium-containing pigment guarantee a more significant anticorrosive effect on galvanized steel in acid rain solution than in the case where they are used separately. According to the data of potentiostatic polarization, this mixture retards the cathodic reaction on steel and anodic on zinc, forming a protective film.

We used the SVE method to study the efficiency of corrosion inhibition by chromate and nonchromate pigments at the sites of through damages of the epoxy coating on galvanized steel. We obtained maps of the potential distribution on the specimens of galvanized steel with epoxy coatings and investigated the placement and dynamics of cathode and anode zones in the neighborhood of through damages. By means of summation of the anodic and cathodic potentials for each scanning of the surface, we evaluated quantitatively the efficiency of chromate and nonchromate inhibiting pigments.

A mixture of nonchromate pigments is more efficient for the protection of galvanized steel (zinc) than of carbon steel. Zinc ions liberated due to the corrosion process favor the synergism of protective action of a mixture of nonchromate pigments. Interacting with calcium and phosphate ions, they form on the metal an adsorbed surface film with good barrier properties.

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