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COMPARISON OF ANTICORROSIVE PROPERTIES OF EPOXY PRIMERS CONTAINING POLYANILINE, POLY (ORTHO-ETHOXYANILINE)OR ZINC PHOSPHATE

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ABSTRACT

The anticorrosive properties of different epoxy primers containing polyaniline, poly (ortho-ethoxyaniline) or zinc phosphate were evaluated on mild steel in saline environment (3.5% wt NaCl).

The obtained results from electrochemical measurements and immersion tests show that primers containing substituted polyaniline provide better corrosion protection compared to conventional zinc primers and polyaniline primers which are supplied by Zipperling Kessler & Co.

The effectiveness of our primers is explained by the good solubility of substituted polyaniline in the selected solvents.

Key words: *Epoxy primers containing substituted polyaniline, polyaniline primers.*

1. INTRODUCTION

Over the last years, several conducting polymers have been tested as corrosion inhibitors and/or anticorrosive coatings namely polyaniline (Pani), polyaniline derivatives and polypyrrole. Pani has been considerably investigated for its aptitude to protect metals against aqueous corrosion [1, 2]. Otherwise, the good corrosion protective properties of coatings containing polyaniline are widely known. A number of studies on the anticorrosion performance of chemically polymerised polyaniline on mild steel have been published [3-11]. However, its practical applications take a long delay because of its insolubility in common organic solvents. Theoretical studies indicate that the substituted Pani has better solubility than unsubstitued Pani, mainly because of the stereo-electronic effect of the substituent on the torsional angle between adjacent phenyl rings which renders the polymer chain more flexible [12]. Our research was motivated by the publication of Dhawan and by our publication according to which among several alkyls the ortho-ethoxy confers to the polymer the best solubility in organic solvents and the best properties as a corrosion inhibitor for mild steel in acidic chloride solution [13,14]. Depending on the aims, Pani was tested as a single coating [15-17], a primer [5, 8, 18, 19] or blended [9, 20], but nothing at all was known about any anticorrosion effect of coatings containing the poly(ortho-ethoxyaniline) (Pea). We have expected that the solubility of Pea in the solvents generally used in primer formulations could enhancing the wettability of the coated metal by increasing the surface of contact between the substrate and the polymer resulting in a higher protection efficiency of a primer against corrosion.

In this work, we have investigated the corrosion protection of mild steel in saline environment (3.5% wt NaCl) by epoxy primers containing a substituted Pani which is Pea and compared with primers containing Pani on the one hand, and with a conventional primer containing organic zinc on the other hand.

The first aim was to determine whether the type of the anticorrosive agent (Pani, Pea or organic zinc) used in the formulation of primers affected the corrosion protection of the coated steel. The second

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aim was to show the effect of the level of the solubility of Pani and Pea in two different solvents namely xylene and dimethyl formamide (DMF), on the efficiency of the obtained primers.

In order to highlight the intrinsic properties of the conducting polymers, we have chosen to evaluate the primers without any top coat.

The combination of the full immersion test, the potentiodynamic polarisation and the cathodic delamination test allowed us to achieve our goal.

2. EXPERIMENTAL

2.1 Synthesis

The polyaniline (Pani) and the poly ortho-ethoxyaniline (Pea) were obtained by following the method of Dhawn and Trivedi [13].

By this method, two solutions were prepared, one with the oxidant agent (ammonium peroxidisulfate) dissolved in 1 M HCl and the other with the monomer: aniline or ethoxyaniline (in excess in relation to the oxidant agent) also dissolved in 1 M HCl. Both solutions were then cooled down in an ice bath under constant stirring and followed by the slow addition of the oxidant solution to the monomer solution. After this process, the mixture was kept at 0 ± 3 °C for 4 hours then filtered under vacuum to obtain a dark green powder, which was washed repeatedly with distilled water.

The deprotonation of the polymers was performed by putting them in contact with 0.1 M NH_4OH solution at 25°C for 16 h and the resulting polymers were filtered and dried under vacuum for 48 h at 40°C.

Finally, in order to increase its solubility in organic solvents such as dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and xylene, Pani was doped using sulfosalicylic acid 4 M.

2.2 Sample preparation

For our study, we prepared five types of steel protection system against corrosion, concerning on primers based on epoxy resin (EE 622) in weight of 30.5% and containing as anticorrosive agents either conducting polymers (in weight of 1, 2 and 3%) or conventional agent (in weight of 7.5%). The main

Primer (anticorrosive agent-solvent)	Anticorrosive agent (% wt)	Solvent (% wt)	Total composition (% wt)
Zinc phosphate* - xylene	7.5	8.8	100
	1	15.3	
Pani - xylene	2	14.3	100
	3	13.3	
	1	15.3	
Pea - xylene	2	14.3	100
	3	13.3	
	1	15.3	
Pani - DMF	2	14.3	100
	3	13.3	
	1	15.3	
Pea - DMF	2	14.3	100
	3	13.3	

Table 1 : Percentage in weight of the anticorrosive agents and the solvents used to formulate the coating systems (epoxy primers).

solvents used to solubilize these agents are xylene (which is widely used in primers) or DMF (which is known for its ability to solubilize Pani and its derivatives). These epoxy-coating systems are given below and also mentioned in detail in Table 1.

- Zinc phosphate* epoxy primer: which is considered as a conventional primer and commercially available.
- Pani epoxy primer (with xylene or DMF as solvent): Pani is actually used as a dispersion in primers supplied by Zipperling Kessler & Co such as CORRPASSIV™.
- Pea epoxy primer (with xylene or DMF as solvent): which is our developed primer.

* Zinc phosphate is commercialised by ENAP-Algeria (Entreprise Nationale des Peintures): singly (as a powder) or incorporated in weight of 7.5% into a coating formulation “epicote”.

All primers were prepared by dissolving first the anticorrosive agent in the solvent, after that the epoxy resin and the others ingredients were added to the solution and the mixture was ball-milled for 4 h. Finally, primers were filtered through fine cotton cloth.

The iron samples with 2 x 2 cm dimension and 1 mm thickness were cut from a piece of mild steel plate. Prior to coating, all samples were polished with 1200 grit emery paper, pretreated in acetone and ethyl alcohol to remove impurities. Finally, the samples were rinsed with distilled water and dried by acetone. Coating thickness was about 45 mm for all samples.

2.3 Immersion test

Full immersion testing of the corrosion protection behaviour of the various primers on steel was carried out in 14 stagnant aerated solutions of 3.5% NaCl at ambient temperature (Figure 1). The test solution was periodically sampled for total-Fe analysis using colorimetric phenanthroline method (ASTM Standard Practice for Laboratory Immersion Corrosion Testing of Metal, G31--72).

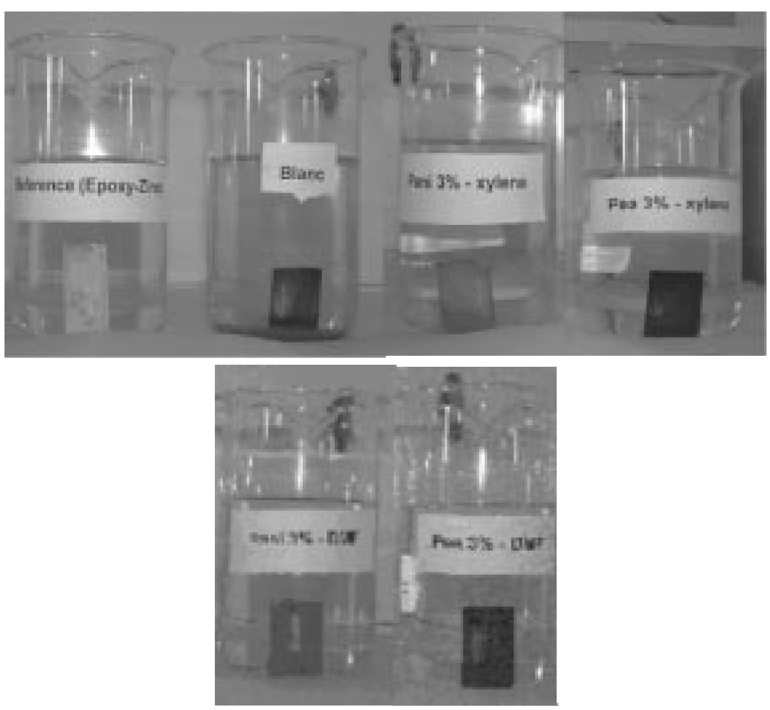

Figure 1 : Photograph of some samples after 30 days of immersion in aerated 3.5% NaCl.

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2.4 Electrochemical corrosion measurements

The electrochemical corrosion measurements were carried out at 25°C in 3.5% wt NaCl aqueous solution. A cylindrical electrochemical cell was used with three electrodes: working electrode (uncoated and coated mild steel); counter electrode (stainless steel cylindrical plaque); reference electrode (saturated calomel (sce) with a luggin capillary). The experiments were performed using a potentiostat/ galvanostat model Autolab, type PGSTAT20. Before polarisation, samples were immersed into the solution and the open circuit potential (OCP) was monitored until a constant value was reached.

2.4.1 Potentiodynamic measurements

Both coated and uncoated mild steel were studied for their potentiodynamic behaviour in NaCl solution. Tafel plots were generated by scanning the potentiel from $E_{i=o}$ to ± 300 mV vs sce with a sweep rate of 1 mV s^{-1}.

2.4.2 Cathodic delamination measurements

The coated steel were scratched at a length of 3 cm and a width of 1 mm, immersed in 3.5% NaCl and cathodically polarised for 24 h at –1 Volt vs sce. To evaluate the delamination resistance of primers, the cathodic current was measured and the delamination surface was observed.

3. RESULTS AND DISCUSSIONS

All data (immersion and electrochemical tests) indicate clearly a decrease in the corrosion rate when the percentage in weight of the conducting polymers used in the coating formulations increase, except for the coating system Pani-DMF. An anomalous behaviour of this primer was observed, the higher protection against corrosion was obtained for the lower weight of Pani (1%).

Here, only the conventional zinc primer and the best primer of each coating system which are:

- Pani (3% wt) – xylene,
- Pea (3% wt) – xylene,
- Pani (1% wt) – DMF,
- Pea (3% wt) – DMF,

will be discussed.

3.1 Immersion test

Results for the full immersion test, wherein corrosion performances of the studied primers were monitored, are reported in table 2 as iron-dissolution (i.e. Total-Fe concentration in the test solution) and are given in Figure 2.

Primer	Total-Fe concentration (mg/l)		
	10 days	30 days	60 days
Uncoated steel	51.22	134.00	201.44
Conventional zinc	0.81	7.31	9.15
Pani – xylene	0.56	6.66	10.03
Pea - xylene	0.31	0.82	1.86
Pani – DMF	0.21	1.83	7.50
Pea - DMF	0.21	0.21	1.13

Table 2 : Total-Fe concentration in the test solution at different immersion time in aerated NaCl 3.5% at a temperature of 25°C.

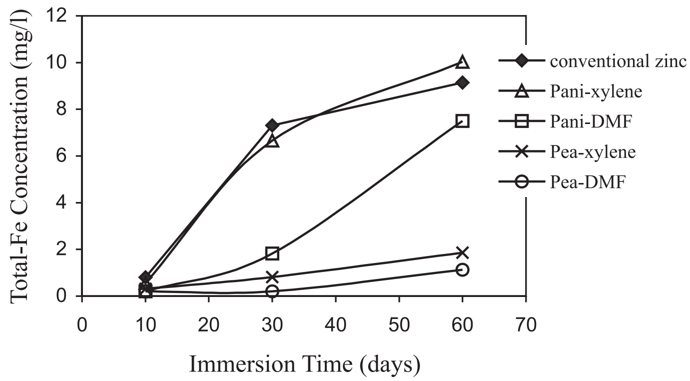

Figure 2 : Total-Fe concentration in the test solution at different immersion time in aerated NaCl 3.5% at a temperature of 25°C.

It is clearly shown in Figure 2 that iron dissolution increase with immersion time in 3.5% NaCl aqueous solution. This figure shows also that whatever the solvent used in the coating formulation, Pea primers gave better corrosion performances compared to that of Pani primers, while the conventional zinc primer was intermediate performer.

Visual observations showed that there were no red-brown corrosion products in tests solutions containing Pea primer coated samples even after 30 days of immersion. The estimated order of the anticorrosive properties of coating systems (based on total-Fe dissolution and visual observations of the specimen and the test solutions) was: Pea-DMF > Pea-xylene > Pani-DMF > Pani-xylene » Conventional (zinc-xylene).

3.2 Electrochemical corrosion measurements

3.2.1 Potentiodynamic measurements

The potentiodynamic polarisation curves (Tafel plots) for samples of mild steel (coated and uncoated) in contact with 3.5% NaCl aqueous solution are shown in Figure 3 and Figure 4. Table 3 lists corrosion potentials observed from the Tafel measurements.

Primer	E_{corr} vs. sce (mV)
Uncoated steel	- 692
Conventional zinc	- 817
Pani-xylene	- 525
Pea-xylene	- 521
Pani-DMF	- 541
Pea-DMF	- 525

Table 3 : Corrosion potentials measurements vs sce for coated and uncoated mild steel immersed in 3.5% NaCl at 25°C.

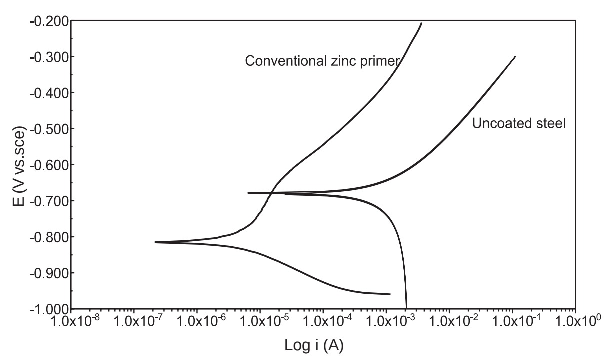

Figure 3 : Tafel plots for mild steel samples (uncoated and coated with a conventional zinc primer) in 3.5% NaCl solution.

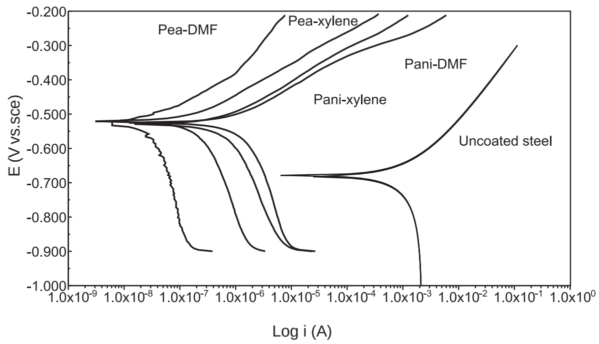

Figure 4 : Tafel plots for mild steel samples (uncoated and coated with conducting polymers based-primers) in 3.5% NaCl solution.

The major observation from Figure 3 and Figure 4 is the coating tendency for the formation of a passive oxide layer for samples covered by primers based on conducting polymers, while there is no tendency for passivation with the conventional primer. Indeed, compared to the uncoated steel, a shift in the corrosion potentials to more positive values (DE » 160 mV) occurs when sample surfaces are covered by primers based on conducting polymers and a shift to more negative value (DE » 125 mV) when it is covered by a conventional one. This passive layer consists of a sandwich structure of Fe_3O_4/g- Fe_2O_3 and are reported by different authors [4, 7, 21].

We can also observe from Tafel plots that a reduction in corrosion current (corrosion rate) occurs when the primer used to protect mild steel from corrosion in saline environment is not conventional.

In addition, the displacement of Tafel plots toward lower values of corrosion current for samples coated with Pea primers compared to Pani primers confirms the results obtained from immersion tests in 3.5% NaCl.

3.2.2 Cathodic delamination measurements

The cathodic delamination was tested to evaluate the performance of primers under rusting and delamination and also, to reflect the role of the anticorrosive agents used in the primer formulations under such conditions. The cathodic current was followed as a measure for delamination at the scratch. The conventional and the four best primers are tested and the results are given in Figure 5.

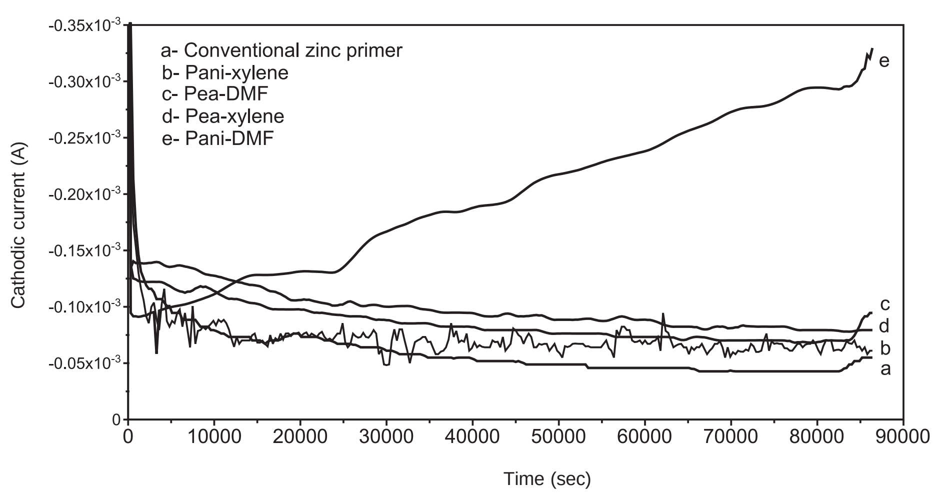

Figure 5 : Delamination test for samples immersed during 24 hours in NaCl 3.5% solution.

It is known that the lower the cathodic current, the higher the delamination resistance. Accordingly, the (Pani-DMF) primer cannot be used to protect mild steel under impressed cathodic conditions in saline environment whereas, the others primers show good properties against delamination even at –1 volt.

It seems to be that the conventional zinc primer have the best resistance delamination, but it should be noted that the value of the applied cathodic polarisation (-1 V) corresponds to an over-protection of 0.5 V for primers containing conducting polymers, whereas it corresponds to an over-protection of 0.2 V for the conventional zinc primer. This is due to the difference existing between the open circuit potential values of the tested primer coated steel samples.

In additional, except for the (Pani-DMF) primer, we can verify by visual observations the strong adherence of the primers to the steel surfaces by the fact that no blistering and no delamination were observed, after 24 hours of immersion in the corrosive environment.

3. CONCLUSION

In this work, a number of epoxy primers were evaluated for their anticorrosive properties on mild steel in saline environment (3.5% wt NaCl). These primers differ from the use of two kinds of anticorrosive agents (conventional or conducting polymer) and two solvents (xylene or DMF) in the coating formulations.

It was found that a protective action of primers based on conducting polymers (Pani or Pea) induce a displacement of the corrosion potentials toward a more noble region for mild steel (cathodic protection) when the conventional zinc primer induces a displacement toward a less noble region (anodic protection).

The results from electrochemical measurements and immersion tests clearly indicate that Pea primers provide better corrosion protection compared to that of the conventional zinc primer and especially compared to that of Pani primers which are a proprietary dispersions supplied by Zipperling Kessler & Co.

In conclusion and as we expected, Pea primers can be preferred over Pani primers. This is probably related to the higher solubility of Pea in the selected solvents.

The corrosion protection behaviour of these primers is studied by electrochemical impedance spectroscopy and our results will be reported at a later date.

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