

CORROSION PROTECTION BY ELECTROPOLYMERISED AND POLYMER PIGMENTED COATINGS – A REVIEW

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ABSTRACT

The aqueous electropolymerisation process can be used for the production of primer coatings on metals. Recent studies have shown that such types of coatings are highly corrosion resistant. Further it is also shown that electropolymerisation coating with pigment is feasible. Besides, the use of polymers such as polyaniline as pigment in paint coatings has been demonstrated. This review summarises the electropolymerisation studies carried out on steel and copper.

I. INTRODUCTION

Electropolymerisation is useful for obtaining adherent and cohesive electron conducting film on metals. In this method, the polymer is obtained *in situ* on the metal from the solution containing monomers. This process is very different from electrophoretic deposition in which the polymer is present in the solution at the beginning of the process. The aqueous electropolymerisation process can be used for the production of primer coating on metals which might be an alternative option to replace the conventional coating systems containing volatile organic solvents. The advantages of aqueous electropolymerisation are: i) the formation of polymer and primer coating in one process; ii) the properties of the coatings can be controlled by varying the electrochemical parameters; iii) the use of aqueous solution eliminates the environmental pollution and easy waste disposal; iv) mild reaction conditions are used and hence the cost of production is low;

v) since the coating is electron conducting, further electrochemical treatments of surfaces are possible; vi) incorporation of reactive metallic powders such as zinc in the coating so that sacrificial protection of substrate is achieved easily. The electropolymerised coatings are found to have high conductivity, good adhesion to the substrate, good paintability and high corrosion resistant property.

The deposition of polyaniline and polypyrrole has been successfully carried out on inert electrodes like Pt, Au etc [1-5]. Due to dissolution of active metals during electropolymerisation, limited studies have been made recently. In this review, the studies carried out on electropolymerisation on steel and copper are summarized.

2. POLYPYRROLE

Initially, the electrodeposition of pyrrole on iron was investigated in different organic solvents. Cheung *et al.* [6] and Ferreira *et al.* [7] have studied the electrodeposition of pyrrole on iron from acetonitrile, propylene carbonate, methanol, tetrahydrofuran, N-N dimethyl formamide, dimethyl sulfoxide, in the presence of tetrabutyl ammonium hexafluoroorthophosphate or tetraethyl ammonium p-toluenesulfonate. They have found that the deposition of polypyrrole film has occurred only in the solvents propylene carbonate, methanol, ethanol and tetrahydrofuran.

The studies of Troch *et al.* [8] have shown that polypyrrole can be deposited on mild steel in aqueous Na_2SO_4 medium and the films are brittle and possessing poor adhesion.

A detailed study on the role of anions on the electrodeposition of polypyrrole from the aqueous electrolytes has been made by Beck *et al.* [9-11]. They reported that polypyrrole coatings could not be deposited on iron from aqueous solution containing anions such as BF_4^- , ClO_4^- , HSO_4^- , SO_4^{2-} , TOS⁻, HCO_3^- , H_2PO_4^- , HPO_4^{2-} and H_2BO_3^- and polypyrrole layers could be obtained from potassium nitrate and oxalic acid electrolytes. Further, it is reported [12,13] that smooth and strong adherent coatings could be obtained from oxalic acid electrolyte.

The electropolymerisation of pyrrole on steel substrate has been carried out in aqueous oxalate solutions in the presence of triethylamine and alkylamine by Su *et al.* [14]. Their results showed that the pH of the reaction medium and applied current density had a great influence on the

electropolymerisation process and the properties of the coatings. Uniform, smooth and strongly adherent coatings were obtained in low pH reaction medium at low applied current density. High current density and high pH of the reaction medium led to brittle and poorly adherent coatings. FTIR studies of the coating have revealed that the polypyrrole coatings contain the counter ions.

The mechanism of polypyrrole coatings on steel from oxalate solution has been studied by Su *et al.* /15/. It has been found by XRD studies that a layer of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ crystals was deposited and passivated the steel sample and the precipitated $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was further oxidized into soluble product when electropolymerisation potential of pyrrole was reached. Electropolymerisation of pyrrole occurred directly on the surface where iron (II) oxalate was decomposed. Further they have shown /16/ that the polypyrrole coatings significantly increase the corrosion potential and reduces the corrosion rate. The coatings were found to inhibit the anodic dissolution reaction and prevent corrosion by isolation and charge transfer mechanism. The coatings formed at pH 2.4 were found to be highly corrosion resistant where the corrosion rates of iron were decreased from 1.05 mmpy to 0.004 mmpy in 1M NaCl. The corrosion resistance of poly(N-methyl pyrrole) coated steel was lower than that of polypyrrole coated steel.

Ferreira *et al.* /17/ have studied the formation of polypyrrole/ TiO_2 composites on mild steel in oxalic acid medium. It has been found that higher pigment concentration incorporated in polymer film is 7.5 % at 5 mA/ cm^2 , pH 4 and stirred baths. XRD studies have indicated that the pigment particles are located inside the film. The SEM micrographs have revealed that the polypyrrole film with TiO_2 are non-porous and compact. The polypyrrole/ TiO_2 films gave more anodic potential than polypyrrole or steel substrates, suggesting that the presence of the pigment improved the protective properties of the film.

3. POLYANILINE

Deberry /18/, studying the electrodeposition of polyaniline (PANI) on stainless steel, observed an anodic protection that reduced significantly the corrosion rate in H_2SO_4 solutions. He also verified that before PANI electrodeposition, a layer of passivated oxide was formed on the steel surface

and he proposed that the PANI film in contact with the oxidized surface stabilized the oxide against the dissolution and/or reduction process.

Troch-Nagels *et al.* /8/, comparing the polypyrrole and polyaniline, observed that PANI itself does not present any corrosion resistance while polypyrrole is strongly resistant.

Sekine *et al.* /19/ also observed that PANI films electrochemically deposited on steel do not satisfactorily protect the surface against corrosion. Lu *et al.* /20/ proposed a mechanism of corrosion protection of steel by PANI films in HCl and NaCl media. The authors concluded that the PANI films could protect the steel surface following a mechanism where the steel passivation occurred with the formation of layers of Fe_2O_3 and Fe_3O_4 . The passivation effect is due to the fact that polyaniline is acting as a redox catalyst and as a noble metal with respect to iron. Further, PANI forms a Iron-PANI complex /21/. Emeraldine base deposited chemically on stainless steel prior to being treated with acids or metal chelating agents protects the metal surface from corrosion in chloride containing acid media /22/. Sazour *et al.* /23/ have studied electropolymerisation of aniline on iron in aqueous solutions containing various inorganic and organic acids under potentiodynamic, potentiostatic and galvanostatic conditions. Smooth adherent coatings were obtained in oxalic acid solution in the potential range -0.6 to 1.5 V. Polyaniline coatings were found to be highly corrosion resistant in a number of corrosive solutions.

PANI has been electrodeposited on iron in oxalic acid media in order to evaluate the protective character of this polymer /24/. The deposition of the polymer layer on iron was performed in a pH 1.4 solution composed of oxalic acid (0.5M), metanilic acid (0.05M) and aniline (0.1M) at a constant potential of 0.3 V vs SSE for 1 hour. PANI film has been found to be efficient for corrosion protection during at least 10 hours in a pH 4.5 sulfate medium. Interaction between the passive layer and polymer has been studied using spectroelectrochemical techniques such as Raman spectroscopy and Reflectivity measurements. Recent studies /25/ have shown that adherent polyaniline coating on iron can be obtained by electropolymerisation of monomers in sulphuric acid media

4. OTHER AROMATIC COMPOUNDS

4.1 Furan

Troch-Nagels *et al.* /8/ have studied the electropolymerisation reaction of furan on mild steel in $\text{H}_2\text{O}/\text{CH}_3\text{OH}$, $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$, 0.05 M H_2SO_4 , 0.08 M Na_2SO_4 . They found that no film was obtained and furan was oxidized at potentials higher than 1.8 V vs SCE.

4.2 Thiophene

Thiophene was electropolymerised on stainless steel from acetonitrile containing 0.1M tetra ethyl ammonium perchlorate and 0.3 M thiophene /8/. Films could be obtained after 10 C Cm^{-2} either at 2.5 V vs SCE or at 0.3 A dm^{-2} .

4.3 2-Aminophenol

Guenbour *et al.* /26/ have studied the electropolymerisation reaction of 2-aminophenol on copper. They found that a coating of high adherence and insulating character was formed on copper. The process involved the deprotonation of the aminophenol molecules which were chemisorbed on the metal surface followed by an anodic oxidation and electropolymerisation. In this process, the polymerization affected the $-\text{OH}$ group by formation of C-O-C bonds while $-\text{NH}_2$ groups were present.

4.4 2-Vinyl-pyridine

Sekine *et al.* /19/ have found that the electropolymerisation of 2-vinyl pyridine film on mild steel is highly corrosion resistant with an efficiency of 90 %. Further they studied the corrosion resistant property of the electropolymerised amines, phenols and hydroxy benzoic acid. They found that in electrooxidation polymerisation films were incomplete, porous and thin films while in electroreduction polymerisation, complete, more compact and thick films were formed.

4.5 5-amino 1-naphthol

The electrodeposition of poly (5-amino-1-naphthol) film on mild steel from aqueous perchloric acid is reported by Menequzzi *et al.* /27/. The polymer films are very adherent to the surface and present the same structure as in the case of platinum electrode. The test for corrosion protection of the polymer coated iron samples was done in 0.4M NaCl + 0.1M HCl.

The particularity of this monomer stems from the presence of two functional groups $-NH_2$ and $-OH$ both can be electrochemically oxidized. In basic medium, the electropolymerisation proceeds through the oxidation of $-OH$ group and yields poly (naph) oxide structure while in acidic medium the selective electrooxidation occurs via NH_2 group. The resulting polymer presents a polyamide structure bearing free OH groups in the chain.

4.6 Fe-Vinyl bipyridine complex

Troch-Nogels *et al.* /8/ have found that no film was formed even on stainless steel at -2 V vs SCE, but a pink coloured film was formed on platinum cathode.

4.7. Phenol

Anodic formation of thick poly oxy-phenylene coatings on iron from phenol-ethylene diamine system has been carried out by Mengoli *et al.* /28/. Thick adhesive coatings on an iron surface have been observed and the thickness of the coatings depended on both the applied potential and also the composition of the solutions. It was possible in a single step to attain the cross linked highly insoluble protective polymer film on the iron surface.

5. POLYMER PIGMENTED COATINGS

Due to environmental restrictions on the use of heavy metal-containing paints, a new class of conducting polymers such as polyaniline have been developed in recent years. The new class of primers containing inherently conducting polymers has more tolerance to pin holes due to the passivating ability of pigments. Mengoli *et al.* /29/ have reported that polyaniline-containing paints offer high corrosion resistant coatings.

Santos *et al.* /30/ have studied the corrosion resistant property of steel coated with polyaniline by spraying a 2% solution of polyaniline in N methyl pyrrolidine. They found that the steel coated with polyamine gained nearly 100 mV in corrosion potential in 3 % NaCl and a low corrosion rate was observed. This change in corrosion potential has been attributed due to the formation of a passivated layer. Further, these studies showed that the PANI film loses water when kept out of the solution and returns to the original state after some time in contact with the solution without losing electrical and mechanical characteristics. This effect is probably due to the presence of air, which keeps PANI in the emeraldine oxidation state.

Wessling *et al.* /31/ have studied the performance of polyaniline primer coatings on steel by salt spray test, electrochemical impedance spectroscopy and Scanning Kelvin-Probe in 3% NaCl. They have found that the coating system with polyaniline primer has been found to be highly corrosion resistant.

A mechanistic investigation of polyaniline corrosion protection using scanning reference electrode technique has been carried out by Kinlen *et al.* /32/. They have found that polyaniline coatings passivate the pinhole defects in coatings. Further they have shown that phosphonic acid salts of polyaniline are more effective for corrosion protection than sulfonic acid salts. A model has been proposed for the protection of polyaniline coatings.

In all the above studies it has been shown that conducting polymer coatings such as polyaniline stabilize the potential of the metal in a passive region and maintain a protective oxide layer on the metal. Both SEM and XPS studies have revealed that an oxide layer has been formed between the PANI coating and the steel surface and is composed mainly of Fe_2O_3 above a very thin Fe_3O_4 layer /33-35/.

It has been reported by Wroblewski *et al.* /36/ that the doped electrically conducting form of polyaniline film (film of thickness 0.005 cm) on steel with epoxy top coat gave excellent performance in 3.5 % NaCl and 0.1 M HCl even at scribed areas. The mechanism of protection of conducting polymer coating has been investigated by Jain *et al.* /37/. It has been stated that the doped conducting polymer will generate an electric field that will restrict the flow of electrons from the metal to an outside oxidizing species thus preventing the corrosion. Among the conducting and non-conducting polyanilines, it has been reported that the non-conducting polyanilines performed well as corrosion resistant coatings /38/. However, studies on the anticorrosive properties of un doped polyaniline casted on mild steel have

shown that the performance of PANI coated system is not good due to poor adhesion /39/. In the review /40/ by McAndrew it was stated that the future for the use of electrically conducting polymers in corrosion resistant coatings appears promising, especially as additives to improve the performance of existing coating system.

6. CONCLUSIONS

Industrial painting of metal substrates can be achieved by direct electropolymerisation of aromatic monomers from aqueous electrolytes. Recent studies have shown that electropolymerisation of aniline and pyrrole on steel can give highly corrosion resistant coatings. Further, these primer coatings are highly conductive and application of top coating by electrodeposition is possible. The possibility of electropolymerisation with pigment particles has been demonstrated. The use of polymers like polyaniline as pigment paint coatings has been shown to offer better corrosion protective coatings.

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