

# Electron conducting organic coating of mild steel by electropolymerization

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The aim was to coat mild steel with an electron conducting polymer in order to replace any possible electrochemical corrosion of the metal by another electrochemical reaction occurring on top of the film. In view of potential industrialization, electropolymerization of a water soluble monomer was studied. In most cases, this was achieved by oxidation, and the substrate had to be passivated. Polyaniline was obtained in nitric acid solution. Films had a good structure but were brittle and powdery on the surface. Except on tin free steel, they were insulating. Polypyrrole was a better candidate. Prepared from a  $\text{Na}_2\text{SO}_4$  solution, films were conductive, ensured good corrosion resistance of the substrate but they were brittle and adhesion to the substrate was not high. Furane, thiophene and iron substituted vinylpyridine complex were tried without success. Further research should consider copolymerization of pyrrole with other monomers.

## 1. Introduction

The aim of this research was to develop a new process to protect mild steel against corrosion. It is well known that corrosion is largely an electrochemical phenomenon. Electrochemical reactions occur at interfaces between an electronic conductor and an ionic conductor. Accordingly, if it is possible to completely cover mild steel with a continuous film of a chemically inert but electron conducting substance, corrosion of the substrate will be avoided, because any electrochemical reaction will occur at the surface of this film without involving the substrate. Other advantages of such an electron conducting film are to allow further electrochemical treatment at its surface, such as electrophoretic painting. Also, reactive metallic powders could be included in the electron conducting film or placed at its surface to achieve sacrificial protection of the substrate without the need for an intimate contact between the metallic grains or with the substrate.

In this paper, electropolymerization is considered as a method to obtain adherent and cohesive electron conducting films. It involves a solution of organic monomer, the transfer of an electron between the substrate and a monomer and the charged monomer leading to the polymerization reaction. For such a process to give a continuous cover of the substrate, the polymer must be insoluble in the electrolyte and the polymerization reaction may not proceed in a direction perpendicular to the substrate.

This process is very different from electrophoresis:

in electropolymerization, the polymer is obtained *in situ* by an electrochemical process, whereas in electrophoresis, the polymer is present in the solution at the beginning of the process.

A literature survey reveals that different monomer solutions can be considered to obtain adherent and electron conducting films. Three types of monomer are especially interesting [1, 2]: benzenic substituted derivatives, heteroaromatic compounds and organo-metallic complexes.

Among benzenic substituted derivatives, aniline can be electropolymerized by oxidation [3-20]. Electronic conductivity of the film varies from  $10^{-13}$  to  $10^{-2} \Omega^{-1} \text{cm}^{-1}$ . Properties depend largely on the support electrolyte: in acid solution, semi-conducting films are obtained on noble metals, but in water-methanol solutions at high pH non conducting films are obtained on mild steel. Phenol can also be electropolymerized by oxidation of phenolate anions at high pH, giving polyoxyphenylene. With an inorganic base very thin and adherent films are obtained. With saturated amines polymerization occurs towards the bulk of the solution. With unsaturated amines wet films are obtained with a poor coverage of the substrate.

Heteroaromatic polymers can easily be obtained by electrochemical oxidation. For pyrrole [21-33], with an organic electrolyte containing acetonitrile and perchlorate ions, polymers are highly conductive: for example  $10^{-2} \Omega^{-1} \text{cm}^{-1}$ , probably because some perchlorate ions act as doping agents. Inorganic acid solutions can also be used. Again, some anions are

observed in the polymer. Other heteroaromatic monomers can be used: indol, azulene, thiophene [34–40] and furane.

Organometallic complexes like vinylpyridine partly substituted by iron or ruthenium or eventually by other metals can also be electropolymerized [41, 42]. The advantage is that the process occurs by reduction instead of by oxidation. However, the monomers are not available on the market and must be synthesized at laboratory scale.

It can be concluded that it is possible to obtain electron conducting films by electropolymerization. However, so far, except for polyoxyphenylene and for polyaniline, they were all obtained on platinum, on semiconductors or on passive metals like stainless steel, where corrosion of the substrate can be neglected. This is not the case on mild steel.

A prospective research programme was conducted in order to evaluate the feasibility of obtaining electron conducting electropolymerized films on mild steel. These films must satisfy to the following conditions:

- good electron conductivity
- good adhesion to the substrate
- good corrosion resistance of the substrate
- good weldability
- plastic deformation of the substrate
- good paintability
- good behaviour during the curing of further paint layers.

Moreover, the process must not be too expensive, and must be amenable to easy industrial application. Accordingly, aqueous electrolytes were favoured.

## 2. Experimental procedures

The electrolytic cell was very simple: a closed 500 ml vessel allowing work under an inert atmosphere, without agitation. The electrodes were 55 mm × 90 mm sheet coupons, 1 mm thick for stainless steel and 0.25 mm for mild steel. They were placed vertically at 20 mm distance and the exposed surface was 13 cm<sup>2</sup>. The temperature was kept constant at 20 °C.

The thickness of the films was determined by three different methods. The first involved weighing 20 samples obtained under the same conditions and measuring the density of the films by sink or float in organic liquids of various densities. The second method was by compressing a certain number of coated samples between two thick steel blocks and observing the cross section after metallographic polishing. The third was based on a conventional magnetic induction thickness measurement apparatus (FORSTER Monimeter S2.310).

The porosity of the films on mild steel was measured by copper cementation after 5 min immersion in a neutral copper sulphate solution at 37 g dm<sup>-3</sup> Cu<sup>2+</sup> or in acid copper sulphate solution (192 g dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, 37 g dm<sup>-3</sup> Cu<sup>2+</sup>) at room temperature. Some samples were examined in cross section after cementation, showing where copper metal nuclei were generated.

Adhesion of the films was determined according to an ASTM scratch test. The film was scratched by a comb in two perpendicular directions in order to obtain two series of six scratches through the film down to the metal substrate. Tearing out was performed by means of a standardized adhesive tape. Results were numbered from zero for perfect adhesion to 5 when more than 65% of the film was torn off. Surface morphology of the films was characterized by SEM after metallization under vacuum. The chemical composition of the films was determined by Auger analysis.

Electrical conductivity was measured by two different methods. The four dots method could only be used when the film was placed on an insulating substrate. This was achieved by embedding the film in a Mecaprex type KM resin and tearing the embedded film from the metal substrate, or by dissolving the steel substrate in sulphuric acid and then depositing the film on a sample holder for optical microscopy. The current was then fed to two copper contacts pressed on the surface of the film and a voltage drop was measured between two other copper contacts parallel to the first ones and placed between them, the whole system having a well defined rectangular shape. With this method the so-called “lateral” conductivity (parallel to the substrate) was obtained. The two dots method involved placing two well defined copper electrodes on each side of the strip, one on the side covered by the film, the other on the bare side. This method allowed measurement of the “transverse” conductivity of the film (perpendicular to the substrate). However, conductivity values depended on the pressure applied to the electrodes. Correct values were obtained when pressures were high enough for conductivity to become independent of the pressure, but this was achieved on few occasions because electric breakdown occurred most of the time before reaching this plateau.

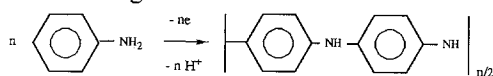
The electrochemical behaviour of the films was also studied. Electronic properties were characterized by polarization curves of coated steel samples in 10<sup>-2</sup> M sulphuric acid. This also allowed determination of the redox properties of the film and evaluation of the kinetics of the O<sub>2</sub>/OH<sup>-</sup> reaction on this film. The electronic nature of conductivity of the films was also checked by electrodepositing zinc from a 80 g dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, 60 g dm<sup>-3</sup> Zn<sup>2+</sup> solution. In this case, results depend not only on conductivity but also on hydrogen overpotential on the film. Accordingly, copper electrodeposition was also studied. To avoid cementation, a cyanide solution was chosen: 74.5 g dm<sup>-3</sup> CuCN, 92 g dm<sup>-3</sup> NaCN, 30 g dm<sup>-3</sup> NaOH, at 20 °C and 6 A dm<sup>-2</sup> cathode current density. Anaphoretic painting was also checked on a Levis industrial bath at pH 8.9 containing 11.2% solids after drying half an hour at 160 °C. Anaphoresis occurred for 2 min at 250 V. It was followed by curing for ten minutes at 190 °C.



Fig. 1. SEM surface micrograph of a polyaniline film obtained on mild steel. Basic solution  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ : 50/50 vol %,  $\text{KOH}$ : 0.035 M; aniline: 0.3 M. Temperature 20°C no agitation. Potentiostatic: 1200 mV/SCE with 0.5 to 0.2  $\text{A dm}^{-2}$ . Magnification  $\times 1000$ .

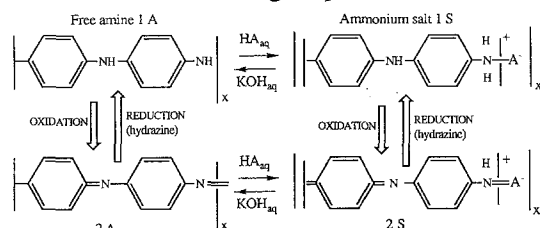
### 3. Polyaniline

This benzenic compound is electropolymerized by oxidation according to the reaction:



According to the literature, the potential needed for making films is between 0.9 and 1.4 V/SCE and the electrolytic solvent is either water or water saturated with methanol.

It should be noted that polyaniline has four different structures according to pH and oxidation:



Only the oxidized form 2S is conducting ( $1$  to  $10 \Omega^{-1} \text{cm}^{-1}$ ), and is suitable for this research. Of course, oxidation and acid solution are the worst conditions in which to deposit a continuous film on mild steel. It was accordingly decided to try first basic solutions, with the hope of converting the films later to a conducting form by dipping in an acid solution. Various electrolytes were tried, with a 50/50 vol % mixture of water and methanol as solvent and 0.035 M  $\text{KOH}$  as supporting electrolyte. Aniline was 0.3 M. Eventually, allylamine was added as corrosion inhibitor and cellasolve to improve homogeneity and the covering power of the films. All electrolyses were at 20°C without agitation. Brown films were obtained both on stainless steel and on mild steel, by electrolysis at constant current density ( $1$ – $2 \text{ A dm}^{-2}$ ), at constant anode potential ( $0.8$ – $1.5 \text{ V/SCE}$ ) or by cyclic voltammetry. They covered all the electrode, but were non-homogeneous: they looked like flattened droplets of polymer on the electrode (Fig. 1). They were insulating, and it was not possible to change this property by dipping in sulphuric acid even at pH from 0 to 1.

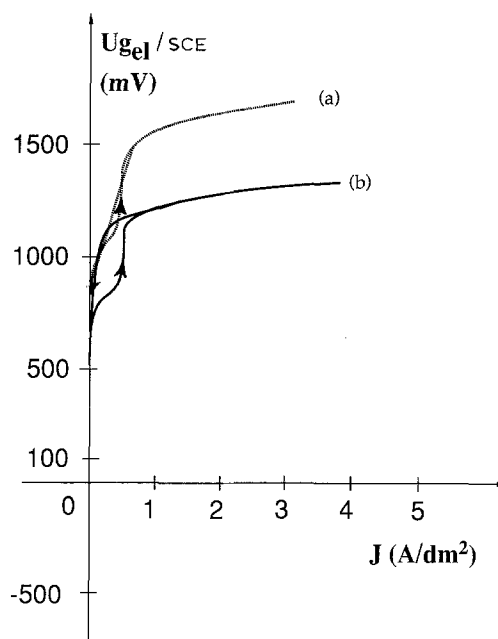


Fig. 2. Potentiokinetic curves of stainless steel at 20°C. (a) 0.13 M  $\text{H}_2\text{SO}_4$ ; 20 vol %  $\text{CH}_3\text{OH}$ ; (b) 0.13 M  $\text{H}_2\text{SO}_4$ ; 0.3 M aniline; 20 vol %  $\text{CH}_3\text{OH}$ .

Neutral solutions were then tried by replacing  $\text{KOH}$  by  $\text{Na}_2\text{SO}_4$  at the same concentration. However, to allow dissolution of the sodium sulphate, the ratio  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  was 70/30 vol %. Despite a higher dissolution of the substrate, films were very similar to those obtained in basic solutions. They were also insulating and could not be made conductive by dipping in acid.

The first acid solution tried was 20 vol %  $\text{CH}_3\text{OH}$  0.13 M  $\text{H}_2\text{SO}_4$ , and 0.3 M aniline. The behaviour of stainless steel was checked in this electrolyte with and without aniline by drawing potentiokinetic curves (Fig. 2).

Aniline oxidation started at 800 mV/SCE. Potentials were kept lower than 1150 mV/SCE to avoid strong corrosion of the substrate and oxygen evolution. Preparing the films at constant potential resulted in a progressive decrease of current density (Fig. 3). On the other hand, if current density was kept constant, the electrode potential increased with time (Fig. 4). Systematic experiments were performed between 800 and 1400 mV/SCE at constant potential. No film was observed below 800 mV/SCE and above 1400 mV/SCE, films were very bad. Current efficiency for films production was near 50%. At constant current density, the optimum range was between 0.05 and 0.3  $\text{A dm}^{-2}$  (initial anode voltage between 1000 and 1200 mV/SCE). The lowest values of current density gave the best films. As soon as the film was formed, the anode potential increased towards oxygen evolution. All the films were black and powdery.

Mild steel must be passivated in order to avoid dissolution of the substrate during aniline oxidation. Immersion in fuming nitric acid was not satisfactory: polyaniline films obtained by subsequent electrolysis in the above-mentioned electrolyte were very brittle and only partially covering. Reproducibility was also

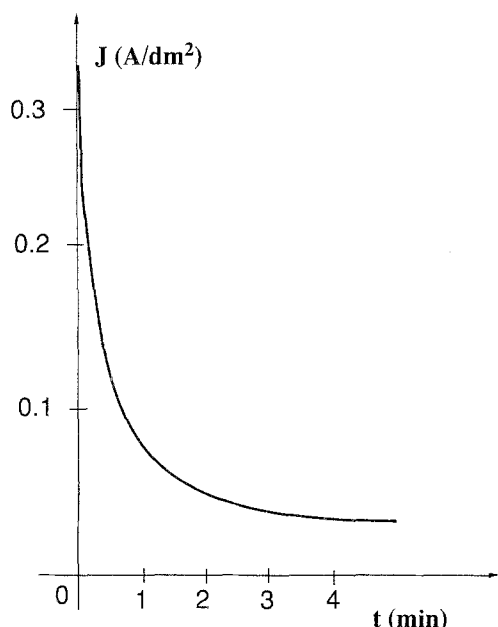


Fig. 3. Current density against time for the electropolymerization of aniline on stainless steel at 1100 mV/SCE in a 20 vol %  $\text{CH}_3\text{OH}$ , 0.13 M  $\text{H}_2\text{SO}_4$  and 0.3 M aniline solution at 20°C with no agitation.

very poor. Electrochemical passivation in borate solution (0.15 M  $\text{H}_3\text{BO}_3$ ; 0.037 M  $\text{Na}_2\text{B}_4\text{O}_7$ ) involving degreasing the sample in trichlorethane, galvanostatic reduction in the borate solution at  $0.05 \text{ A dm}^{-2}$  for 10 min followed by anodic oxidation at  $1 \text{ A dm}^{-2}$  for 2 s was also studied. Figure 5 shows that continuous dissolution of the substrate occurred when no aniline was present in the sulphuric acid solution. Figure 6 shows that passivation was better in the presence of aniline. It was not possible to obtain polyaniline films by cyclic voltametry after borate passivation; only electrolysis at constant current ( $1\text{--}2 \text{ A dm}^{-2}$ ) or constant anode potential (1200 to 1500 mV/SCE) resulted in bad quality films: very powdery and only partly covering, they contained a high concentration of iron salts due to anodic dissolution of the substrate during electrolysis. Corrosion inhibitors were then added to electropolymerization sulphuric acid solution: formol reacted with aniline and formed a precipitate.  $\text{SbCl}_3$  and allylamine had no effect on the films.

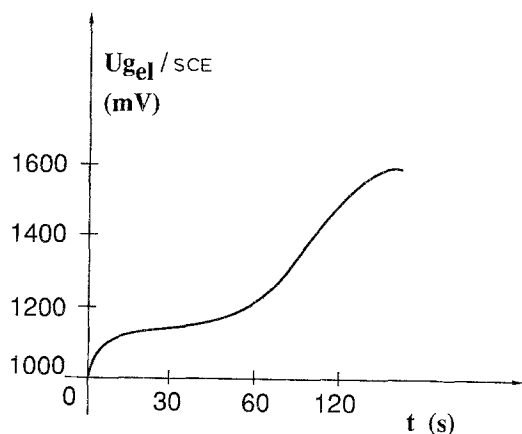


Fig. 4. Anode potential against time for the electropolymerization of aniline on stainless steel at  $0.3 \text{ A dm}^{-2}$  in a 20 vol %  $\text{CH}_3\text{OH}$ , 0.13 M  $\text{H}_2\text{SO}_4$  and 0.3 M aniline solution at 20°C with no agitation.

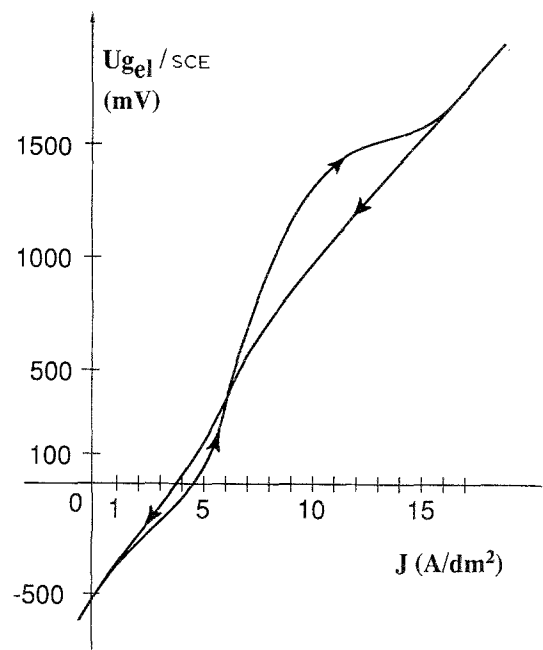


Fig. 5. Potentiokinetic polarization curve of mild steel previously passivated electrochemically in a borate solution. This curve in a sulphuric acid solution without aniline: 0.13 M  $\text{H}_2\text{SO}_4$ , 20 vol %  $\text{CH}_3\text{OH}$  at 20°C with no agitation.

It was then decided to replace the sulphuric acid solution by a nitric acid one (0.1 M  $\text{HNO}_3$ ; 0.3 M aniline) for the electropolymerization process, without previous passivation. Figures 7 and 8 show that aniline oxidation occurred in the same potential range as in sulphate solution and also that anodic dissolution of the mild steel decreased. It was possible to obtain

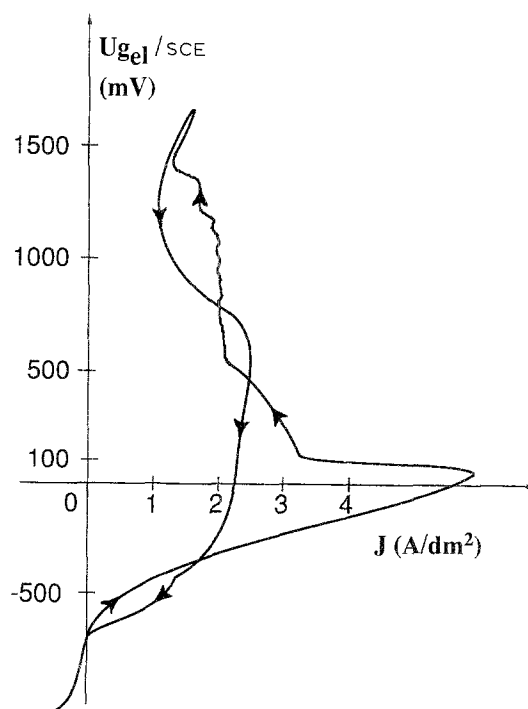


Fig. 6. Potentiokinetic polarization curve of mild steel previously passivated electrochemically in a borate solution. This curve in a sulphuric acid solution with aniline: 0.13 M  $\text{H}_2\text{SO}_4$ , 20 vol %  $\text{CH}_3\text{OH}$ ; 0.3 M aniline at 20°C with no agitation.

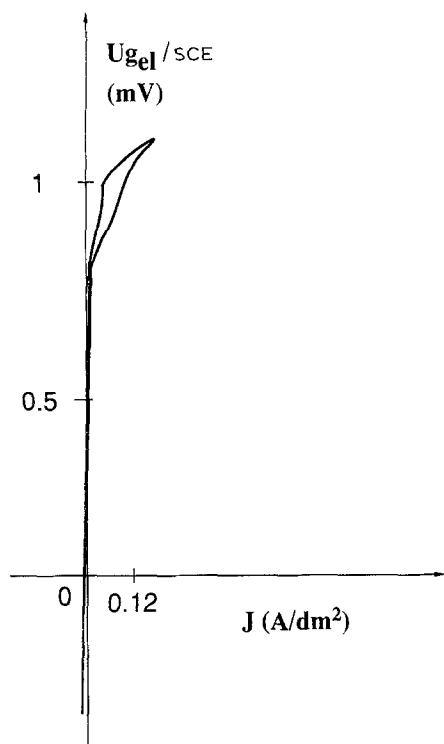


Fig. 7. Potentiokinetic polarization curve of stainless steel in a 0.1 M  $\text{HNO}_3$ , 0.3 M aniline solution at 20°C with no agitation.

reproducible covering films on degreased and eventually etched mild steel from this solution. When working at constant anode potential, current density decreased against with time as shown in Fig. 3, while working at constant current density resulted in progressive increase in anode potential as in Fig. 4. All films were black in colour. Satisfactory current densities were 0.1 to 1  $\text{A dm}^{-2}$ , or anode potentials were 900 to 1500 mV/SCE.

Properties of the films obtained in nitric acid solution can be summarized as follows:

(i) At  $0.7 \text{ C cm}^{-2}$ , the thickness was between 1.5 and 2  $\mu\text{m}$ , with a good agreement between weighing and induction measurements. Cross sections were useless because the film was broken away during cutting and polishing.

(ii) In neutral solution, the porosity measured by copper cementation was low and depended on film thickness:  $0.7 \text{ C cm}^{-2}$  was quite good, although a few copper crystals were still observed. Metallographic cross sections showed copper crystals to be initiated at the film/steel interface. When films were dipped in acid solutions, they were badly attacked, and strong copper cementation occurred.

(iii) Adhesion could not be measured because the surface of the films was powdery, even after curing ten minutes at 170°C.

(iv) Although powdery, films showed a good surface structure on SEM micrographs (Fig. 9). Auger analysis showed noticeable concentrations of oxygen and iron. Auger depth profile analysis showed a progressive increase in iron concentration and a similar decrease in carbon concentration in the whole film thickness.

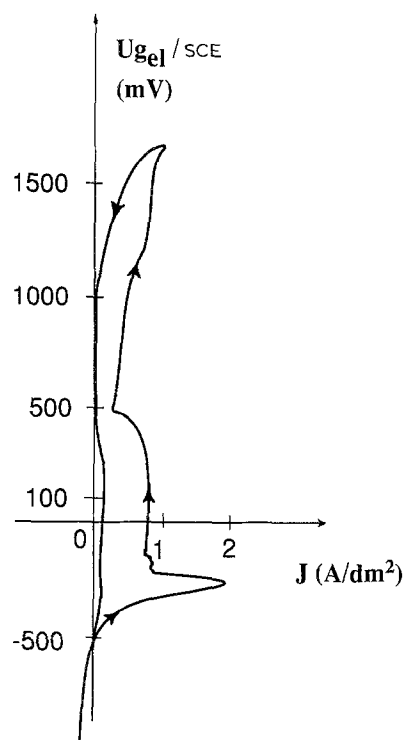


Fig. 8. Potentiokinetic polarization curve of mild steel in a 0.1 M  $\text{HNO}_3$ , 0.3 M aniline solution at 20°C with no agitation.

(v) The mechanical properties of films were bad: they were brittle.

(vi) The lateral and vertical conductivities of films were very low.

(vii) Polarizing anodically mild steel samples covered by polyaniline showed anodic dissolution of the substrate to occur only slightly slower than for bare steel (0.01 M  $\text{H}_2\text{SO}_4$ ; 1  $\text{A dm}^{-2}$  at 0 mV/SCE).

(viii) It was not possible to paint mild steel covered by polyaniline films by anaphoresis: films were insulating in their oxidized and/or reduced forms.

It can be concluded that polyaniline films did not meet the requirements for mild steel protection. However, anode potentials used for polymerization were

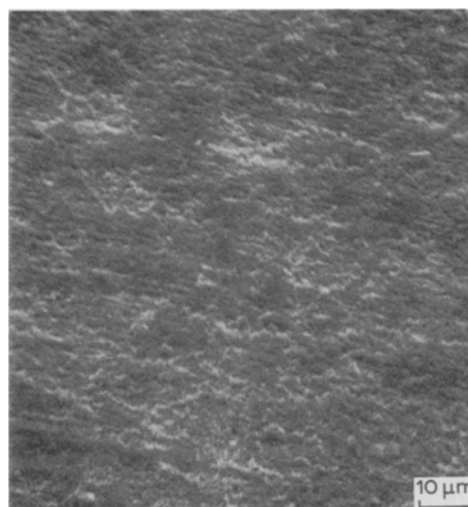


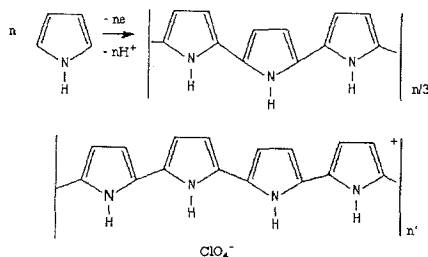
Fig. 9. SEM surface micrograph of a polyaniline film obtained on mild steel. Nitric acid solution: 0.1 M  $\text{HNO}_3$ ; 0.3 M aniline at 20°C with no agitation. Potentiostatic: 1450 mV/SCE and 0.8 to 0.2  $\text{A dm}^{-2}$ . Magnification  $\times 1000$ .

rather high in most experiments due to the need to passivate the substrate. This could have resulted in some peroxidation of the films. To check this possibility, a few more experiments were performed on tin free steel (TFS – mild steel covered electrolytically by a very thin passivating film of Cr-Cr<sub>2</sub>O<sub>3</sub>, approximately 50 nm thick).

On these substrates, polyaniline films were obtained in sulphuric acid solutions already described. They completely covered the electrodes which could then be painted by anaphoresis. However, films were porous, powdery and brittle and, accordingly, it was decided to study another monomer.

#### 4. Polypyrrole

Pyrrole electrochemical oxidation can occur in organic and in aqueous solution. In acetonitrile containing perchlorate ions, polymer films can be obtained with a conductivity in the range of  $10^2 \Omega^{-1} \text{cm}^{-1}$ . This is due to doping the polymer by oxidation and to electrostatic incorporation of anions in its structure:



Polypyrrole can also be obtained from acid aqueous solutions (H<sub>2</sub>SO<sub>4</sub>, HCl, HBr). In this case, chemical analysis of the films show again that anions are included. In this research, only aqueous solutions were studied.

In sulphuric acid solution (0.01 M H<sub>2</sub>SO<sub>4</sub>; 0.5 M pyrrole), potentiokinetic curves from stainless steel showed that oxidation of pyrrole started at 500 mV/SCE. The speed of this reaction increased continuously with anode potential and gave rise to a black film whose thickness increased with the duration of the electrolysis. Forward and reverse parts of the curve were the same. Moreover, the current remained constant when the films were made at constant anode potential and vice versa. Good films could be obtained at current densities in the region of  $10 \text{ A dm}^{-2}$  with only some magnetic agitation. However, no film could be obtained on mild steel, even prepassivated: only substrate dissolution was observed.

A less corrosive electrolyte was accordingly chosen: 0.08 M Na<sub>2</sub>SO<sub>4</sub>; 0.5 M pyrrole. Figure 10 gives the potentiokinetic curves on stainless steel in solutions with and without pyrrole. It can be seen that pyrrole oxidation starts at 800 mV/SCE and that the current of the reverse curve is higher than for the forward curve. Potentiostatic and galvanostatic films were made at anode potentials ranging from 800 to 1400 mV/SCE and at current densities ranging from 0.5 to  $10 \text{ A dm}^{-2}$ . All films were black and covered the substrate entirely, but adhesion was poor. Figure 11 shows the potentiokinetic curves on mild steel. With-

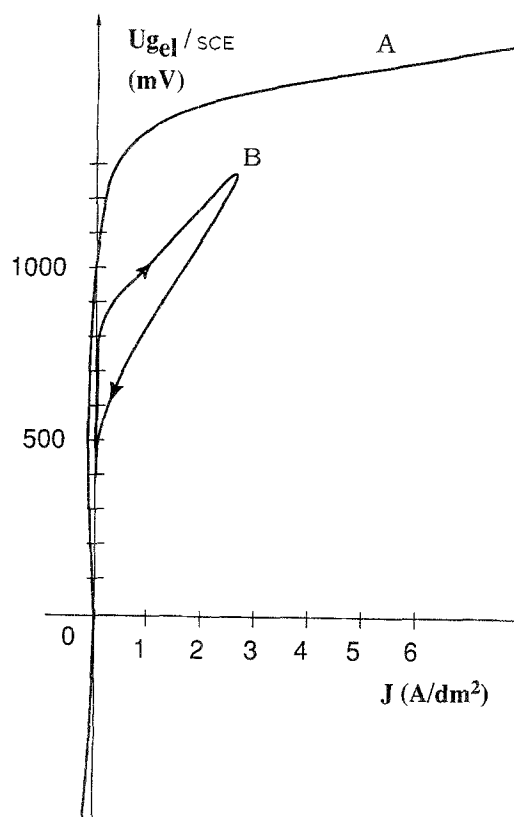


Fig. 10. Potentiokinetic polarization curve of stainless steel in a 0.08 M Na<sub>2</sub>SO<sub>4</sub> solution without pyrrole (curve A) or with 0.5 M pyrrole (curve B) at 20°C with no agitation.

out pyrrole, continuous anodic dissolution of steel occurs. With pyrrole, anodic dissolution of the substrate was reduced and a black film of polymer started to appear at 700 mV/SCE. Potentiostatic and galvanostatic experiments were performed in the range of 800 to 1400 mV/SCE and 0.5 to  $5 \text{ A dm}^{-2}$ . The current

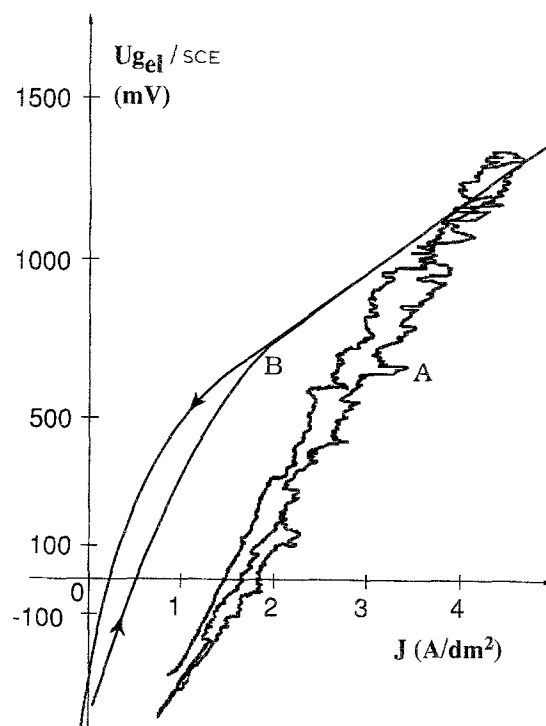


Fig. 11. Potentiokinetic polarization curve of mild steel in a 0.8 M Na<sub>2</sub>SO<sub>4</sub> solution without pyrrole (curve A) or with 0.5 M pyrrole (curve B) at 20°C with no agitation.

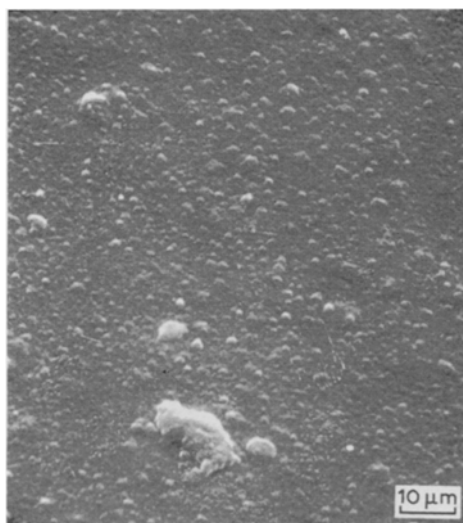


Fig. 12. SEM surface micrograph of a polypyrrole film obtained on mild steel in a 0.08 M  $\text{Na}_2\text{SO}_4$ ; 0.5 M pyrrole at 20°C with no agitation. Potentiostatic: 1100 mV/SCE and 1.5 A  $\text{dm}^{-2}$ . Magnification  $\times 1000$ .

remained constant when working at constant anode potential and vice versa. Films were all black in colour. They were not powdery, but were easily detached from the substrate by means of a glue tape. Figure 12 shows that films were quite homogeneous and fine grained with a few local protuberances. Further experiments were made in order to improve adhesion. It was possible to derive a critical thickness of the films above which adhesion became very bad: 1.4 C  $\text{cm}^{-2}$  for films made at 900 mV/SCE and 0.5 A  $\text{dm}^{-2}$ ; 0.5 C  $\text{cm}^{-2}$  at 5 A  $\text{dm}^{-2}$  and 0.3 C  $\text{cm}^{-2}$  at 10 A  $\text{dm}^{-2}$  on degreased mild steel. Prepassivation of mild steel was found deleterious, and increased the anode potential necessary for making the film. On the contrary, electrolytic pre-etching (30 s at 50 A  $\text{dm}^{-2}$  in 1 M  $\text{H}_2\text{SO}_4$ ) proved quite satisfactory: good adhesion could be obtained for higher thicknesses than stated above.

Properties of the films made in this neutral sulphate solution on mild steel can be summarized as follows:

(i) At 0.7 C  $\text{cm}^{-2}$ , the thickness was of about 2.2  $\mu\text{m}$ , with a good agreement between the three methods of measurement.

(ii) In neutral solution, the porosity of the films was very low and decreased after curing at 170°C for 10 min. In acid solution, the film was rapidly destroyed.

(iii) Adhesion to the substrate depended on the pre-etching of the substrate and on the postcuring. Without curing and etching, ASTM scratch test values were 5, and remained at 5 with curing alone. With etching and no curing, the value was 3. It became 1.5 to 2 when pre-etching and curing were used together. No change in morphology was observed.

(iv) Films were not powdery in surface and had a good surface structure (Fig. 12). Auger analysis showed carbon, nitrogen, sulphur and oxygen. These two latter elements were probably due to  $\text{SO}_4^{2-}$  anions. They were distributed homogeneously in the whole thickness of the films. No iron was visible.

(v) Mechanical properties of the films were bad:

they were brittle. Curing improved this property slightly.

(vi) Lateral electrical conductivity of films obtained at 0.7 C  $\text{cm}^{-2}$  was 1  $\Omega^{-1}\text{cm}^{-1}$ .

After curing, the conductivity had fallen to 0.1  $\Omega^{-1}\text{cm}^{-1}$ . These values were lower than those indicated in the literature, but were quite satisfactory for organic materials. Values for the vertical electrical conductivity were erratic: no satisfactory steady value could be derived as a function of the mechanical pressure due to breakage of the film.

(vii) Polarizing anodically mild steel samples covered by polypyrrole showed anodic dissolution of the substrate to occur 15 times slower than for the bare substrate (0.01 M  $\text{H}_2\text{SO}_4$ , 0.05 A  $\text{dm}^{-2}$  at 0 mV/SCE). Current remained low up to 400 mV/SCE. Above this value, oxidation of the film was observed. The film was destroyed when oxygen evolution occurred, at about 2 V/SCE.

(viii) It was possible to paint mild steel covered by polypyrrole films by anaphoresis. Conditions for painting were the same as for bare mild steel.

It can be concluded that polypyrrole is a good candidate for mild steel protection. However, adhesion, mechanical properties and electrical conductivity should be improved.

Further experiments were made. In a tetraethylammonium perchlorate solution (0.05 M  $\text{Et}_4\text{NClO}_4$ ; 0.4 M pyrrole), films were less adherent than in  $\text{Na}_2\text{SO}_4$ . They were also slightly powdery on the surface. At the interface steel/film, some iron hydroxide precipitate was observed due to higher dissolution of the substrate. Auger analysis showed that chlorine and oxygen were homogeneously distributed in the films, probably as  $\text{ClO}_4^-$  anions.

Sodium sulphonate was also tried in order to increase the conductivity. However, these solutions are acid, and films were only obtained on stainless steel. Conductivity was about 50  $\Omega^{-1}\text{cm}^{-1}$ .

Incorporation of metallic particles in the films during production was difficult, because polymerization is obtained by oxidation, and metal deposition is due to reduction. This was tried by an alternating current method, but metal was only deposited in the open pores of the film.

## 5. Other heteroaromatic compounds

Furane was studied in three different types of electrolytes. In  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  or  $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$  at 33 vol % alcohol, 0.05 M  $\text{H}_2\text{SO}_4$  or 0.08 M  $\text{Na}_2\text{SO}_4$  with as supporting electrolyte and 0.5 M furane; no film was obtained. Furane was oxidized at potentials higher than 1.8 V/SCE, and corrosion of the substrate and oxidation of the solvent were the main reactions.

In dimethylformamide as the solvent, with 0.1 M tetraethylammonium perchlorate and 0.3 M furane, the only reaction observed on stainless steel and on mild steel was corrosion of the substrate with precipitation of iron salts at the surface.

In acetonitrile, with the same composition as for

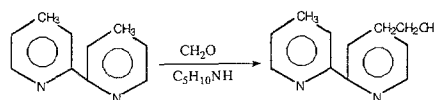
dimethylformamide, dissolution of steel was the main reaction. Very thin ( $0.1\ \mu\text{m}$ ) films could only be obtained on stainless steel at  $2\ \text{V/SCE}$  for  $10\ \text{C cm}^{-2}$ . Electrical conductivity was  $10\ \Omega^{-1}\ \text{cm}^{-1}$ , but the films were very brittle.

Thiophene is insoluble in aqueous solutions. It is only oxidized at potentials higher than  $1.6\ \text{V/SCE}$ . Accordingly, only acetonitrile was used as a solvent, with  $0.1\ \text{M}$  tetraethylammonium perchlorate and  $0.3\ \text{M}$  thiophene. Films could only be obtained on stainless steel after  $10\ \text{C cm}^{-2}$  either at  $2.5\ \text{V/SCE}$  or at  $0.3\ \text{A dm}^{-2}$ . These very high anode potentials could not be considered for surface treatment of mild steel.

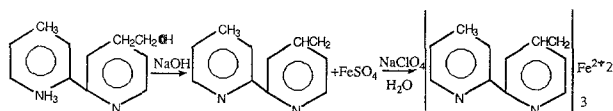
## 6. Organometallic complexes

Electropolymerization of  $[\text{Fe}(\text{vinylbipyridine})]^{2+}$  complexes was considered because films could be obtained by reduction instead of by oxidation. During reduction, the oxidation state of the metal ion remains unchanged and electrical conductivity results from electron jump between the two valency state of the metal ions.

The organic ligand was synthesized according to



followed by the reaction leading to the monomer including iron



The ligand was prepared starting from 4,4'-dimethyl-2,2'-bipyridine available on the market. Two fractions were obtained, respectively at 80 and 50% of the desired ligand. Purification by chromatography was not possible because of the reverse reaction. Complexation to the monomer including iron was made on this impure ligand. The monomer, deep red in colour, was not purified either.

According to the literature, reduction of the monomer occurs only at very negative potentials, between  $-1.5$  and  $-3\ \text{V/SCE}$ . Monomers are, moreover, insoluble in water. Acetonitrile was used as the solvent, in the presence of  $0.1\ \text{M}$  of methanol or of tetraethylammonium perchlorate and  $10^{-3}\ \text{M}$  of the monomer. With stainless steel electrodes, reduction seemed to start at  $-2\ \text{V/SCE}$ , but no film appeared on the cathode. Iron salt precipitate appeared in solution due to anode corrosion. With platinum electrodes, polarization curves were similar as with stainless steel. After two hours of electrolysis at  $-2.2\ \text{V/SCE}$  and  $0.5\ \text{A dm}^{-2}$  the platinum cathode showed a slightly pink colour without true formation of a film: the colour seemed due to an increase in complex concentration near the cathode, staying on the electrode after evaporation of the solvent.

## 7. General conclusions

Electropolymerized polyaniline films were obtained on mild steel either after prepassivation or directly in nitric acid aqueous solution. Films did not meet the requirements for industrialization of the process: they were brittle, did not allow anaphoretic painting except on tin free steel, and did not increase corrosion resistance of the substrate.

Polypyrrole was a better candidate. Films could be obtained in sodium sulphate aqueous solution without pretreatment of the substrate. They were conductive enough to allow anaphoretic painting without changing the usual conditions for bare mild steel. Corrosion resistance was substantially increased. However, adhesion to the substrate was poor and films were brittle. Adhesion could be increased by pre-etching the substrate and by curing. Brittleness remained a problem.

Other possibilities considered (furan, thiophene and iron vinylbipyridine complexes) proved unsatisfactory.

Further research should be done with polypyrrole with the aim of improving the mechanical properties. Copolymerization with other monomers should be considered.

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