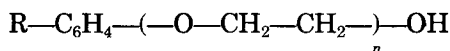


Improved Polyaniline Coatings by *In Situ* Electropolymerization

In situ electropolymerization onto metal electrodes is attracting increasing interest because of the wide range of possible applications revealed by the appropriate choice of monomers and electrolysis conditions.¹ When the technique is aimed at the anticorrosion protection of a metal, coatings with high cohesion and strong adhesion to the substrate are required. These properties mainly confront penetration by water, oxygen and ions, and later polymer detachment due to underskin corrosion.²

In this respect the polyaniline and sulfur-bridged polyaniline coatings described in two previous papers in this journal^{3,4} were inadequate and therefore provided little protection.

In the present note we describe how the use of monomers containing thermally curable groups may secure cohesion, whereas satisfactory adhesion may be achieved by adding nonionic surfactants of Triton type to the electrolytic solutions. They have the following general structure



where R = 1,1,3,3-tetramethylbutyl, and proved capable of increasing the adhesion of polyoxyphenylene coatings onto Fe, Cu, and Zn.⁵

EXPERIMENTAL

All chemicals were reagent grade. Coating runs were performed by constant voltage (two electrodes) in an undivided cell, using Fe sheet samples as anodes with a useful dipped area = 25 cm². Polishing procedure involved degreasing by acetone, followed by cathodic polarization in aqueous KOH at 20 mA/cm² for 2 min.

Cyclic voltammeteries were performed on a stationary Fe disc electrode (area = 0.125 cm²), using an SCE as reference.

IR spectra of the coatings were recorded with a Perkin-Elmer 682 Infrared Spectrophotometer in two ways: in KBr pellets or by the single reflectance technique. Physical properties of the coatings were determined according to ASTM procedures.

RESULTS

Homo- and Copolymerization of *N*-(2-Hydroxyethyl)aniline

The current decrease recorded by electrolyzing a water/methanol (1.5:1) mixture containing *N*-(2-hydroxyethyl)aniline (HEA) 0.17*M*, allyamine 0.37*M*, ammonium sulfide 0.045*M*, and ethoxyethanol 0.24*M*, with 4.0 V applied, is shown in Figure 1 (curve a). A dark brown coating is formed, whose thickness decreases from the edges to the center of the sheet, due to un-homogeneous electric field and poor throwing power. Current yield is ca. 0.15 mg/C, corresponding to 20–25% current efficiency.

However, the Fe anode becomes homogeneously coated when one of the following carboxy substituted anilines (0.055*M*) is added to the above electrolytic solution: 4-aminophenylacetic acid (APA), anthranilic acid (ANA), or 3-aminobenzoic acid (ABA). As may be seen from Figure 1 (curves b–d), more gradual passivations take place, although current efficiency is not improved. The concentrations of Figure 1 guarantee optimum performance of the system, and large variations from the indicated values cause disadvantages: Iron sulfide forms when the ammonium sulfide concentration exceeds 0.06*M* or when allyamine is < 0.25*M*; oxygen evolution becomes faster (and current efficiency lower) by increasing the allyamine concentration; soluble coupling products diffuse away from the anode in the absence of sulfide.

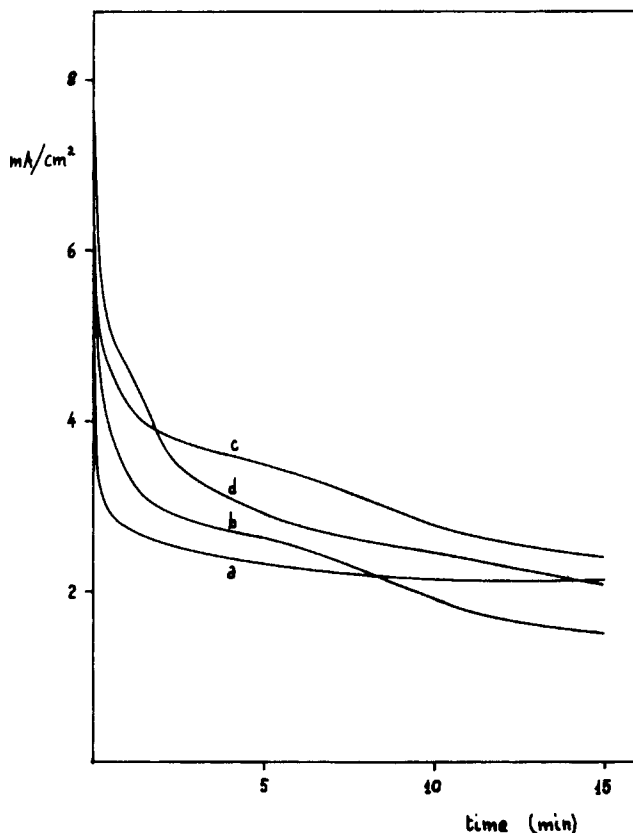


Fig. 1. Current decrease recorded at Fe. Solution composition was: (a) HEA 0.17*M*, allylamine 0.37*M*, ammonium sulfide 0.045*M*, ethoxyethanol 0.24*M*; water/methanol 1.5:1; (b) a + APA 0.055*M*; (c) a + ANA 0.055*M*; (d) a + ABA 0.055*M*.

Coating Composition

Coating samples were purified as described in Ref. 4, to free them from pollutant molecular sulfur and other entrapped species. Elemental compositions and \bar{M}_n (measured by vapor pressure osmometry) of purified samples are shown in Table I. Although experimental compositions do not fit those calculated for [monomer-2H], thus suggesting the incursion of electrochemical and homogeneous chemical side reactions, the following points must be noted:

(a) The oxygen/nitrogen ratio is higher in the presence of carboxy substituted anilines, as expected, but always keeps close to unity, suggesting a very high content of HEA in the copolymers.

(b) The sulfur content of the homopolymer is in the range observed for primary and secondary anilines,⁴ whereas 30–50% less sulfur is found in the copolymers. (This is tentatively explained by competition between the HS⁻ and carboxylate anions at the anodically polarized electrode.)

Most of the IR bands of HEA are also found in the spectrum of its homopolymer. Significant differences are observed only in the aromatic C—H out-of-plane bending region: A strong band at 820 cm⁻¹, due to parasubstituted units, is seen in the polymer together with weak bands at 750 and 690 cm⁻¹. The latter bands, which are strong in the HEA spectrum (monosubstitution), are not unexpected when considering the low molecular weights shown in Table I and their attribution to terminal units. Two additional medium-weak bands are seen at 1660 and 1360 cm⁻¹. These may suggest the oxidation of the alcoholic function to (H-bonded?) aldehyde.

IR spectra of the copolymers are indistinguishable from the spectrum of the homopolymer, thus confirming that the coatings mainly consist of HEA. This is not surprising because the

TABLE I
Elemental Composition and Molecular Weight of Purified Coating Samples

Monomers	Experimental composition ^a					\bar{M}_n
	C	H	N	O	S	
HEA	62.57	5.51	11.09	11.08	6.72	610
HEA/ANA	66.42	5.55	10.83	12.11	3.24	710
HEA/APA	65.03	5.54	10.44	12.07	4.80	575
HEA/ABA	65.35	5.52	10.67	12.43	4.22	

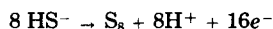
^a Theoretical compositions for monomer-2H are: HEA: C, 71.11%; H, 6.67%; N, 10.37%; O, 11.85%; ANA and ABA: C, 62.22%; H, 3.70%; N, 10.37%; O, 23.70%; APA: C, 64.43%; H, 4.70%; N, 9.40%; O, 21.48%.

—NH— group of HEA is likely to be oxidized at a lower potential than the amine function of carboxy-substituted anilines which, on the contrary, are not suitable for electrochemical homopolymerization alone.

Use of Triton

The addition of Triton (X100 or X405) to the electrolytic solutions does not cause significant variations in current vs. time curves. HEA homopolymerization is less efficient (current yields decrease to 0.10–0.12 mg/C), whereas copolymerizations are unaffected.

A significant effect of Triton appears in Figure 2, showing the first and the 15th CV scans in basic (pH = 10.5) sulfide solutions in the absence (a) and presence (b,c) of Triton X405. The anodic peak I at –0.25 V is ascribed to the reaction



according to Shoesmith.⁶ However, it must be noted that:

(1) Oxidation currents are lower in the presence of Triton (possibly because of a partial surface blockage).

(2) A reduction peak (II) is seen at –0.7 V in Figures 2(b) and (c). This peak is absent when the anodic scan is limited to –0.4 V.

(3) The relative height of peak II with respect to I increases at higher scan rates (Fig. 2(c)). Peak II is hardly seen at a scan rate ≤ 10 mV/s.

It may be deduced that the sulfur layer formed at peak I potential is readily dissolved in the presence, but not in the absence, of Triton, possibly as polysulfide. The surfactant is thus likely to favor good adhesion both by removing the weakly adhering sulfur layer and by securing strong interaction between metal and polymer.⁵

Physical Properties, Reproducibility of Coatings

A standard curing procedure (30 min heating at 180°C) was applied to coated samples before physical testing. Both esterification reactions and Triton thermooxidation⁵ are likely to occur in these conditions.

Table II summarizes the physical properties of copolymer coatings (homopolymers were poorer because of high porosity and lack of homogeneity). The following points deserve special attention:

(a) Adhesion is much better and salt fog resistance almost doubled for coatings obtained in the presence of Triton.

(b) Thin films are porous, but porosity drops at thicknesses $> 5 \mu\text{m}$.

(c) Hexamethoxymethylmelamine (Cymel 303), added to some solutions to improve cross-linking efficiency, gave detectable positive results.

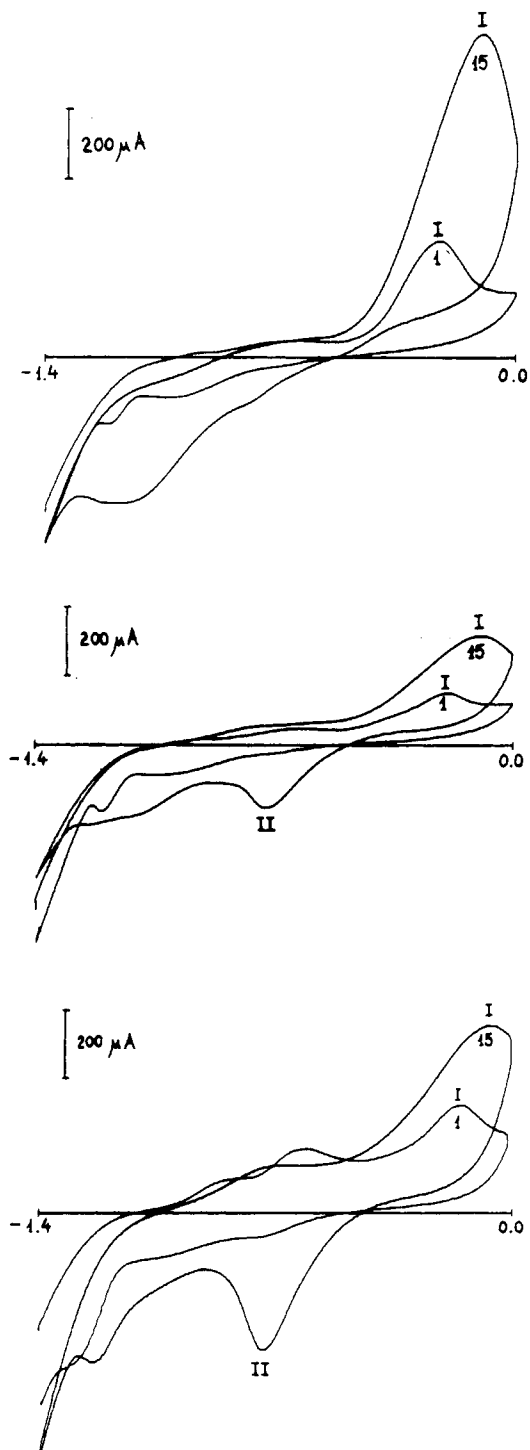


Fig. 2. Cyclic voltammetry patterns obtained at Fe. Solution composition was: (a) allylamine 0.37M, ammonium sulfide 0.045M; water/methanol 1.5:1; (b) and (c) a + Triton X405 0.002M. Scan rate: (a) and (b) 50 mV/s; (c) 200 mV/s.

TABLE II
Physical Properties of Copolymer Coatings

Solution components ^a Carboxy aniline	Triton	Cymel 303	Thickness (μm)		Pores/ cm^2	Hardness ASTM D3363	Adhesion + elasticity ASTM D522	Salt fog resistance ^b (h) ASTM B117
			ASTM D1186	D1186				
APA (0.055M)	—	—	6.2	6.2	6	6H	Poor	90
APA (0.055M)	X100 (0.002M)	—	3.5	3.5	200	6H	Very good	48
APA (0.055M)	X100 (0.002M)	(0.07M)	6.5	3.5	7	6H	Good	160
APA (0.055M)	X405 (0.002M)	(0.07M)	6.2	3.0	200	6H	Very good	48
APA (0.055M)	X405 (0.002M)	—	6.2	3.0	0	6H	Good	190
ANA (0.055M)	X100 (0.002M)	—	6.0	3.1	5	6H	Good	70
ANA (0.055M)	X405 (0.002M)	—	6.0	3.0	20	5H	Very good	170
ABA (0.055M)	X405 (0.002M)	(0.07M)	6.0	3.0	0	5H	Good	100
ABA (0.055M)	X405 (0.002M)	(0.07M)	6.0	3.0	200	6H	Very good	90
		(0.07M)	6.0	6.0	5	6H	Good	170

^a All the solutions contained: HEA 0.17M; allylamine 0.37M; ethoxyethanol 0.24M; ammonium sulfide 0.045M in water/methanol 1.5:1.

^b Etched samples.

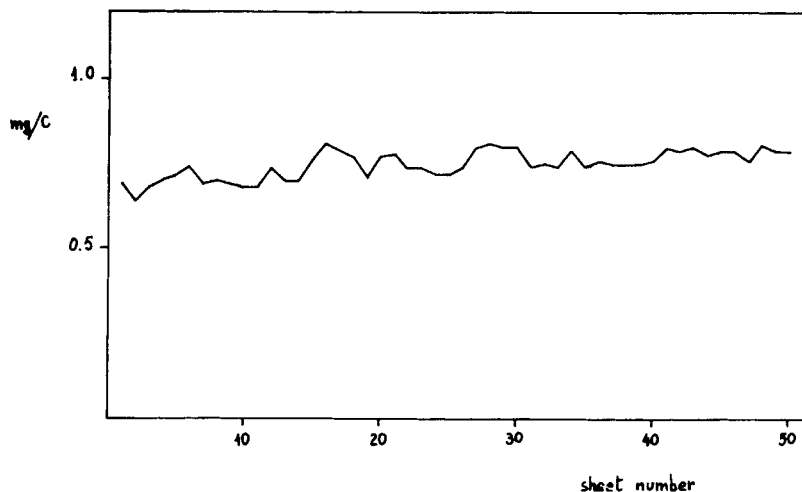


Fig. 3. Coating yields as a function of the progressive number of the anodized Fe sheet, obtained after a 30-min electrolysis in HEA 0.17M, allylamine 0.37M, ammonium sulfide 0.045M, ethoxyethanol 0.24M, and Triton X405 0.002M. Water/methanol 1.5:1.

Further merits of the copolymer coatings are reproducibility of coating performances and stability of the electrolytic baths. Figure 3 shows coating yields (in an HEA/APA solution) as a function of the progressive number of the anodized sample. Physical properties keep constant through 50 consecutive coating runs, whereas a slight increase in film thickness is observed. On the basis of such data it may be concluded that, as regards achieving protecting coatings on Fe, the described system is not far from the performances of *in situ* electropolymerization of phenols.⁵

The financial support of the "Progetto Finalizzato Chimica Fine e Secondaria" (Chimica Fisica delle Superfici) is gratefully acknowledged.

References

1. G. Mengoli, 34th ISE Meeting, Erlangen (BRD) 18-23 Sept. 1983, nr. III 5.
2. H. Leidheiser, Jr., *Corrosion*, **38**, 374 (1982).
3. G. Mengoli, M. T. Munari, P. Bianco, and M. M. Musiani, *J. Appl. Polym. Sci.*, **26**, 4247 (1981).
4. G. Mengoli, M. M. Musiani, B. Pelli, and E. Vecchi, *J. Appl. Polym. Sci.*, **28**, 1125 (1983).
5. G. Mengoli, M. M. Musiani, B. Pelli, M. Fleischmann, and I. R. Hill, *Electrochim. Acta*, **28**, 1733 (1983).
6. D. W. Shoesmith, P. Taylor, M. G. Bailey, and B. Ikeda, *Electrochim. Acta*, **23**, 903 (1978).

MARCO M. MUSIANI
GIULIANO MENGOLI
FERDINANDO FURLANETTO

Istituto di Polarografia ed Elettrochimica
Preparativa del C.N.R.
Corso Stati Uniti
4-35100 Padova, Italy

Received January 12, 1984
Accepted August 7, 1984