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Appraisal of the polypyrrole/cataphoretic paint bilayer system as a protective coating for metals

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Very adherent modified polypyrrole $(PPy)_m$ films have been electrosynthesized on oxidizable metals such as mild steel (MS) and zincated steel (Zn) by electrochemical oxidation of pyrrole (Py) on the substrate. In the case of mild steel, the adherence of the coating is maintained in both the oxidized and reduced states of the polymer, allowing the cataphoretic print technique, which is particularly useful in the automotive industry, to be used. When submitted to the salt spray test, the bilayer system $(MS/(PPy)_m$/cataphoretic paint) appears to be as good as the reference system where the PPy layer has been replaced by a phosphating layer.

Keywords: *cataphoretic paint*, *corrosion protection*, *mild steel*, *polypyrrole films*, *zincated steel*

1. Introduction

Conducting adherent polymer films are generally obtained by electrochemical oxidation of heterocyclic monomers on noble (Pt, Au) or inert solid substrates (graphite, glassy carbon). Owing to their broad field of application they have been extensively studied during the last ten years [1, 2]. Conductive in the doped state, they become insulating after reduction to the neutral state, and thus behave as ordinary organic coatings with predictable anticorrosion properties.

However, although the electrosynthesis of polymer films such as polypyrrole (PPy), polythiophene (PT) or polyaniline (PANI) is easy to carry out on noble or inert electrodes, it is much more difficult with oxidizable metals like Fe, Zn, Cu or Al. Indeed, the oxidation potential of the metal is much more negative than that of the monomer and, therefore, dissolution of the metal will occur and stabilize the potential of the electrode at a negative value where monomer oxidation does not occur.

Nevertheless, in the case of iron or steel it was shown recently that a judicious choice of the electrolytic medium can reduce the dissolution rate of the metal without impeding monomer oxidation. Adherent PPy films were obtained on iron or steel in basic organic solvents (methanol or tetrahydrofuran, both in the presence of $N(Bu)_4PF_6$) [3, 4], whereas poorly adherent PPy films were obtained in CH_3CN [5] and PC [6] with iron and zinc. More recently, a significant improvement was achieved with the use of aqueous media. Beck *et al.* showed that PPy films could be formed on iron or steel by using KNO_3 [7] or oxalic acid [8] as electrolytes. The adherence strength of PPy layers is much higher in the presence of oxalic acid than in the presence of NO_3^-. However, in both cases the adherence of the PPy layers did not satisfy the usual requirements for good anticorrosion protection and, in particular, for the application of a cataphoretic paint on top of the film. Indeed, PPy films peeled off the electrode when the reduction potential reached a value of −0.5 V vs SCE.

After several unsuccessful attempts we found that the adherence was considerably improved when the iron surface was treated with dilute nitric acid [9–11]. At the same time, Beck *et al.* showed that pretreatment of iron with MnO_4^- and electrolysis with oxalic acid also made PPy adhere strongly to iron [12]. In the case of zinc the situation is much more difficult since Zn is more electronegative than iron, and its dissolution is rapid at the oxidation potential of pyrrole. Nevertheless, it was found that chemical treatment of Zn with Na_2S made it possible to electropolymerize pyrrole in sodium oxalate and to obtain adherent PPy films [12, 14]. This result was confirmed recently by de Bruyne *et al.* [15] and we improved upon it by using a short electrochemical treatment instead of a chemical treatment [16].

The reason for this improved adherence in the case of steel is not yet well understood but seems to be correlated with the presence of nitride species firmly anchored at the iron surface and resulting from the nitric acid treatment [17].

In this work we have studied the protection of mild steel and zincated steel substrates by PPy films obtained by oxidation of pyrrole in aqueous media. Two kinds of PPy films were synthesized. The first was pure PPy, while the second was a modified PPy,

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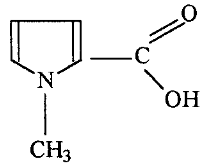
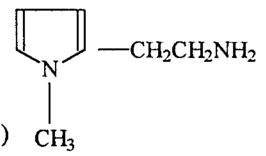
$(PPy)_m$, obtained by oxidation of a mixture of pyrrole, *N*-methylpyrrole-2-carboxylic acid (I) and *N*-methyl-2[(2-ethylamino)](II)pyrrole in a ratio of 1 : 0.1 : 0.1 at a total concentration of 0.1 M.



(I)



(II)

The polymer obtained was heated at 180 °C in order to cause chain coupling condensation of NH_2 and COOH groups (Scheme 1). The protection properties were appraised by comparing the results of the salt spray test on the classical (M/phosphating/cataphoretic paint) and (M/PPy/cataphoretic paint) (M = mild steel or zinc).

2. Experimental details

Electrosynthesis of PPy or modified PPy films on mild steel samples (30 cm^2 area, PSA B 53 3055, carbon <0.10%) electrozincated steel (PSA B 53 3210) has been described previously [10, 11]. The cataphoretic paint was provided by Pittsburg Plate Glass Industries (PPG 717 958) and applied according to the manufacturer's instructions. The salt spray test was performed according to the PSA B17 10 58 and NF X 41-002 norms. Adherence of PPy films to the substrate was measured by a normalized Sellotape test (PSA norm D25-1075). A 100% adherence means that no loss of adhesion is observed when the tape is pulled over the film previously scratched so as to break the film up into small squares. The corrosion test at open potential was performed in 0.5 M NaCl using a saturated calomel electrode (SCE) as the reference electrode.

3. Results

The coated samples were submitted to two different corrosion tests: variation of the open potential in a NaCl solution and salt spray experiments.

3.1. *Variation of the corrosion potential with time*

Prior to coating, the mild steel samples were treated with 10% HNO_3 and then PPy was synthesized by electrochemical oxidation of 0.1 M pyrrole in 0.1 M KNO_3 + 2.5×10^{-2} M Triton X 405 at a constant current density of 4 mA cm^{-2}. Modified PPy films were obtained with a 1 : 0.1 : 0.1 mixture of pyrrole, aminopyrrole and pyrrole carboxylic acid. The films were obtained in their doped state and were reduced at −0.7 V in 0.1 M NaOH before carrying out the corrosion test at open potential in 0.5 M NaCl.

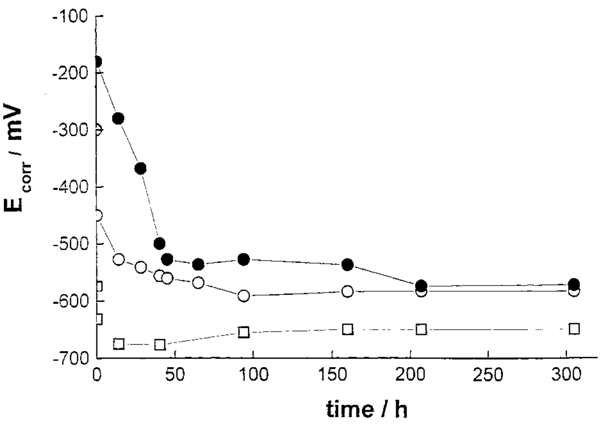


Fig. 1. Time–corrosion potential curves of various coated mild steel plates in 0.5 M NaCl. key: (□) MS, (○) (MS/PPy) and (●) $(MS/PPy)_m$.

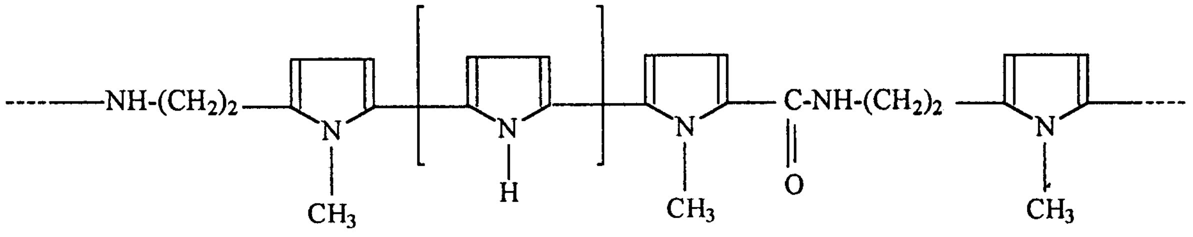
In the case of a bare mild steel plate the corrosion potential E_{corr} decreases rapidly from −575 to −625 mV in a few minutes and then after about 20 h reaches a pseudo steady state at about −675 mV (Fig. 1). With a standard PPy-coated mild steel plate an apparent protection continues for about 40 h and the potential of the electrode decreasing from −300 to −580 mV, and then remaining fairly constant.

The protection was markedly improved when the mild steel plate was coated with modified PPy, $(PPy)_m$. In this case no corrosion was observed after eight days' immersion in the brine solution, and the potential decreased slowly from −175 to −520 mV (Fig. 1). However, after longer times, a reddish corrosion appeared at some points on the plate, but no visible general corrosion was detected when the film was peeled off the substrate.

From these results it can be concluded that some pitting corrosion occurs but, as with phosphating, no lateral propagation of the corrosion occurs, and this was confirmed when an X-scratch coated surface was treated with salt solution.

3.2. *Salt spray tests*

3.2.1. PPy coatings. All the PPy films synthesized on mild steel (MS) or zincated steel (Zn) plates were



Scheme 1

Table 1. Electrosynthesis and treatment conditions used for obtaining PPy films on mild steel and zincated mild steel

Substrate	*Treatment*	*Electrosynthesis conditions*
Mild steel	HNO_3 (10%)	$j = 4\,mA\,cm^{-2}$ 0.1 M KNO_3 + 0.1 M Py + 2.5×10^{-2} M Triton X 405
Galvanized or electrozincated mild steel	Na_2S (0.2 M)	$j = 10\,mA\,cm^{-2}$ 0.1 M $K_2C_2O_4$ + 0.5 M Py

reduced in 0.1 M NaOH as previously, rinsed in distilled water and dried with an air jet. Electrosynthesis conditions for obtaining PPy films are summarized in Table 1.

In the case of mild steel, the salt spray test was applied for 500 h on standard and modified polypyrrole coatings, about 3–15 μm thick. In both cases, the iron PPy coatings appeared to be severely damaged; however, the modified polypyrrole coating $(PPy)_m$ was less attacked than that of standard polypyrrole $(PPy)_s$. These results clearly show that an iron plate coated with $(PPy)_s$ is not sufficiently protected when a salt spray corrosion test is performed. In the case of zincated steel plates, the salt spray test was not carried out, because the protection of zinc by an organic coating is still much more difficult than that of steel.

3.2.2. Bilayer coatings consisting of a PPy film and a cataphoretic layer, (M/PPy/Cat).

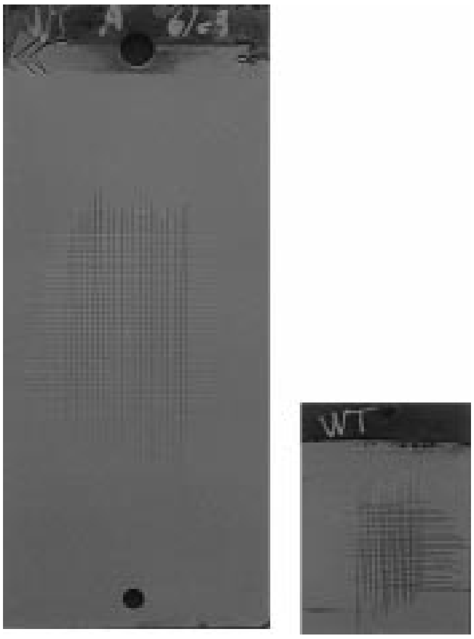
In this case the PPy film may be considered as a primer upon which an additional paint layer has been deposited by cataphoresis (Cat).

As previously, the metallic plates (M) were coated with a $(PPy)_s$ or $(PPy)_m$ film, 3–15 μm thick, on which a paint layer was applied by cataphoresis following the recommendations of the supplier. The properties of the (M/PPy/Cat) coating were compared with the classical coating ($M/PO_4/Cat$) in which a phosphated steel plate was covered with the same cataphoretic paint layer. The mild steel (MS) and zincated steel (Zn) plates were preliminarily treated with dilute HNO_3 and Na_2S, respectively. Results are summarized in Tables 2 and 3.

Table 2. Comparison of the behaviour of scratched (Zn/PPy/Cat) and (Zn/PO_4 /Cat) coatings submitted to the action of water (21days) or salt spray test (500 h)

(a) Adherence immediately after curing at 180 °C for 30 min
(b) Lateral propagation of corrosion (LPC) in millimeter at the streak

Results	*PPy/Cat*	*PO_4 /Cat*
PPy thickness/μm	3–15	
Total thickness/μm	28–37	23–27
Adherence (a)	95–35%	100%
Salt spray test		
LPC (b)	6–9	9–10
blistering	strong	weak
Immersion in distilled water		
adherence	95–35%	100%
blistering	0	0



(a) (b)

Fig. 2. Comparison of scratched ($MS/PO_4/Cat$) (a) and (MS/PPy/Cat) (b) coatings submitted to the action of water (21 days).

Table 3. Comparison of the behaviour of scratched (MS/PPy/Cat) and ($MS/PO_4/Cat$) coatings submitted to the action of water (21 days) and salt spray test (500 h)

(a) Adherence immediately after curing at 180 °C for 30 min
(b) Lateral propagation of conversion (LPC) in millimeter at the streak

Results	*PPy/Cat*	*$(PPy)_m$ /Cat*	*PO_4 /Cat*
PPy thickness/μm	3–6	3–6	–
total thickness/μm	47–57	47–57	24–25
adherence (a)	100–95 %	100–95 %	100%
Salt spray test			
LPC (b)	1–5	1–5	1–2
Blistering	0	0	0
Immersion in distilled water			
adherence	100–95 %	100%	100%
blistering	0	0	0

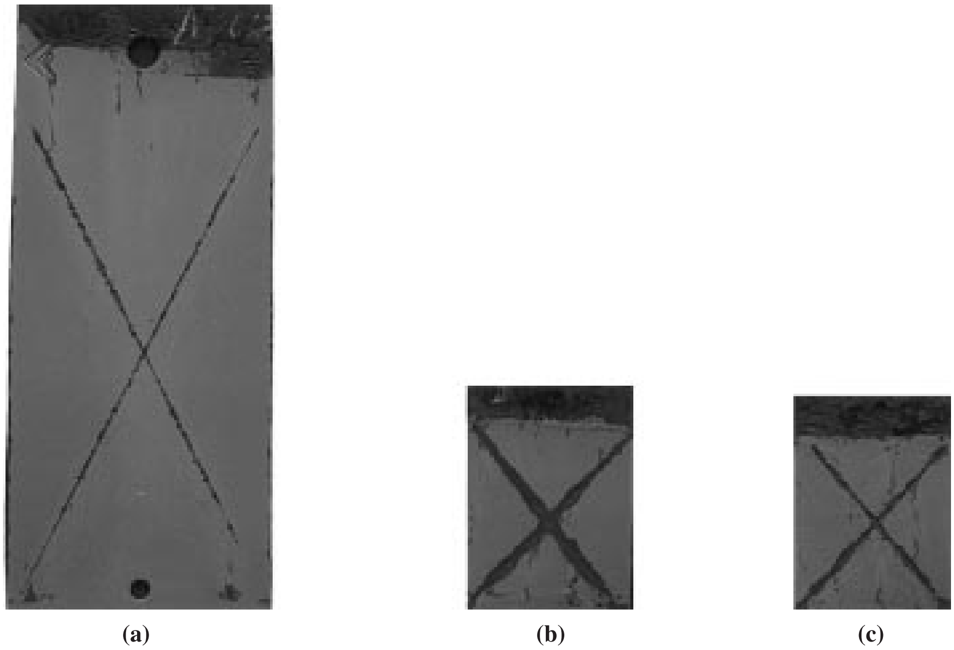


Fig. 3. Comparison of scratched ($MS/PO_4/Cat$) (a), (MS/PPy/Cat) (b) and ($MS/(PPy)_m/Cat$) (c) coatings submitted to the action of a salt spray test (500 h).

(*a*) *Zincated steel*
The quality of the protection is poor in the case of the ($Zn/(PPy)_s/Cat$) system and corresponds to a loss of adherence. This result is probably due both to the cathodic treatment of $(PPy)_s$ resulting from the cataphoretic paint application and to the heating of the whole paint bilayer at 180 °C (Table 2).

(*b*) *Mild steel*
In this case the results are very good (Table 3). Adherence of the (PPy/Cat) coating to the steel substrate is much the same as (PO_4/Cat). In particular, there is no blistering and the behaviour towards the salt spray test is similar to that of the (PO_4/Cat) coating.

Figure 2 shows clearly that the scratched ($MS/(PPy)_s/Cat$) coating remains insensitive to the action of water for a three-week period and seems as good as a (PO_4/Cat) coating (Fig. 2(a)). The effect of the salt spray test carried out for 500 h is more severe. In the case of standard PPy ($MS/(PPy)_s/Cat$) (Fig. 3(b)), some lateral corrosion propagation occurs, and appears more pronounced than in the case of a phosphated MS ($MS/PO_4/Cat$) (Fig. 3(a)). The lateral corrosion is considerably reduced with a modified PPy ($MS/(PPy)_m/Cat$), and in this case the process compares fairly well with a ($MS/PO_4/Cat$) coating (Fig. 3(c)). This latter result is promising and shows that dramatic improvements can be achieved if the PPy is suitably modified.

4. Conclusion

This study shows that strongly adherent PPy films can be formed electrochemically by oxidation of pyrrole on mild steel or zincated mild steel. The feasibility of cathodic overcoating by electrodeposition of paint on PPy films deposited on these materials has been demonstrated. However, in both cases, good adherence of PPy to the substrate is achieved only after specific treatment of the electrode (dilute HNO_3 for mild steel, Na_2S for a zinc surface). Comparison of the PPy/cataphoretic paint bilayer with a classical phosphating/cataphoretic paint system shows that similar protection was obtained with a modified PPy coating. These results establish that the process is possible and prove that after they have been reduced and dedoped conductive polymers may constitute efficient protective coatings against corrosion of iron or mild steel.

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