

# Anodic Synthesis of Polyaniline Coatings onto Fe Sheets\*

GIULIANO MENGOLI, MARIA TERESA MUNARI, PAOLO BIANCO,  
and MARCO M. MUSIANI, *Istituto di Polarografia ed Elettrochimica  
Preparativa del C.N.R. Corso Stati Uniti, 4-35100 Padova, in collaboration  
with C. R. FIAT Orbassano, 50-Torino, Italy*

## Synopsis

Aniline Black coatings were obtained on Fe anodes by electrolyzing a basic solution of aniline in a water-methanol medium. Allylamine (an inhibitor of Fe corrosion), although not essential to the process, imparts better efficiency to it. The deposited polymers contain 15–20% azobenzene and exhibit semiconductor properties. The three nitroaniline isomers need a more efficient corrosion-inhibition system. They may be polymerized to adherent films in the presence of both allylamine and  $K_2CrO_4$ .

## INTRODUCTION

The anodic oxidation of aniline to polymeric products (Aniline Black) has been known for a long time.<sup>1</sup> This reaction is performed in sulfuric acid at Pt electrodes, and the polymer is obtained in a dissolved or dispersed form. Only a few investigators, by oxidizing aniline both in aprotic and aqueous media, have recently reported filming of Pt anodes by Aniline Black.<sup>2,3</sup> By taking the electric properties of the polymers<sup>4,5</sup> into account, these works aimed at obtaining either modified or semiconducting electrodes for multipurpose use.

Data related to synthesis of polyaniline coatings on Fe are reported here: passivation of Fe and use of a suitable corrosion inhibitor can achieve aniline oxidation at a nonnoble metal anode. The aim on one hand was to obtain adhering films of a reacting polymer onto the most technologically interesting and common metal by a single-stage process and on the other, to assess the corrosion protection given by these films to the substrate.

## EXPERIMENTAL

### Chemicals

All compounds used in this study were commercially available reagent-grade chemicals. The reaction medium consisted of water-methanol mixtures.

The Fe samples had standard dimensions of  $23.5 \times 2.5 \times 0.05$  cm, although the surface dipped in the anodization bath was not more than  $25 \text{ cm}^2$ . The Fe samples, when not otherwise stated, were cleaned before coating in a degreasing acid bath.

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## Apparatus and Procedure

The electrolyzer consisted of a cylindrical vessel filled with 100 ml of the experimental solution in which the Fe sheet, immersed in the middle, constituted the anode, and a Pt coil which surrounded the sheet was the cathode.<sup>6</sup> A constant potential difference was applied between these electrodes, and the current decrease caused by resistance of the forming film was monitored by an ammeter. Once electrolysis was stopped, the coated sheets were rinsed in water and then either dried at room temperature or cured in an oven.

The constitution of the coating material, once it was recovered from the substrate, was investigated by instrumental methods including pyrolysis coupled with mass spectrometry.<sup>7,8</sup>

## RESULTS

### Aniline Black Coatings

#### *Features of the Process*

The application of an anodic potential to a Fe sheet immersed in an alkaline medium, according to a Pourbaix diagram,<sup>9</sup> brings about passivation of the metal (for not exceedingly high potentials applied). However, the passivating layer of Fe oxides does not hinder charge transfer, and thus, on a passivated Fe sheet, anodic oxidation may occur which, considering the relative redox potentials, would otherwise not occur on the bare metal. Indeed, by anodizing on an Fe sheet sample 100 ml water-methanol equal volumes containing 0.33 mol/L aniline and 0.035 mol/L KOH (system A) by voltages in the 4–8 V range, the current decreases with time (see dashed curves of Fig. 1) owing to the formation of an insulating film of black material. The best current yields (mg of product/C) are obtained for the smallest voltages applied; on increasing the voltage, the yields drop (see dashed curve of Fig. 2). When aniline concentrations lower than  $\approx 0.3$  mol/L are used in the process, some rust forms concurrently, whereas for aniline concentrations  $>0.4$  mol/L, loose deposits are formed. The reproducibility of coating performances using system A is rather poor in that the system degrades

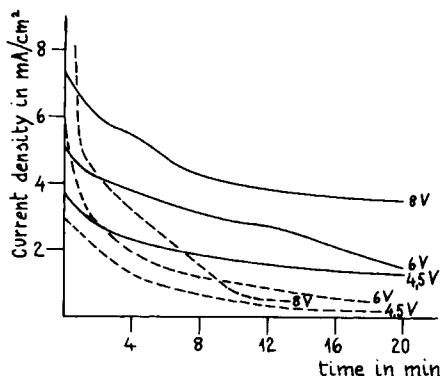


Fig. 1. System A (---): Current decrease during electrolysis at Fe sheet anodes at various voltages applied. System B (—): Identical runs.

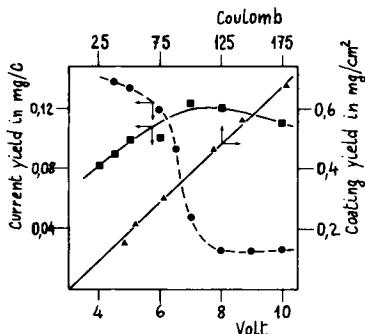


Fig. 2. (●) Current yield (mg/C) for system A as function of voltage. (■) Current yield for system B. (▲) Coating yield as function of the coulombs passed.

very rapidly; on the other hand, poor reproducibility and inhomogeneity have been tested elsewhere for films obtained at Pt.<sup>2</sup>

The features of the process are greatly improved when allylamine (0.53 mol/L) and Cellosolve\* (0.3 mol/L) are added to the electrolytic solution (system B). Under these conditions, (1) the current decrease with time, especially for the highest voltages applied, is less sharp (Fig. 1, plain curves); (2) the current yield becomes much more independent of the voltage (Fig. 2, plain curve); (3) coating performances are reproducible: several dozen sheets could be coated in the same 100 ml of solution without any degradation of film coherence or yield loss. This last fact may also be deduced from the linear relationship between growth of film (mg/cm<sup>2</sup>) and coulombs passed shown by the straight line of Figure 2; this plot was obtained from samples anodized for different lengths of time.

#### *Coulombic Yields*

Assuming that aniline oxidation involves 2 F/mol, an efficiency for film formation of 25–30% may be deduced from the coulombic yields of Figure 2. Indeed, having coated many sheets in the same solution for a total charge transfer of 2400 C, only 310 mg dried material could be recovered, corresponding to a 27% current yield. However, a further 470 mg of oxidation products (azobenzene and tar) was found dissolved or dispersed in the system corresponding to a 42% current yield. (The solution darkens as the coating process continues. Analysis of the tar gave composition and structural features similar to those of the coatings.) No Fe<sup>2+</sup> (less than 1 mg, by spectrophotometric determination of the ortho-phenanthroline complex) was practically present in solution. Therefore, at least 70% of the current is engaged by anodic coupling of aniline; the remaining current is probably consumed either by further oxidation of the products (see below) or possible oxidation of some water.

#### *Controlled Potential Data*

Some voltametric runs were carried out on microscale on a rotating Fe disc (vs. SCE) for determining the current–potential curves related to the process. Thus, curve 1 in Figure 3 shows that, in the absence of aniline, the anode reaction

\* This compound (ethylene glycol monoethyl ether) improves film spreading and homogeneity.

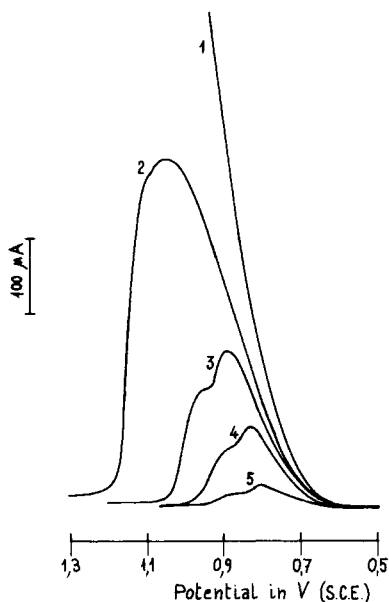


Fig. 3. Current-potential curves (SCE reference) obtained by a rotating (1000 r/min) Fe microanode (area  $0.03 \text{ cm}^2$ ) and a potential scan rate of  $3.3 \text{ mV/sec}$ . Curve 1: Water-methanol (1:1 by volume) containing allylamine ( $0.49 \text{ mol/L}$ ), KOH ( $0.1 \text{ mol/L}$ ), and cellosolve ( $0.3 \text{ mol/L}$ ). Curve 2: As before, with the addition of aniline ( $0.16 \text{ mol/L}$ ). Curves 3, 4, and 5: Successive potential scans without cleaning the electrode.

is sustained by water discharge (the presence of allylamine does not change this picture). Upon addition of aniline (curve 2), no new electrode process may be detected, but passivation of the anode starts to take place. Such passivation progressively increases when successive potential scans are run without cleaning the electrode (curves 3 and 4) until it becomes completely insulated (curve 5).

On dipping the electrode filmed in this way into an  $0.03 \text{ mol/L AgNO}_3$  solution and scanning toward cathodic potentials, a deposit of silver is formed which cannot subsequently be stripped anodically. The plain curve in Figure 4 refers to the Ag deposition on the filmed Fe; the dotted curves illustrate the same process on a bare electrode. The polymeric film therefore exhibit the semi-conducting properties already tested elsewhere.<sup>2,5</sup>

#### *Analysis of the Products*

After having recovered the coating material from the sheets by DMF or acetone, it was precipitated in water and then dried under vacuum at room temperature to avoid the irreversible modifications which easily occur with aniline polymers. It was thus found by gas-chromatographic analysis that the product always contains minor amounts of azobenzene (10–20%) and a major polymeric fraction. The latter was examined by comparing it to an emeraldine sample prepared by chemical oxidation (persulfate<sup>10</sup>) in sulfuric acid followed by neutralization with KOH of the emeraldine sulfate.

Table I shows the elemental analysis data obtained for both polymers. The chemical compositions of both (which are very close to each other) differ from the theoretical provision of a head-to-tail polyaniline,  $\text{H}-(\text{C}_6\text{H}_4-\text{NH})_n\text{H}$ . This

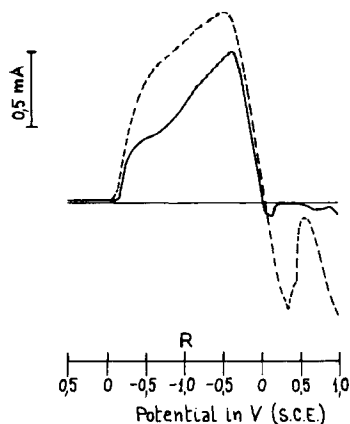


Fig. 4. Current-potential curves recorded in  $\text{AgNO}_3$  (0.03 mol/L) hydroalcoholic solution at Fe rotating disc electrode by a potential scan rate of 16.7 mV/sec: (---) bare electrode; (—) filmed electrode. At point R, the potential scan direction was reversed; the silver deposition rate does not decrease immediately after point R, probably being controlled by crystallization kinetics.

fact may partly be attributed to hydrolysis of the quinoneimine groups typical of these polymers to the corresponding quinone groups.<sup>11</sup> It must furthermore be considered that during polymer formation,  $\text{OH}^-$  groups may enter the chains and that the final product has a high affinity for many inorganic ions.<sup>12</sup>

On submitting the polymer to mass spectrometry at low temperatures (100–150°C), only fragmentation products of azobenzene (from the coating material) and aniline (from emeraldine) may be observed. On increasing the pyrolysis temperature to 300°C and ionizing with a 70 eV beam, more significant fragments are obtained: the relative  $m/e$  values are reported in Table II. Peak series corresponding to the structures  $\text{C}_6\text{H}_5(\text{NHC}_6\text{H}_4)_n\text{NH}_2$  and  $\text{C}_6\text{H}_5(\text{NHC}_6\text{H}_4)_n\text{H}$  and the dehydrogenated structures derived therefrom (which might contain quinoneimine and quinone units) are common to both samples and have the highest relative abundances. Moreover, the electrochemical product shows strong peaks of the series 285, 376, 467 and 299, 390, 481, respectively, which may be due to pyrolysis condensation products, as suggested for polysulfonanilides.<sup>6</sup>

Table III shows the molecular weight of the electrochemical sample obtained by vapor pressure osmometry in acetone at 40°C. In agreement with this datum, Figure 5 shows the GPC pattern standardized by polystyrene; for comparison, the GPC of emeraldine sample is plotted in the same figure.

TABLE I  
Elemental Analysis Data

Sample	Theoretical composition, %			Experimental composition, %		
	C	H	N	C	H	N
Emeraldine	79.12	5.49	15.38	69.14	4.42	13.05
Polyaniline coating	79.12	5.49	15.38	69.01	4.88	12.40
Coating from 2-nitroaniline	52.94	2.94	20.59	54.17	3.49	19.70
Coating from 3-nitroaniline	52.94	2.94	20.59	51.81	3.60	18.93
Coating from 4-nitroaniline	52.94	2.94	20.59	49.67	3.52	17.52

TABLE II  
Pyrolysis–Mass Spectrometry Data from Emeraldine and Polyaniline Coatings (70 eV Ionization Energy)

<i>m/e</i>	Relative intensity, %		<i>m/e</i>	Relative intensity, %	
	Emeraldine	Coating		Emeraldine	Coating
51	14	12	261	9	4
52	12	11	273	10	3
65	25	21	274	4	4
66	32	32	275	48	12
77	17	18	276	9	3
78	45	51	284	2	4
91	20	18	285	2	12
92	25	22	286	—	4
93	100	100	289	16	—
94	9	10	290	4	—
106	4	4	299	—	11
107	29	8	300	—	6
108	41	4	301	—	4
167	60	16	347	7	1
168	29	17	349	27	2
169	61	33	351	—	7
180	7	5	364	—	2
181	12	7	374	—	3
182	21	7	375	—	4
183	26	11	376	—	9
184	82	25	377	—	3
185	12	5	379	5	—
194	—	4	388	—	3
195	1	3	390	—	6
196	2	2	391	—	3
197	3	1	392	—	3
198	7	1	440	9	1
199	25	1	442	—	3
208	—	4	452	—	1
209	—	4	457	—	1
258	10	4	467	—	4
260	41	15	481	—	2

### Coatings from Nitroanilines

#### Features of the Process

The coating process described so far was also tried using substituted anilines. Nitroanilines were selected, as from data in the literature<sup>13,14</sup> they seem less likely to produce the corresponding azoderivatives: the head-to-head oxidative coupling side reaction, in fact, hinders head-to-tail polymer growth.

TABLE III  
Molecular Weight Data<sup>a</sup>

Monomer	$\bar{M}_n$
Aniline	500
2-Nitroaniline	800
3-Nitroaniline	850
4-Nitroaniline	480

<sup>a</sup> Molecular weights were measured in acetone at 40°C by vapor pressure osmometry.

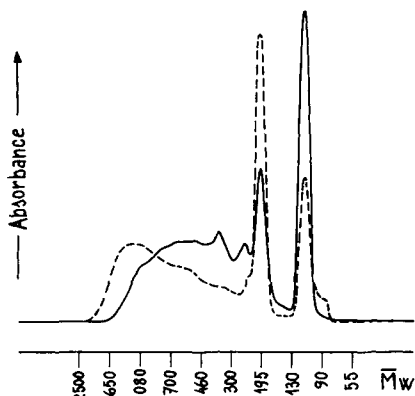


Fig. 5. GPC of a polyaniline sample (plain curve) and an emeraldine sample (dashed curve). Chromatographic conditions: column,  $\mu$ -Styragel, 500 Å; solvent THF, 1 ml/min; detector, UV 300 nm.

It was therefore found that simple hydroalcoholic alkaline solutions of nitroanilines do not lead to film formation. In the presence of allylamine, the Fe sheet anodes are coated in any case, but film features are poor due to thinness and dishomogeneity. On the contrary, homogeneous, coherent, and thicker coatings are obtained when the Fe sheets are either dipped in  $K_2Cr_2O_7/H_2SO_4$  for 1–2 min or anodized briefly in  $K_2CrO_4$ /water before the process. Moreover, it was found that such “conversion coating”<sup>15</sup> may be carried out in situ by adding the nitroaniline solution of  $K_2CrO_4$  (0.01–0.03 mol/L), thus achieving both pretreatment and organic coating of the Fe samples with a single anodization. It must be noted that during the electrolysis, film formation is paralleled by noticeable oxygen evolution from water discharge. Indeed, the average coulombic yields generally are little above 0.1 mg/C, which corresponds to a current efficiency of 15–20% (on the basis of 2 F/mol stoichiometry).

For instance, on electrolyzing by 4.0 V a mixture of 3-nitroaniline (0.11 mol/L), allylamine (0.49 mol/L), KOH (0.1 mol/L),  $K_2CrO_4$  (0.025 mol/L), and Cellosolve (0.3 mol/L) in water–methanol (1:1 by volume), the coulombic yields range from 0.12 to 0.13 mg/C; film thickness increases from 0.15 to 0.30 mg/cm<sup>2</sup> on varying the anodization time from 20 to 100 min. At 5 V applied, the coulombic yield drops below 0.1 mg/C. Since the coating process is paralleled by oxygen evolution, the oxidation of nitroanilines might also occur indirectly, through OH<sup>•</sup> radical intermediates of water oxidation. This is reasonable when considering that the anode reaction of nitroanilines takes place at a 0.5 V more positive potential than for aniline. On the other hand, an indirect oxidation of nitroanilines by  $CrO_4^{2-}$ , which would thus be reduced to  $Cr^{3+}$  to be recycled by the anode, must be disregarded for the following reasons:

- (1) Polymer formation occurs only in situ (on the sheet surface).
- (2) No product of nitroaniline oxidation is recovered after repeated coating runs from the solution which remains clear and stable.
- (3) No consumption of either  $CrO_4^{2-}$  or nitroaniline was tested (spectrophotometrically) within several hours for unreacted solutions.

Figure 6 shows the current trend during anodization of the system: 2-nitroaniline (0.11 mol/L), allylamine (0.49 mol/L), KOH (0.1 mol/L),  $K_2CrO_4$  (0.025

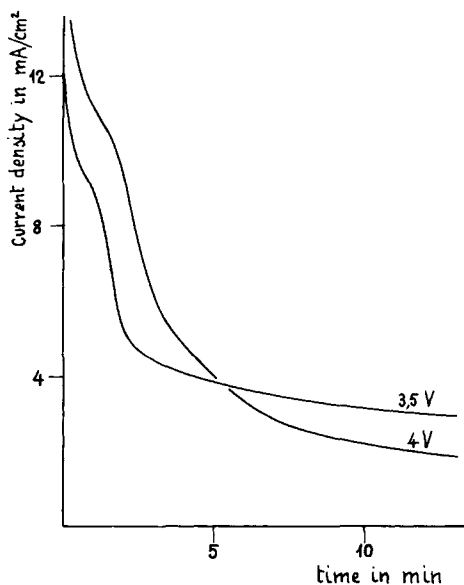


Fig. 6. Current decrease during electrolysis of a water-methanol (1.5–1 by volume) solution containing 2-nitroaniline (0.11 mol/L), allylamine (0.49 mol/L), KOH (0.1 mol/L),  $K_2CrO_4$  (0.025 mol/L), and cellosolve (0.3 mol/L) at Fe sheet anodes, at 3.5 and 4.0 V applied.

mol/L), and Cellosolve (0.3 mol/L) in water-methanol (1.5:1 by volume). In this case, too, for 3.5–4.0 V applied, current yields do not exceed 0.13 mg/C.

The behavior of 4-nitroaniline is similar.

#### *Analysis of the Coatings*

Table I shows elemental analysis of the coating material recovered from the sheets. These data are not in disagreement with theoretical expectations for a polynitroaniline. The IR spectra, too, are very close to those of the monomers. The main difference here is reduced absorption by NH; in particular, the band at  $1620\text{ cm}^{-1}$  becomes very feeble.

On submitting coating samples to pyrolysis coupled with mass spectrometry, only fragments from nitroanilines and their azo derivatives ( $m/e$  92, 93, 94, 138, 150, 240, 256, and 272) could be observed at  $140\text{--}150^\circ\text{C}$  and 70 eV. On increasing the pyrolysis temperature to  $400^\circ\text{C}$ , no other significant fragment was detected as the samples carbonized without vaporizing.

As regards molecular weights ( $M_n$ ), data for the three isomers are shown by Table III; the lower weight for 4-nitroaniline polymer is probably related to the block of the para position in the monomer, whereby coupling can only occur in the ortho position.

Figure 7 shows the GPC of the polymer obtained from 2-nitroaniline.

#### *Physical Properties of the Polymer Coatings*

When dried at room temperature, the coating material obtained either from aniline or the nitroanilines is easily scratched or dissolved from the substrate; however, its resistance may be greatly increased by thermal curing. Thus, when



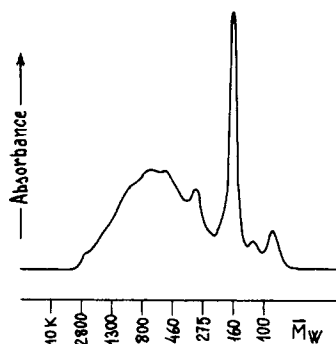
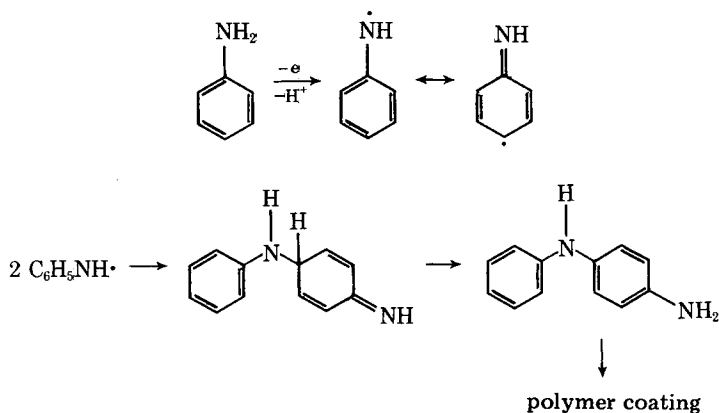


Fig. 7. GPC of a poly(2-nitroaniline) sample. Chromatographic conditions as in Fig. 5.

the coated samples are cured in an oven, monomers and azo derivatives are removed and the polymers, through melting and crosslinking processes, become insoluble and in general gain a fine gloss; their colors range from deep black (for Aniline Black) to pale or reddish brown (for polynitroanilines). The most interesting physical properties of the cured samples are shown in Table IV.

## DISCUSSION

The analytical data of the coatings prepared from aniline indicate that they mainly consist of polyaniline chains (making due allowance for azobenzene), which form through an anodic coupling mechanism according to the following scheme:



This process clearly requires continuous interaction of the growing heads ( $\text{—NH}_2$ ) with the anode and ceases either when the polymer precipitates (so that the amine head can no longer oxidize) or when a head-to-head coupling reaction leads to azo groups.

Some fragments detected by mass spectrometry as well as the elemental composition further suggest the occurrence of a large number of quinoneimine (and quinonediimine) units in the chains. These moieties, which are probably formed by further oxidation of polyaniline chains, account for a current consumption exceeding 2 F/mole and may also explain the semiconducting prop-

TABLE IV  
Physical Properties of Coatings

Sample No.	Monomer	Thickness, $\mu\text{m}$	Porosity, microholes/ $\text{cm}^2$	Hardness <sup>a</sup>	Adhesion <sup>b</sup>	Salt fog resistance, h <sup>c</sup>
1	Aniline <sup>d</sup>	4.5	200	H	fair	60
2	Aniline <sup>d</sup>	4.0	100	H	fair	60
3	Aniline <sup>d</sup>	6.0	100	HB	fair	60
4	Aniline <sup>d</sup>	8.5	100	HB	fair	80
5	2-Nitroaniline	6.0	high	HB	poor	24
6	2-Nitroaniline	5.0	high	HB	poor	24
7	2-Nitroaniline	4.0	high	HB	poor	24
8	3-Nitroaniline	2.0	high	HB	fair	48
9	3-Nitroaniline	3.0	50	HB	fair	48

<sup>a</sup> Determined by graphite standards.

<sup>b</sup> Cross cut adhesion.

<sup>c</sup> ASTM Method B 117.

<sup>d</sup> All samples were prepared by electrolyzing system B.

erties of the films. In fact, quinoneimine and quinonedimine units probably resist oxidation (thus hindering anodic charge transfers), whereas, being reducible, they do allow the cathode process.

For nitroanilines, the situation is similar; molecular weights and elemental analysis suggest a polynitroaniline structure for the coatings. Elemental analysis furthermore may indicate a reduced occurrence of quinoneimine units in the polymer. The fact is reasonable, considering that NH bridges between two nitrobenzene moieties typical of the polymer must be less suitable for further oxidation than those in polyaniline chains. On the other hand, a higher resistance toward oxidation is also provided by nitroaniline monomers, which therefore explains the low current efficiency of coating formation (largely paralleled by water discharge).

With regard to the importance of allylamine for the realization of the process, the role of this compound as an inhibitor of Fe dissolution during the anodic synthesis of polyoxyphenylene coatings on Fe has already been suggested.<sup>16</sup> The data of the present work confirm this view; in fact, considering that anilines themselves are only slightly effective as Fe corrosion inhibitors,<sup>17</sup> the improvements obtained in the presence of allylamine are explained. It is clear that in the case of nitroanilines whose anodic oxidation is more critical, pretreatment of the substrate not only increases passivation but probably makes the surface more suitable for bonding the organic layer.

With regard to allylamine, its importance in the deprotonation stages of intermediate cation radicals (see scheme above) must be mentioned, too. Furthermore, a possible incorporation of such products in the polymer through reaction with quinoneimine intermediates as suggested in the anodic synthesis of polyoxyphenylenes<sup>16</sup> cannot be disregarded. In this way, the nitrogen content of the coatings, higher than expected, might be explained.

In conclusion, according to the data reported above, the protection given to the substrate by these anodic film coatings is not negligible. The main limit seems to be microporosity. Since this is probably due to the presence of entrapped monomers and azo derivatives, when conditions suitable for avoiding

such handicap are found, the protective features of these coatings may hold some interest.

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