JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) 1069–1075

Phenol electropolymerization on phosphated mild steel via zinc electrodeposition

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Received 8 February 1993; revised 22 February 1993

Phenol electropolymerization to polyoxyphenylene coatings on phosphated steel and phosphated galvanized steel, normally impossible under the conditions allowing effective coating formation on either steel or zinc, is activated by cathodic deposition of zinc. A critical zinc amount has been found to be necessary to suppress electrochemical processes competitive with electropolymerization and induce coating formation with nearly 100% efficiency. SEM analysis showed that this critical amount of zinc corresponded to the formation of a low number of zinc nuclei emerging at the surface of the phosphate layer, on which, however, polyoxyphenylene was formed as a continuous coating. A.c. impedance tests showed that initial barrier properties are worse for coatings grown on zinc-plated phosphated samples than for those grown on steel from the same solutions. However, the long term corrosion resistance is much better in the former case, the improvement being largely associated with zinc cathodic protection

1. Introduction

Corrosion protection of mild steel articles, notably car bodies, by electrochemical deposition of paints is commonly realized on pretreated, rather than bare, metal surfaces. Among the different surface treatments phosphating is the most effective one, producing a twofold action, i.e. improvement of the metal-paint adhesion and reduction of the area available to electrochemical reactions involved in the corrosion process [1–3].

The nature of phosphate coatings (especially their cation content) has evolved with time in order to cope with the requirements of the paint deposition processes (anodic or cathodic) and various methods of coating application have been developed. However, a common feature to all phosphate coatings is the existence of a coating-free fraction of the metal surface which, according to different authors, may vary between very wide limits (0.5–30%, [2, 4]). This coating-free area, unavoidably associated with the growth mechanism of the phosphate coatings, is the locus of corrosion reactions, yet allows the electrochemical deposition of paints and might, in principle, enable other electrochemical reactions to occur. Thus, Leidheiser *et al.* [4] have shown that zinc deposition may be easily performed and suggested that the sequence phosphating/Zn-plating/painting might be a viable alternative to the common Zn-plating/phosphating/painting sequence. It might be supposed that, thanks to phosphate-free areas, electropolymerization reactions should be feasible on phosphated steel. Phenol electropolymerization has been investigated as a corrosion protection method [5] leading to coatings of interesting protective properties [6] which it would be attractive to further improve by a phosphate pretreatment. Some unsuccessful attempts at growing polyoxyphenylene films onto phosphated steel have been mentioned previously [7]. In the present paper we describe how the approach by Leidheiser *et al.* [4] allows polyoxyphenylene coating deposition to be realized onto Zn-modified phosphated metals (either steel or galvanized steel).

2. Experimental details

The phosphated steel samples were provided by Chemetall GmbH, Frankfurt, Germany. The treatment applied to either steel or galvanized steel consisted of the following stages: alkaline cleaning; manganese modified zinc phosphating, applied by spray; finally, after-rinsing by a Cr(VI)/Cr(III) solution.

Samples of variable geometry and size were used for different experiments:

(i) 0.7 cm^2 disc electrodes, obtained by insulating all but a circular region of phosphated plates, were employed in cyclic voltammetry.

(ii) Rectangular sheets were used for constant voltage electrolyses aimed at coating synthesis [5] (an active area of 20 cm^2 consisting of both planar faces and edges was exposed to the electrolyte).

(iii) 0.6 cm diameter rods were employed for the a.c. impedance corrosion testing; a 10 cm^2 area was exposed to 0.5 M NaCl solutions thermostated at 25° C.

The phosphate layer thickness was 0.17–0.2 mg cm^{-2}, and the coating-free area, measured as the ratio of the diffusion limited oxygen reduction currents at phosphated and bare steel [8] was between 4 and 7%.

Zinc was deposited on both phosphated steel and phosphated galvanized steel according to [4], from a solution containing 77 g dm^{-3} $ZnCl_2$, 132 g dm^{-3} NH_4Cl, 66 g dm^{-3} citric acid and NH_4OH to adjust the pH to 7, at a constant current of 40 mA cm^{-2}. Constant voltage electropolymerization runs with a two-electrode arrangement and thermal curing of the samples were carried out following previously reported procedures [5]. Hydroalcoholic solutions typically containing 1 M phenol and 0.6 M allylamine were employed.

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were performed with a Philips XL 40 scanning electron microscope equipped with an EDAX PV99 energy-dispersive X-ray spectrometer.

A.c. impedance corrosion tests were carried out at the corrosion potential of the coated samples with a 1250 frequency response analyser and an 1186 electrochemical interface (both by Solartron).

All potentials are referred to the saturated calomel electrode (SCE).

3. Results and discussion

It is shown in [4] that zinc electrodeposits on phosphated steel nucleate on the phosphate-free areas and then develop through the layer pores up to the outer surface, where they may then coalesce. A continuous zinc layer covering the whole electrode surface is only formed after extensive deposition. This picture was fully confirmed in our experiments in spite of the somewhat different nature of the phosphate layers. Thus, Zn-plated phosphated steel samples were prepared in which the amount of zinc could be easily controlled by measuring the zinc deposition charge (current efficiency was >90%). The Zn-plated phosphated steel samples were then used as anodes for the electropolymerization experiments.

Figure 1 compares the cyclic voltammetries recorded on zinc (a), phosphated galvanized steel (b) and Zn-plated phosphated steel (0.4 C cm^{-2} zinc deposition charge) (c); (results obtained on steel and phosphated steel are similar to (a) and (b), respectively). On bare zinc (a) an anodic current flows at $E > 0.8$ V vs SCE, due to phenol oxidation and some minor solvent discharge. Successive cycles induce a gradual, but marked, current decrease and, after prolonged cycling, zinc becomes coated by a thick polymer film. A marked zinc dissolution/passivation peak is not observed, which is at variance with results for solutions containing ammonia instead of allylamine [6]. On phosphated galvanized steel (b) the current onset is somewhat delayed and a much lower current than in case (a) flows from the first cycle. This result is not surprising, since the active electrode area is much smaller in case (b). Also, in this case there is increasingly low current over successive cycles, but the electrode appearance does not change even on prolonged cycling. The behaviour observed on Zn-plated phosphated steel (c) is much closer to (a) than to (b): an initially large anodic current smoothly decreases during successive cycles, while a polymer coating is formed. A major difference between (a) and (c) is only found in the first cycle; in the latter case an anodic peak due to zinc dissolution/passivation is observed. This result suggests that the electrodeposited small zinc crystals are more prone to dissolution than the zinc sheet. A comparable anodic peak was also observed when the electropolymerization was carried out on anodes obtained by electrodeposition of zinc on mild steel and, therefore, was in no way linked with the phosphate layer. The zinc dissolution charge (Q_{dis}) was compared with the zinc deposition charge (Q_{dep}) for a series of electrodes prepared by varying Q_{dep} from 0.25 to 2.5 C cm^{-2}. The ratio Q_{dis}/Q_{dep}, measured at a sweep rate of 50 mV s^{-1}, decreased from 0.11 to 0.06 when the zinc amount was increased by a factor of 10 and became even lower for faster sweep rates. Thus, it may be concluded that most of the deposited zinc is not dissolved away under the electropolymerization conditions, i.e. when a large positive potential (around 2 V vs SCE) is suddenly applied. The absence of the zinc dissolution peak in cycles other than the first one proves that the produced polyoxyphenylene protects zinc from electrodissolution.

Figure 2 shows the current-time curves recorded under constant applied voltage on various anodes: zinc (dotted line), phosphated steel (dashed line) and Zn-plated phosphated steel with variable amounts of deposited zinc (solid lines). By increasing the zinc amount the observed behaviour gradually changes from that of phosphated steel to that of zinc. By measuring the transferred charge and the weight of deposited polymer, the electropolymerization current yields were obtained for each experiment. These are plotted against the zinc deposition charge in Fig. 3, which also shows the data obtained by plating zinc on phosphated galvanized steel. Current yield was zero in the absence of electrodeposited zinc, irrespective of the nature of the metal underlying the phosphate layer. A sharp increase of current yield to nearly attain the stoichiometric value of 0.47 mg C^{-1} occurred for a deposition charge as low as 0.05–0.1 C cm^{-2}, corresponding to < 0.02 mg cm^{-2} zinc. The marked similarity between the results obtained on either phosphated steel or phosphated galvanized steel suggests that a critical amount of electrodeposited zinc exists which induces a jump in the electropolymerization current efficiency. It might be supposed that this amount was that necessary to completely fill the phosphate layer pores; under this hypothesis

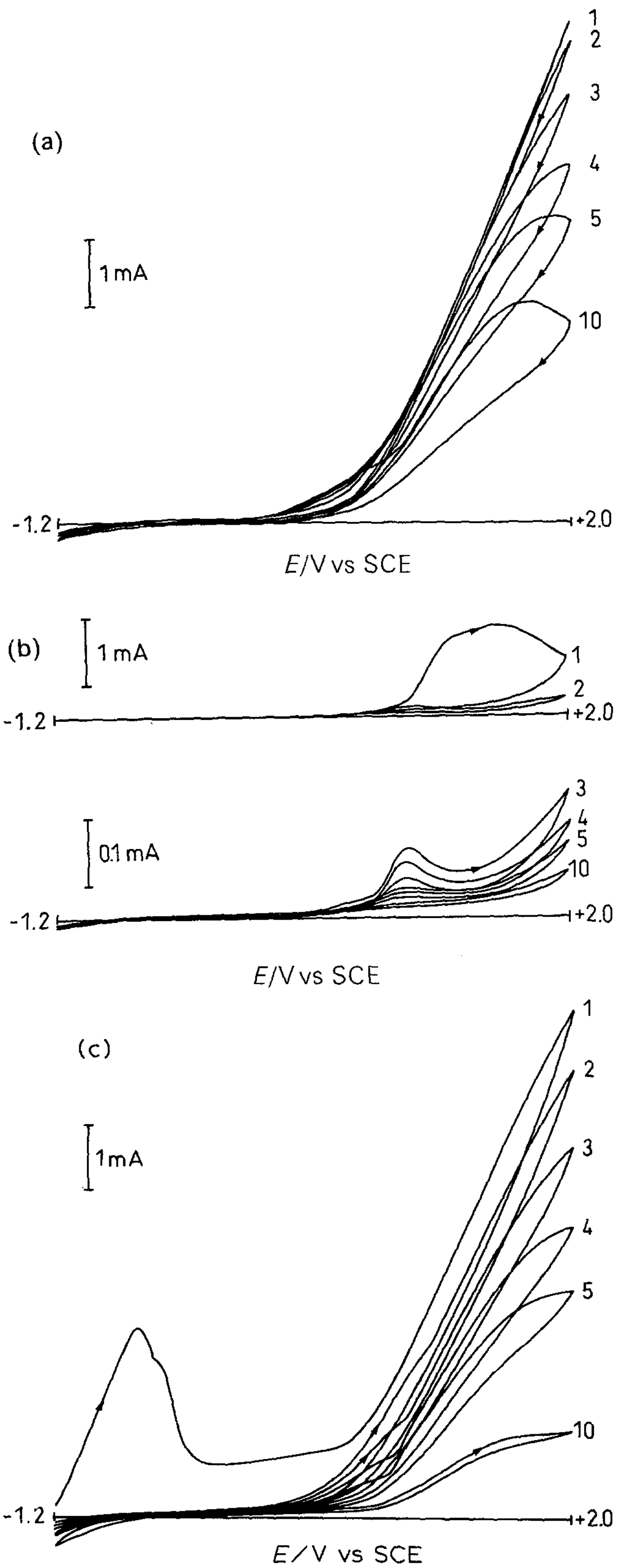

Fig. 1. Cyclic voltammograms recorded on Zn (a), phosphated steel (b) and Zn-plated phosphated steel (c) electrodes (0.7 cm^2 area) in 1 M phenol, 0.6 M allylamine, 0.6 M methoxyethanol hydroalcoholic solutions (pH 10, water/methanol ratio = 2.5). Sweep rate 50 $mV\,s^{-1}$; cycle numbers are indicated on the curves.

it may be calculated that about 5% of the layer volume was due to pores (a value in the same range as that of phosphate-free areas).

Figure 4 compares the growth rates of polyoxyphenylene coatings on zinc and Zn-plated phosphated steel electrodes prepared with two different zinc deposition charges (0.1 and 0.25 $C\,cm^{-2}$), the former near the critical value and the latter well above it. Although in both cases current yields are near the stoichiometric one (Fig. 3) growth rates are markedly different. Thus, while the critical amount of electrodeposited zinc is sufficient to almost entirely suppress

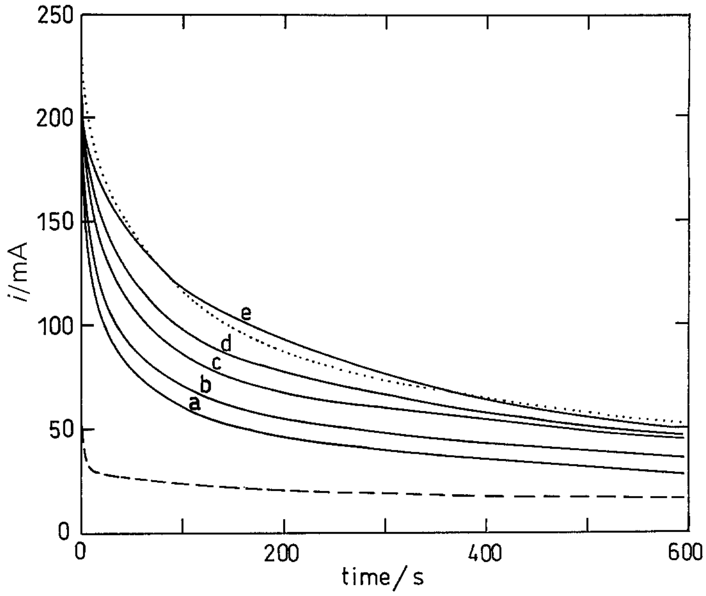

Fig. 2. Current-time curves recorded during constant voltage electrolysis (4 V) on Zn (dotted line) phosphated steel (dashed line) and Zn-plated phosphated steel (solid lines) in the same solution as for Fig. 1. Zn deposition charges: (a) 0.1, (b) 0.17, (c) 0.24, (d) 0.5 and (e) 2.5 C cm^{-2}.

any parasitic process, it cannot give a growth rate as large as that observed on a homogeneously active electrode.

Zinc-plated phosphated steel samples were analyzed by SEM both before and after electropolymerization. Figure 5(a) and (b) show samples obtained by deposition of 0.025 and 0.125 mg cm^{-2} of zinc, respectively. For the former, corresponding to a zinc amount just above the critical value, zinc covers only a few percent of the surface: Zn-free areas larger than 100 μm^2 are common. Large Zn-free areas are still present for a five times higher amount of zinc, as shown by Fig. 5(b). This picture, showing the boundary between the Zn-plated and the 'bare' phosphate areas, also emphasizes that the phosphate crystal morphology is not altered by the zinc deposition stage.

Figure 5(c) shows a phosphated steel sample Zn-plated on its whole surface (zinc amount = 0.125 mg cm^{-2}) and then submitted to electropolymerization only on its left half. Despite the zinc deposit being present only as isolated nuclei, polyoxyphenylene formed as a continuous film coating on both zinc and phosphate crystals. The sample of Fig. 5(d) was Zn-plated only on its right half and then submitted to electropolymerization on its whole surface. It is evident that the presence of zinc nuclei was essential to polyoxyphenylene formation, while the phosphate layer was not affected under the electropolymerization conditions. It must be stressed that the defects visible in the polymer film at the boundary between polymer coated and uncoated areas (Fig. 5(c) and (d)) were not detected far from this boundary.

SEM data show that each layer is stable under the

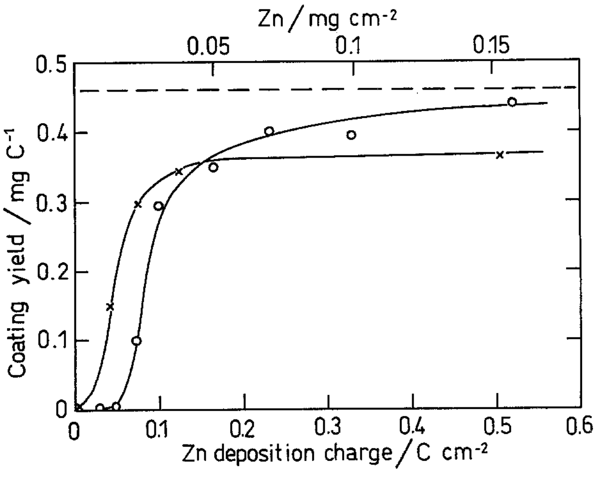

Fig. 3. Dependence of the polyoxyphenylene coating yield on the zinc deposition charge on phosphated steel (○) and phosphated galvanized steel (×). The dashed line represents the theoretical coating yield for 100% efficiency. Zinc coverage was calculated for a 0.3 mg C^{-1} deposition yield. Electropolymerization solution as for Fig. 1.

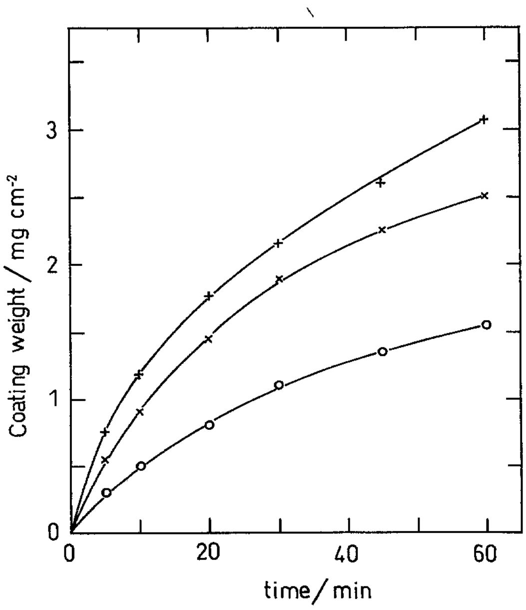

Fig. 4. Dependence of the coating weight on electropolymerization duration for Zn (+), and Zn-plated phosphated steel (×, ○). Zn deposition charge 0.1 (o) and 0.25 C cm^{-2} (x). Electropolymerization solution as for Fig. 1.

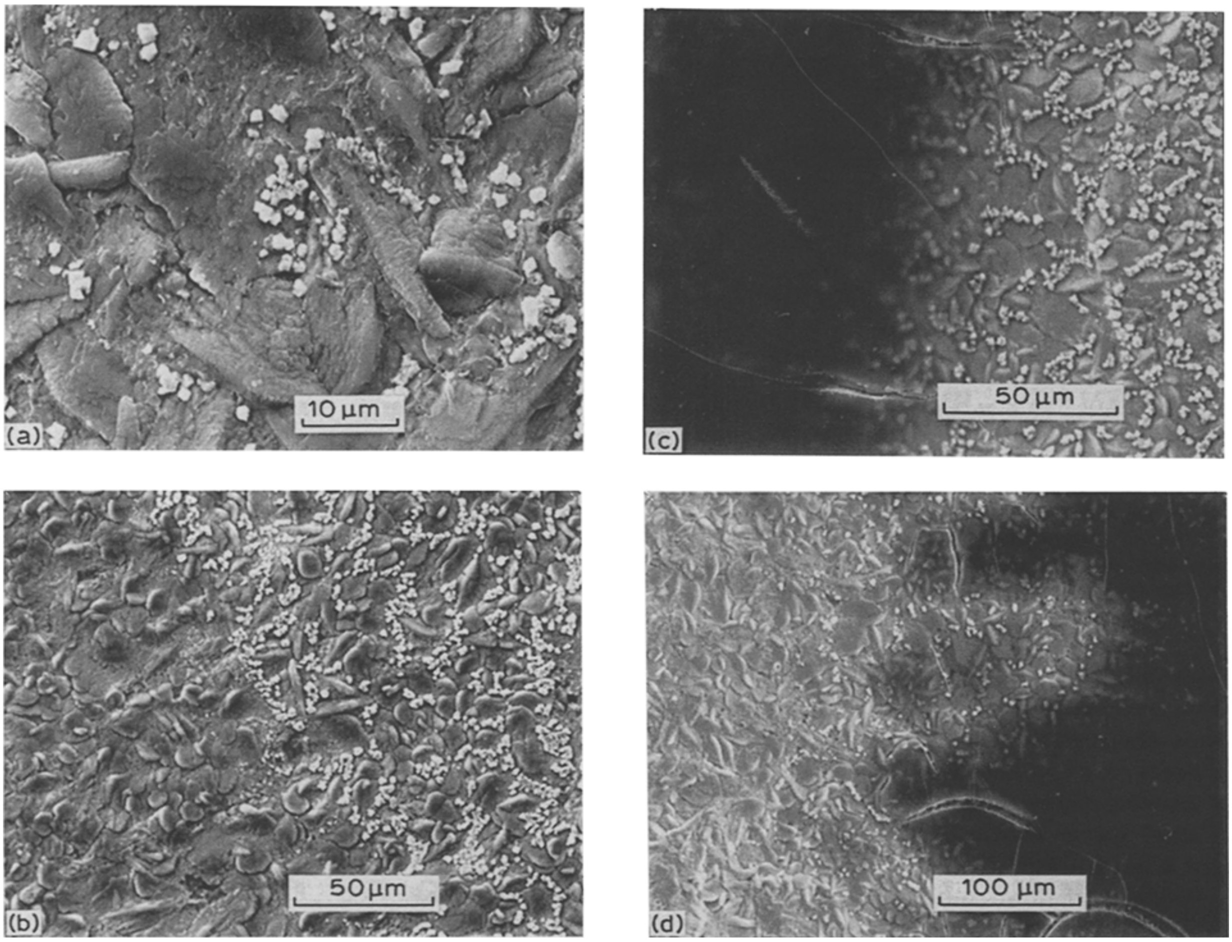

Fig. 5. SEM micrographs of Zn-plated phosphated steel samples; Zn deposition charge 0.08 (a) and 0.4 C cm^{-2} (b–d). Electropolymerizations (c and d) were carried out in the same solution as for Fig. 1.

conditions used for the deposition of the following ones. Further confirmation was provided by EDX analysis of polyoxyphenylene coated Zn-plated phosphated steel samples, which showed peaks due to P, Zn and Mn in the ratios observed before electropolymerization, though all signals were of low intensity because of the overlying polymer.

The above electrochemical and SEM data highlight two points deserving some discussion: (i) the growth of a homogeneous polymer film on an inhomogeneously active substrate, and (ii) the lack of an effective electropolymerization in the absence of zinc deposition.

Unlike conductive polymers, which grow in a similar way to metal deposits, polyoxyphenylene films develop as electrolyte-swollen ionically-conductive gels [5, 6, 9]. As long as the transport of monomers and oligomers through this gel is fast enough to allow their approach to the electrode surface, electron exchange and coupling of the formed radicals, the electropolymerization may proceed. Electropolymerization stops when the polymer layer becomes so thick and/or crosslinked that transport is severely hindered. With such a growth mechanism a polymer coating may be expected to develop on the whole surface, even if a limited fraction of the electrode area is active in charge transfer. On the other hand, polymer molecules formed away from the electroactive (Zn) areas are likely to be unable to reach very high molecular weight.

Concerning the second point, the possibility that polyoxyphenylene is formed inside the phosphate layer pores cannot be ruled out (though with a very poor current efficiency, Fig. 3). A polyoxyphenylene amount of 3×10^{-6} g cm^{-2}, not detectable by weighing, would be sufficient to fill the whole pore volume. However, it is clear that effective electropolymerization does not take place onto phosphated steel or phosphated galvanized steel samples. Several hypotheses might be advanced in order to explain this failure. The first involves a local pH change: when phenol and water (or the corresponding anions) are oxidized at the bottom of an occluded pore, a pH decrease must be expected. This might oppose phenol polymerization [10] and induce allylamine protonation preventing it from exerting its interfacial role [11]. However, the use of electropolymerization solutions buffered at pH 10–10.5 did not change the picture. A second hypothesis might be that the chromate after-rinsing of phosphated steel selectively inhibits the phenol oxidation, while allowing other reactions like oxygen evolution or zinc deposition. However, phosphated steel samples not submitted to after-rinsing were also inactive towards phenol electropolymerization, while application of chromate after-rinsing to either mild steel or zinc

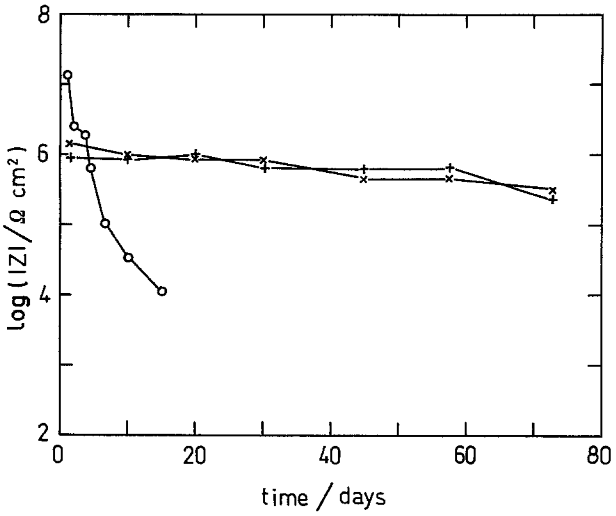

Fig. 6. Dependence of the impedance modulus (measured at 0.01 Hz) of polyoxyphenylene coated steel (○), Zn-plated phosphated steel (+) and Zn-plated steel (×) on the duration of the immersion in 3% NaCl. Zn deposition charge 1 C cm^{-2}.

(with no phosphate treatment) did not prevent electropolymerization. A possible explanation is that when electroactive areas are located at the bottom of pores (possibly filled in part by polymer) transport of growing oligomers is severely restricted, while that of small species is comparatively free (oxygen evolution is not hindered on the phosphate-free areas).

Polyoxyphenylene coatings of comparable thickness (15 μm) were deposited on steel and Zn-plated phosphated steel from solutions containing, in addition to phenol and allylamine, a non-ionic surfactant (alkylphenylpolyethoxyethanol) previously found to improve metal-coating adhesion [12]. Once exposed to 3% NaCl the corrosion potential of the coated samples was in the range −0.55/−0.60 V for the former and in the range −0.95/−1.0 V for the latter. In agreement with [7], the impedance diagrams obtained for the steel samples consisted of two loops which, following a classical interpretation [13], may be interpreted as due to the coating (high frequency) and the corrosion reaction (low frequency) impedances: the coating resistance measured after 24 h was 200–300 kΩ cm^2. Zinc-plated phosphated steel samples showed markedly lower coating resistance, increasing with the amount of deposited zinc. By increasing the zinc deposition charge from 0.1 to 2.5 C cm^{-2} the coating resistance increased from 5–10 to 80–120 kΩ cm^2. Therefore, the coatings grown on the inhomogeneous Zn-plated phosphated steel samples appeared to offer much lower resistance to electrolyte penetration than those grown on mild steel. A coating material consisting largely of low molecular weight material might lead to such a result. Figure 6 summarizes the time variation of the impedance measured at 10 mHz for steel, Zn-plated phosphated steel samples and, in addition, for Zn-plated steel samples. This impedance does not exactly represent the polarization resistance Rp since, owing to mass transport phenomena involved in the corrosion of zinc [14], in the absence of forced convection Rp can only be obtained at very low frequency. On prolonging the exposure to NaCl solutions the impedance of mild steel samples declined much faster than that of Zn-plated ones. Figure 6 also shows that the impedance of Zn-plated samples was independent of the phosphating treatment. The improved behaviour with respect to untreated steel must therefore be ascribed to the zinc deposit, while the effect of the phosphate layer cannot be appreciated.

4. Conclusions

It has been shown that the electrodeposition of small amounts of zinc activates phosphated steel and phosphated galvanized steel towards electropolymerization of phenol to polyoxyphenylene coatings. A critical amount of zinc, roughly corresponding to that necessary to fill the phosphate layer pores induces electropolymerization on the whole electrode surface, though large Zn-free areas remain after the zinc deposition.

The reason why effective electropolymerization does not occur on phosphated steel not submitted to zinc deposition remains partly unclear; a reason might be found in the hindrance of mass transport within the pores, while selective passivation by chromate after-rinsing and local pH effects appear to be irrelevant.

Corrosion tests carried out by a.c. impedance show that polyoxyphenylene coatings formed onto Zn-plated phosphated steel have worse barrier properties than those obtained onto steel. This result is likely to reflect microscopic coating inhomogeneities caused by the inhomogeneous reactivity of the Zn-plated phosphated steel electrode surface. For prolonged exposure to a corrosive environment, the performance of Zn-plated phosphated steel is markedly better than that of steel, though the improvement is to be ascribed largely to the cathodic protection provided by zinc. Therefore, it must be concluded that, even if electropolymerization has been made feasible onto phosphated steel by Zn-deposition, the phosphate layer does not cause an improvement in the protective performance of coatings prepared by electropolymerization as it does in the case of electrophoretic paints, the loss in barrier properties being a major disadvantage. It is worth noting that coatings of much better barrier properties than those obtained from the phenol-allylamine system employed in this work may be obtained on steel from ammonium sulfide containing solutions. However, the latter system is unsuitable for zinc [6].

Although the investigation of the corrosion behaviour of polyoxyphenylene coated phosphated samples has not allowed the role of the phosphate layer to be clearly evaluated, the study of the electropolymerization of phenol on electrodes of very peculiar reactivity, with small active areas (located or not at the bottom of pores) separated by inert ones, has allowed the gathering of new data on a problematic process like the electrochemical growth of non-conductive polymer layers.

Acknowledgements

This work was financially supported by Italian CNR – Progetto Finalizzato Chimica Fine II.

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