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The influence of amines on the anodic coupling of phenols to polyoxyphenylene films

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The formation of protective polyoxyphenylene coatings onto Fe, Zn and Cu sheets by anodic oxidation of phenol/amine systems has been investigated. It was found that thick homogeneous coatings are obtained only when a suitable amine is present in the electrolysis solution. The amine not only stops the anodic formation of passivating metal oxides which inhibit polymer growth, but also enters into the structure of the coatings. The polymer chains obtained from phenols are, in fact, highly modified by amine molecules grafted onto the phenoxy units.

1. Introduction

We have recently found that good polyoxyphenylene coatings on Fe sheet anodes may be achieved by electrolyzing mixtures of phenols neutralized with ethylenediamine in aqueous alcoholic medium [1, 2].

The synthesis *in situ* of passivating polymer films by anodic oxidation of alkaline phenoxides has been reported previously [3–8]: such coatings were, however, of doubtful technological interest because of the poor physical features (extreme thinness) and the large current consumption involved.

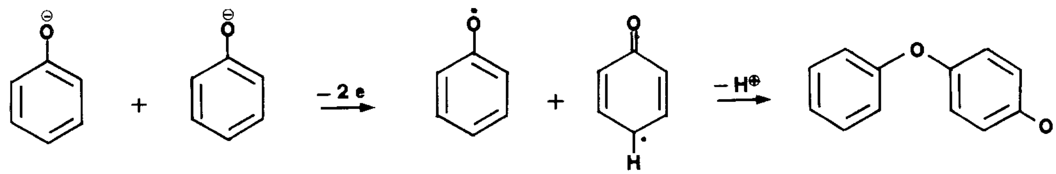
In contrast, the electrolysis of systems based on phenol (as the main monomer)/2-chlorophenol/ethylenediamine gives outstanding results in that:

(a) thick homogeneous coatings, reaching more than 20 μm can be obtained;

(b) the current yield is very near to that calculated from Scheme 1 (0.5 moles of phenols polymerized per Faraday).

This behaviour (which is mainly due to the presence of ethylenediamine) was tentatively explained by assuming that ethylenediamine is adsorbed at the surface of an Fe anode in competition with phenoxide anions: thus the formation of passivating films would be inhibited by the entrapped ethylenediamine, whose solvation allows the passage of current until thick polymer films are formed [2]. Support for this view was obtained by elemental analysis of the films, which in some instances contained ten times more ethylenediamine than the electrolysis solutions: the fate of the amine entered into the polymer was, however, not clarified. When mixtures of phenols were neutralized using amines other than ethylenediamine, non-adhering oil products were generally obtained [2]: it was also noted that the phenol/2-chlorophenol/ethylenediamine system gave unsatisfactory coatings on metals other than Fe.

Such results could not be considered as definitive: the new findings described in this paper probably widen the applied importance of poly-



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oxyphenylene coatings and give a further explanation of the role of the amine in their formation.

2. Experimental

2.1. *Chemicals*

Phenols, amines and the other organic compounds were reagent grade chemicals commercially available, and were used as supplied. The solvent was deionized water mixed with methanol. The metal samples were cut from sheets of Fe, Cu and Zn and had the standard dimensions 23.5 x 2.5 x 0.05 cm: before use the Fe samples were cleaned as previously described [2], whereas Zn and Cu sheets were simply degreased with acetone.

2.2. *Apparatus and procedure*

The coating was performed in a single compartment glass cylinder already described [2]: a standard volume of 100 cm^3 of solution was generally electrolyzed in this cell; a metal sheet was the anode and a Pt coil fastened to the glass and surrounding the anode was the cathode. The electrolyses were performed by applying a constant voltage to the electrodes [2, 9], the current transients being monitored by an ammeter.

Once coated and rinsed by pure water, the sheet samples were dried in an oven at 120–150° C for 15–20 min. Chemical analysis of the coatings was carried out by the usual laboratory techniques; physical determinations of adhesion and hardness and salt fog resistance tests were performed according to ASTM methods.

Some electrolytic and voltammetric runs were carried out in small compartmented cells equipped with a working microelectrode of either Fe, Cu or Zn (having an area of ~ 0.2 cm^2) and a SCE as reference electrode.

3. Results

3.1. *Phenol/allylamine system*

3.1.1. Preliminary observation. From a systematic investigation of the influence of various amines on the anodic oxidation of phenol it was found that allylamine is the most suitable for producing protective coatings. In fact the phenol/allylamine system is more simple than the phenol/2-chlorophenol/ethylenediamine system previously described [1, 2] and gives rise to coatings with similar or better features: the phenol/allylamine system, furthermore, has a far higher range of applicability as will be shown below.

3.1.2. Variables of the process at Fe sheet anodes. The morphology of the coatings obtained from the phenol/allylamine system is affected by the experimental conditions such as the methanol/water ratio, temperature, pH and additions of cellosolve [2]. Such parameters were, however, found to have no important influence when varied within the following ranges (which correspond to the best coating performance): temperature 20–30° C, methanol 20–30 vol%, pH 10–10.5, cellosolve 1–3 vol%. Under these conditions the voltage applied during the electrolysis and the concentrations of either phenol or allylamine are the main variables controlling polymer film formation and the rate of polymer deposition.

The effect of voltage is shown in Fig. 1 in terms of the current transients recorded during the electrolysis of a water/methanol (30%) solution containing phenol 1.19 M, allylamine 0.69 M; cellosolve 0.15 M. For any voltage from 2.5 to 4.5 V (plain curves of Fig. 1) the current decreases smoothly with time: only after long electrolysis (⩾ 30 min), when thick (15–20 μm) insulating coatings have been built up, does the current decrease to a negligible fraction of the initial value. The yield of polymer coated onto each Fe sheet

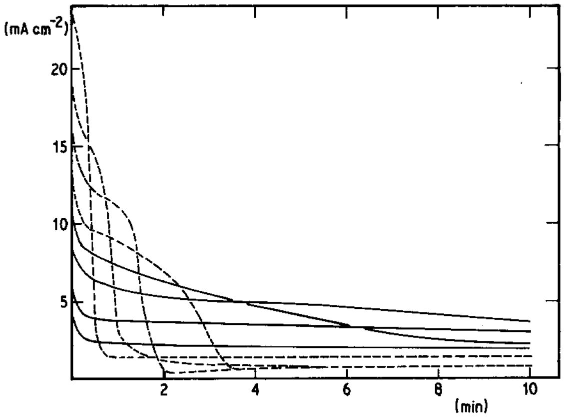

Fig. 1. Current transients during the electrolysis of a phenol/allylamine solution for increasing applied voltages. The voltage was: for the continuous curves 2.5, 3.0, 3.5, 4.0 V; for the dotted curves 4.5, 5.0, 6.0, 7.0 V.

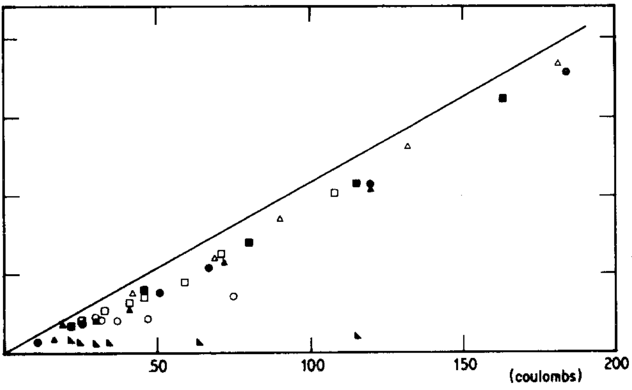

Fig. 2. Coating yields (mg cm^{-2}) as a function of the charge transferred to 100 cm^3 of water/methanol solution containing phenol 1.18 M and allylamine 0.42 M. The straight line refers to a theoretical yield of 0.5 polymerized phenol M per F. The voltage (V) applied was: ▲ 2.5; ● 3.0; △ 3.5; ■ 4.0; □ 4.5; ○ 5.0; ► 6.0.

approaches the theoretical stoichiometry of scheme 1 (Fig. 2). Conversely, when the voltage is higher than 4.5 V (dotted curves of Fig. 1) the sharp current drop with time indicates some accelerated passivation phenomena. The films obtained at these higher voltages are far thinner (0.5–2 μm) and the related coulombic yields are well below the theoretical stoichiometry (Fig. 2).

The effects of voltage are similar for solutions of other compositions: however systems containing higher concentrations of either phenol or allylamine generally tolerate higher voltages without any loss in coating performance.

Fig. 3 shows the influence of phenol concentration on the coating kinetics at fixed voltage. The coulombic yield was constant in such experiments: therefore the increase of coating weight (mg cm^{-2}) which occurs with the increase of phenol concentration is simply caused by the passage of more charge.

Allylamine has a fundamental role in producing coherent, thick coatings. Thus, when a solution of phenol neutralized with an inorganic base was electrolyzed, depending on the voltage applied, either fast passivation or spongy deposits were obtained: a slight addition of allylamine, however, allowed the growth of a thick homogeneous polymer coating onto the sheet anode.

Also the influence of allylamine concentration is remarkable, especially when the electrolysis is carried out at a voltage ⩾ 5 V. One can in fact observe in Fig. 4 that on increasing the allylamine concentration the passivation rate of Fe sheet anodes is slowed down, so that large charges may be passed and more substantial coatings may be achieved. However, when the allylamine concen-

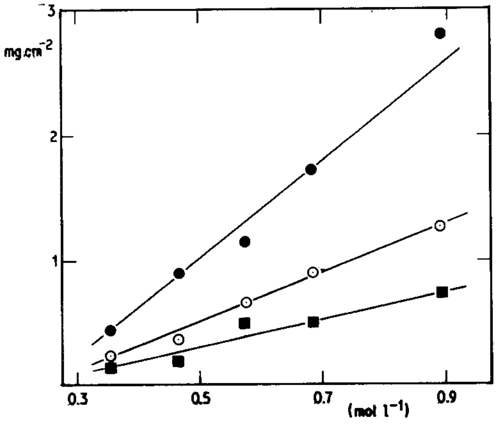

Fig. 3. Coating yields (mg cm^{-2}) obtained for increasing concentrations of phenol from a water/methanol (20%) solution containing allylamine 0.8 M and cellosolve 0.15 M. The straight lines refer to the yield calculated for three fixed electrolysis times with 4 V applied: the times were respectively 5, 10 and 30 min.

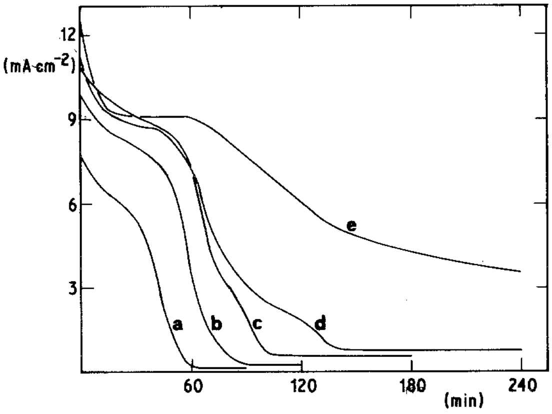

Fig. 4. Current transients during the electrolysis of a 1.14 M phenol solution with 5 V applied for increasing concentrations of allylamine. Allylamine concentrations were, starting from the left-hand curve: 0.27, 0.47, 0.67, 0.80, 1.07 M.

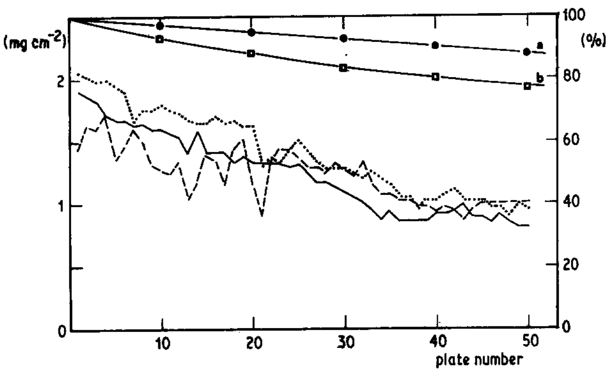

Fig. 5. Polymer yield (mg cm^{-2}) obtained after a fixed electrolysis time as a function of the number of the samples coated .... Fe sheets; ———— Zn sheets; – – – Cu sheets. Curve a, volume decrease (%); curve b, monomer decrease (%) for Zn.

Table 1. Analysis data of a phenol–allylamine solution utilized for repeated coating runs

Metal sheet	*Total charge transferred* (C)	*Residual phenol (by GC)* (%)	*Residual phenol (by difference with polymer obtained)* (%)	*Metal dissolved* (mg)
Fe	3492	78	75	0.01
Zn	3218	83	77	4.90
Cu	2856	82	80	0.36

tration exceeds that of phenol (that is, when the pH is much increased) fast passivation may again occur, as observed previously with ethylenediamine [2].

3.1.3. Coatings obtained on metals different from Fe: reproducibility of the process. The system phenol/allylamine enables the production of coherent polymer films on metals such as Cu and Zn, for which a protective and insulating coating may be technologically interesting. On electrolyzing phenol/allylamine concentrations similar to those of Fig. 1 it was found that the coulombic yield of the coatings agrees, in the voltage range 2.5–4.5 V, with the theoretical stoichiometry of scheme 1, whereas for higher voltages a decreased yield is observed: clearly this behaviour may be explained in terms of the phenomena observed for Fe.

In view of the commercial interest in the phenol/allylamine system, the stability of the solution and the reproducibility of coating performance have been tested using the following experiments. Using 100 cm^3 of a water/methanol (20%) solution containing phenol 0.68 M, allylamine 0.8 M and cellosolve 0.15 M, 50 Fe sheets were coated in succession by anodizing each one for 30 min at a voltage of 4 V: the same experiment was repeated using Cu and Zn sheets. It was found that during the entire process the coulombic yield was constant, but the average rate of polymer formation showed a steady decrease as may be observed in Fig. 5. Table 1 summarizes some analytical data determined at the end of the experiments. The phenol consumption as determined by gas chromatography are very near to those estimated from the total weight of polymer coated onto the sheets*. Therefore phenol does not take part in a side reaction. With respect to the consumption of the other components of the electrolysis solution, the decrease of allylamine concentration was only 2–3% and still less for cellosolve. Moreover, the pollution by metal ions dissolved from the sheets was negligible as can be seen from Table 1, and should not affect the process. The solution used for coating Cu sheets, however, showed after some days the formation of small amounts of polymer. On the basis of these results the loss of kinetic efficiency in the plots of Fig. 5

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* In fact the weight of polymer material would give a phenol consumption higher than that determined by GC: the reasons for this will be clarified in subsequent pages.

must be mainly due to a decrease in the monomer concentration. Since the phenol concentration may be easily restored during the process, no serious handicap exists in practical applications.

3.1.4. Voltammetric data. Potentiostatic and potentiodynamic runs carried out at microelectrodes of Fe, Cu and Zn show some points in common:

(a) When a water/methanol solution with KOH as base electrolyte is oxidized, extensive formation of passivating oxides on the three metals is suggested by the relatively low values of limiting current.

(b) The addition of allylamine to the solutions depolarizes the electrode with a sharp rise of the anodic current from 0.5–0.9 V (SCE).

(c) When phenol is present in solution, a slow passivation of the anode takes place.

The detailed behaviour at each metal can be seen in Figs. 6–8.

The current–potential curves obtained by linear sweep voltammetry at Fe shown in Fig. 6, agree completely with (a)–(c) above. It can also be noted that the high current after addition of allylamine (curve b) is due to water oxidation since electrolysis led to oxygen evolution but neither dissolution of Fe nor Fe oxide formation.

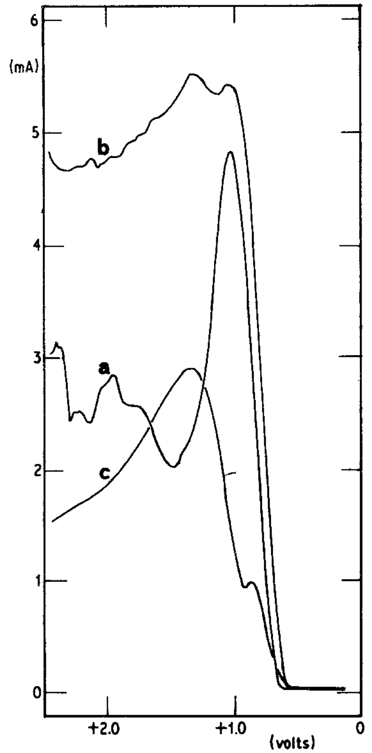


Fig. 6. Voltammetric current–potential curves obtained at a Fe microelectrode potential sweep rate 86 mV s^{-1}. Curve a, water/methanol (25%), KOH 0.1 M; curve b, water/methanol (25%), KOH 0.1 M, allylamine 0.8 M. curve c, water/methanol (25%), KOH 0.1 M, allylamine 0.8 M, phenol 0.68 M.

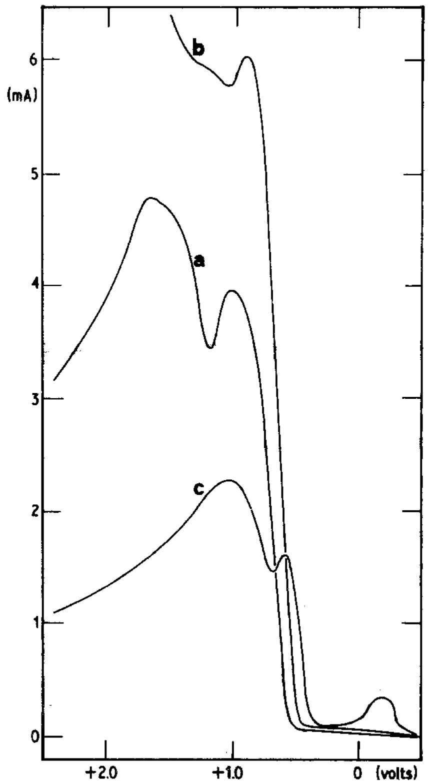


Fig. 7. Voltammetric current–potential curves obtained at Cu under the same conditions described for Fe. Curve a, b and c refer to the same situations as Fig. 6.

Fig. 7 shows the voltammetric curves obtained at Cu. A prepeak may be due to the presence of phenol (curve c). If a potentiostatic electrolysis is, however, carried out at the potential of this peak, the current decreases only slightly as no insulating film builds up: however, after extensive electrolysis (⩾ 30 min) some solid organic deposit may be observed at the anode surface. Conversely when either potential sweep or potentiostatic experiments are carried within the potential range of the large current after addition of allylamine, the coating takes place efficiently. The anode reaction occurring when only allylamine is present in solution involves copper oxidation (to Cu hydrates and amino complexes) as shown by potentiostatic electrolysis.

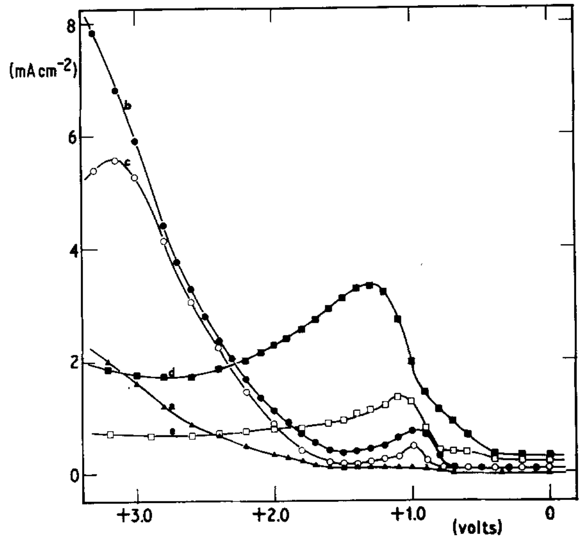


Fig. 8. Pseudo steady state current–potential curves obtained at Zn. Curve a, water/methanol (25%), KOH 0.1 M; curves b and c, the same solution in the presence of allylamine 0.27 M; curves d and e, the background solution in the presence of phenol 0.68 M and allylamine 0.80 M. The full points of the curves represent the current recorded after 30 s of electrolysis at each potential, the empty points represent the current after 3 min.

Fig. 8 shows the current–potential curves obtained potentiostatically at Zn using a (pseudo) steady state technique. Curve a shows that in an alkaline water–methanol medium, Zn is extensively passivated at all positive potentials. Curve b shows the depolarization promoted by allylamine, which is mainly related to water discharge: curve c, however, shows that in the presence of allylamine some passivation does occur at longer electrolysis times. The addition of phenol gives rise to a current from ~ 0.5 V (curve d), which drops for longer electrolysis times (curve e): under such conditions the electrode becomes coated with a coherent film.

3.2. *Coatings from substituted phenols*

In the presence of allylamine the formation of coatings was also achieved using substituted phenols. Thus interesting data, particularly on the mechanism of polymerization, could be obtained using either dimethylphenols or phenols bearing halogen substituents.

The polydimethyloxyphenylene coatings prepared from 2,6-dimethylphenol, the features of which were poorer than those of polyoxyphenylenes, could be dissolved (100%) by methylene dichloride and in part (~ 50%) by acetone. The fraction soluble in acetone was shown by vapour pressure osmometry to have $\overline{Mn} = 800$, whereas the insoluble fraction had $\overline{Mn} = 3200$. Both the fractions when dissolved in deuterated chloroform gave NMR patterns similar to those reported in the literature [10] : the ratio of the integrals referring respectively to the aliphatic and aromatic protons was 3/2, which constitutes a significant test of the linearity of the polymer chains.

The anodic oxidation of some phenols bearing halogen substituents showed some different features. For instance, after having coated several sheets using 2-bromophenol/allylamine mixtures, low concentrations of Br^- were found in solution, indicating the occurrence of some process in addition to the carbon–oxygen coupling of Scheme 1. This phenomenon was even more evident in the oxidation of 2,6-dimethyl-4-bromophenol: coatings were easily obtained on Fe although this monomer has no ring position whereby the unpaired electron of the phenoxy radical intermediate may be localized.

It should be noted that the coatings obtained from these brominated phenols have a poor finish as they appear burned and pitted: it is likely that the Br^- is oxidized and the resulting $Br^{\bullet}$ and Br_2 attack both the polymer and the substrate. Such degradation may be reduced by electrolyzing at low current density and low charge transfer thus avoiding Br^- accumulation at the sheet surface. Under these conditions the coulombic yield rises above the stoichiometry of Scheme 1 (Fig. 9): a further yield increase may be obtained on electrolysing using short current pulses (Fig. 9) so that Br^- produced in the polymerization may diffuse away from the surface of the metal.

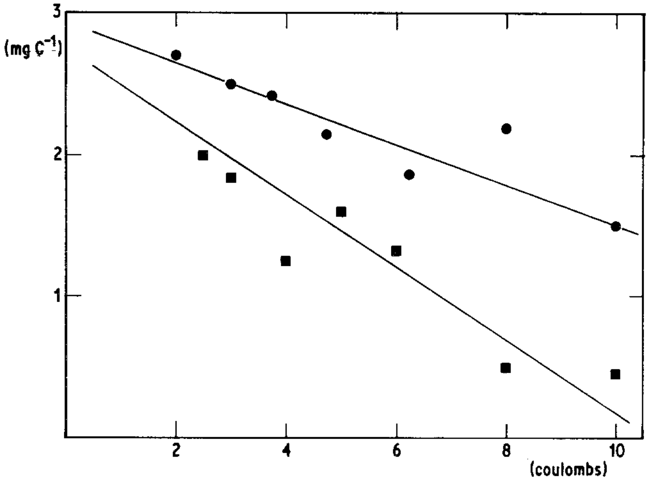


Fig. 9. Coating coulombic yield (mg C^{-1}) as a function of the charge transferred. Electrolysis of 100 cm^3 of water/methanol (30%) solution containing 2,6-dimethyl-4-bromophenol 0.2 M, allylamine 0.8 M and KOH 0.2 M. ■ with 2 V applied; ● by pulsing the voltage every 7 s.

Also the oxidation of 2,6-dichlorophenol produces halide ions, but to a smaller extent than in the case of brominated phenols.

3.3. *Coatings obtained utilizing other amines*

It is possible to produce anodic coatings based on phenol using certain other amines: however, the range of conditions in which coherent films are obtained is much more restricted than for allylamine. In fact, using defined concentrations of phenol and amine, polymer films may frequently be formed but they do not always adhere to the metal substrate.

Benzylamine and propylamine resulted in good coatings on Fe and Zn sheets and ethanolamine on Zn. The results on Cu were much poorer in every case. For such systems the dependence of the coating process on the voltage applied is similar to that observed for allylamine. Under favourable conditions the coulombic yields agree with the stoichiometry of Scheme 1 as shown in Fig. 10: the compositions used for these runs are reported in the legend.

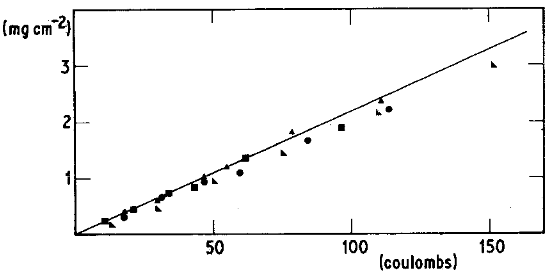


Fig. 10. Coating yields (mg cm^{-2}) obtained at Zn sheets as a function of the charge transferred to 100 cm^3 of various phenol/amine compositions in water/methanol: ■ phenol 0.75 M, propylamine 0.41 M (3.0 V applied); ▸ phenol 1.5 M, ethanolamine 0.65 M (3.5 V); ● phenol 0.62 M, allylamine 0.73 M (4.0 V); ▲ phenol 1.02 M, benzylamine 0.34 M (4.0 V).

3.4. *Physical properties and composition of the coatings*

Most of these coatings have a very good appearance and a fine gloss, their colour varying from yellow to brown-yellow. The physical properties of some samples prepared from various phenol/amine compositions are reported in Table 2: the hardness and the cross cut adhesion are very good, the salt fog resistance is fair but the adhesion under stress is rather poor. Hence the interesting properties reported for coatings typical of the phenon/2-chlorophenol/ethylenediamine are maintained or improved.

A chemical analysis of the coatings is reported in Table 3, one should note the following points:

(a) The samples obtained from 2,6- and 3,5-dimethylphenol have a composition similar to that predicted theoretically for the corresponding polyoxyphenylenes.

(b) The samples prepared from 2-bromophenol have lost ~ 30% of the bromine.

(c) The coatings prepared from phenol and various amines always contain considerable amounts of nitrogen and from 10 to 20% of the amine enters into the film composition.

The coatings prepared from phenol were completely insoluble in common solvents except tri-

Table 2. Physical properties of coating obtained from phenol–amine compositions

Metal	*System* (M)	*Thickness* (μm)	*Hardness*[*]	*Adhesion*[†]	*Adhesion + elasticity*[‡]	*Salt fog resistance*		
						20 h	*44 h*	*60 h*
Fe	Phenol (0.75), propylamine (0.41) (3.0 V)	4.2	5 H	good	fair	good	some corrosion due to porosity	corrosion on ~ 50% of the surface
Fe	Phenol (0.42), allylamine (0.50) (3.0 V)	5.0	6 H	good	fair	good	some corrosion due to porosity	corrosion on ~ 50% of the surface
Fe	Phenol (1.02), benzylamine (0.34) (4.0 V)	13.5	6 H	good	poor	good	some corrosion due to porosity	corrosion on ~ 50% of the surface
Zn	Phenol (0.75), propylamine (0.49) (3.0 V)	7.0	6 H	good	poor	some porosity no blisters	corrosion due to porosity	corrosion on 100% of the surface
Zn	Phenol (0.62) allylamine (0.73) (4.0 V)	12.0	4 H	good	fair	some porosity no blisters	corrosion due to porosity	corrosion on 100% of the surface
Zn	Phenol (1.02), benzylamine (0.34) (4.0 V)	14.5	5 H	good	fair	some porosity no blisters	corrosion due to porosity	corrosion on 100% of the surface
Cu	Phenol (0.62), allylamine (0.73) (4.0 V)	9.0	5 H	good	poor	good	good	some blisters

[*] Determined by graphite standards.

[†] Cross cut adhesion.

[‡] By conical mandrel test.

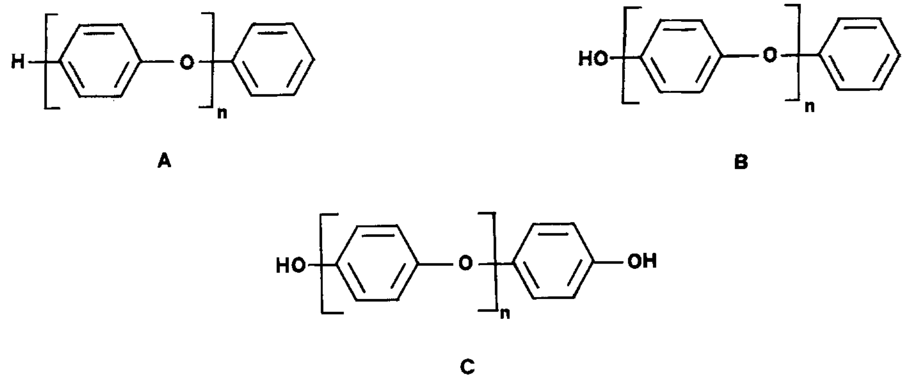
Table 3. Elemental analysis of the coatings

Sample number	*Bath composition* (M)	*Purification number*	*Theoretical composition (%)*			*Experimental data (%)*			*[Amine]/[monomer units] in the polymer*
			C	*H*	*O*	*C*	*H*	*N*	
1 Fe	2,6-Dimethylphenol 0.40, allylamine 0.85	–	80.00	6.67	13.33	76.36	6.62	absent	–
2	2,6-Dimethylphenol 0.40, allylamine 0.85	1	80.00	6.67	13.33	79.39	6.72	absent	–
3	3,5-Dimethylphenol 0.49, allylamine 0.85	–	80.00	6.67	13.33	76.43	6.62	absent	–
4	3,5-Dimethylphenol 0.49, allylamine 0.85	1	80.00	6.67	13.33	77.65	6.91	absent	–
5	2-Bromophenol[†] 0.29, allylamine 0.85	–	42.10	1.75	9.37	47.37	3.07	5.51	0.38
6	Phenol 0.62, allylamine 0.73	–	78.26	4.35	17.39	77.08	5.60	2.60	0.17
7 Zn	Phenol 0.62, allylamine 0.73	–	78.26	4.35	17.39	76.20	5.10	2.65	0.18
8 Cu	Phenol 0.62, allylamine 0.73	–	78.26	4.35	17.39	76.48	5.57	3.37	0.23
9	Phenol 0.75, propylamine 0.41	–	78.26	4.35	17.39	71.67	5.14	2.03	0.15
10	Phenol 0.75, propylamine 0.41	1	78.26	4.35	17.39	73.39	4.64	1.24	0.08
11	Phenol 1.02, benzylamine 0.34	–	78.26	4.35	17.39	71.73	4.41	2.65	0.19
12	Phenol 1.02, benzylamine 0.34	1	78.26	4.35	17.39	71.22	4.26	2.01	0.14
13	Phenol 1.02, benzylamine 0.34	2	78.26	4.35	17.39	68.27	4.01	1.92	0.14
14	Phenol 1.02, benzylamine 0.34	3	78.26	4.35	17.39	70.81	4.30	1.97	0.14
15	2,6-Dichlorophenol[‡] 0.34, allylamine 0.73	–	44.72	1.24	9.94	43.49	2.16	1.61	0.19

[*] The data referring to unpurified samples might be affected by some metal trace scratched from the sheets.

[†] Theoretical Br content 46.78; experimentally found 33.10.

[‡] Theoretical Cl content 44.10; experimentally found 35.90.



(2)

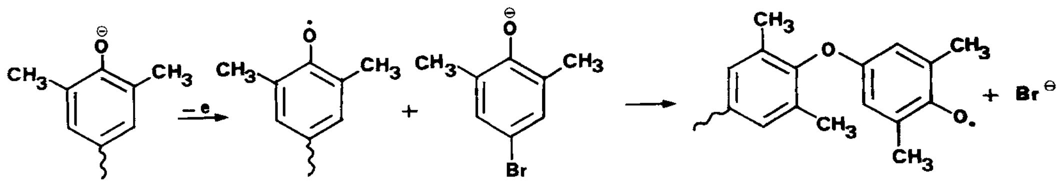
fluoroacetic acid and samples prepared using either benzylamine or propylamine could be completely dissolved in this solvent. As these samples could be precipitated by addition of water to their CF_3COOH solution, the polymers could be purified by dissolution and precipitation from any species adsorbed or entrapped in the chains. Table 3 (no. 11–14) shows the elemental analysis of a sample purified in this way and only an initial slight decrease of the amine content is seen.

Purified polymers from the phenol/propylamine system were furthermore examined by pyrolysis/mass spectrometry [11]. Thus the spectra obtained by directly introducing the samples into the ionic source (mass spectrometer: Hitachi Perkin-Elmer RMU 6) at 300–500° C, with energies in the range 15–70 eV, other than the pyrolysis products reported in Scheme 2 [12], showed significant new peaks. Peaks were observed having m/e values 57 units higher than those typical of series A, B and C ($n \geq 4$). These masses correspond to structures wherein a propylamino group replaces a hydrogen of a phenoxy unit. For the polymer obtained from the phenol/benzylamine system, phenoxy moieties bearing benzylamino groups could not be detected, because of the easy fragmentation of the amine–benzyl bond as shown by a strong peak at m/e = 91. The intensity of this peak was higher than the intensities of fragments at m/e = 106 and 107, in contrast to the typical pattern of free benzylamine.

4. Discussion

After emphasizing the similarities that exist between the anodic polymerization of phenols and the synthesis of polyoxyphenylenes carried out by chemical catalysis, the discussion will be focused on the role of the amine, which is not only fundamental to the outstanding behaviour of the electrochemical systems but it has no analogue in the literature on the chemical polymerization of phenols. The similarity of the products obtained in this work from 2,6-dimethylphenol with those described in the literature [10, 13–15], the pyrolysis/mass spectrometry fragmentation pattern of the products obtained from phenol, as well as the coulombic yields, leave little doubt that the polymerization takes place by alternating one electron oxidation steps with coupling steps according to Scheme 1.

The C—X bond cleavage observed during the polymerization of 2-bromophenol and 2,6-dimethyl-4-bromophenol also has an analogue in chemical polymerization [16–19]. In the case of 2,6-dimethyl-4-bromophenol the coulombic yield shows a stoichiometry of



(3)

monomer polymerization well above the usual 0.5 mol F^{-1} (see Fig. 9) and this suggests the occurrence of chain propagation steps according to Scheme 3.

With regard to the function of the amine, two points must be discussed (i) the role of the amine at the electrode; (ii) the subsequent fate of the amine in the coating composition.

With respect to the first point, amine adsorption on Fe sheet anodes has already been suggested as the key step in the inhibition of the fast passivation phenomena normally observed during phenol oxidation [2]. The evidence obtained in this paper from voltammetric data allow a more complete picture. In fact:

(a) At least for Fe anodes in alkaline medium, the application of a potential above 0.5 V (SCE), causes the formation of passivating metal oxides (this is in agreement with literature data [20]).

(b) The addition of amine inhibits metal oxidation, but allows for the occurrence of other anode reactions (this is also known, as aliphatic amines may inhibit Fe corrosion [21]). Therefore, when phenol is present in a solution containing amines it may be oxidized at Fe, but the metal surface freed from the competitive growth of oxides is passivated only when a thick polymer film is formed. Confirmation of this view is obtained from both the influence of the applied voltage and the effect of amine concentration. When the voltage is raised, the potential applied to the Fe anode rises so that amine desorbs [22] and Fe is oxidized: thus the formation of metal oxides together with polyoxyphenylenes leads to fast passivation (Fig. 1) by thin films of poor physical features*. It is reasonable that such effects may be reduced by increasing both amine (see Fig. 4) and phenol concentrations. The phenomena involved at a Zn sheet anode are probably similar, whereas some difference exists at Cu. On Cu, in fact, polyoxyphenylenes might be synthesized in part by an indirect oxidation of phenol through copper ions, or copper–allylamine complexes formed *in situ*†. This is not surprising when considering that copper I (in the presence of oxygen) and copper II amine complexes [10, 13–15] are widely used catalysts in the chemical polymerization of phenols. The higher instability of the bath when Cu sheets have been coated, and the high specificity to the amine (only allylamine works properly with Cu sheets) seem to support this mechanism.

The presence of large amounts of nitrogen in the purified coatings indicate that most of the amine is strongly bound to the polyoxyphenylene chains. In fact, the purification using a strongly acid solvent such as CF_3COOH, not only removes the entrapped amine but should also have hydrolyzed any imine bond formed while drying in the oven. A further definitive test for the existence of strong bonds between phenoxy moieties and amine was given by the mass spectra.

Some evidence for the mechanism by which a bond may form between a phenoxy unit and amine, is given by the absence of amine from the polymers obtained from 3,5- and 2,6-dimethylphenol. It is necessary to propose a route to form a stable bond between the amine and a ortho or meta position in the ring.

A radical reaction seems very unlikely since it would involve the formation of unstable amine radicals through radical transfer steps from the very stable phenoxy radicals: moreover, if radical transfer could take place, allylamine should have been affected by vinyl polymerization. Therefore the reaction must be of different character.

It is known that the subsequent growing steps of polyoxyphenylene chains involve not only head-to-tail coupling (Scheme 1) but in addition the quinol–ether equilibration of polymeric phenoxy radicals [13, 23, 24] (Scheme 4). Indeed the quinoid intermediate (I) should be open to nucleophilic attack from the amine, as in the easy room temperature reaction between quinones and amines [25]* and the attack would take place in the meta position according to Scheme 5. Indeed, when the two meta positions are blocked the reaction does not occur. But what about the absence of nitrogen in polymers obtained from 2,6-dimethylphenol? For this compound the electrodonating effect of the methyl groups may

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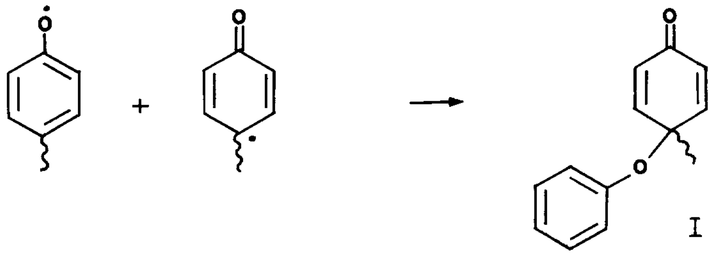
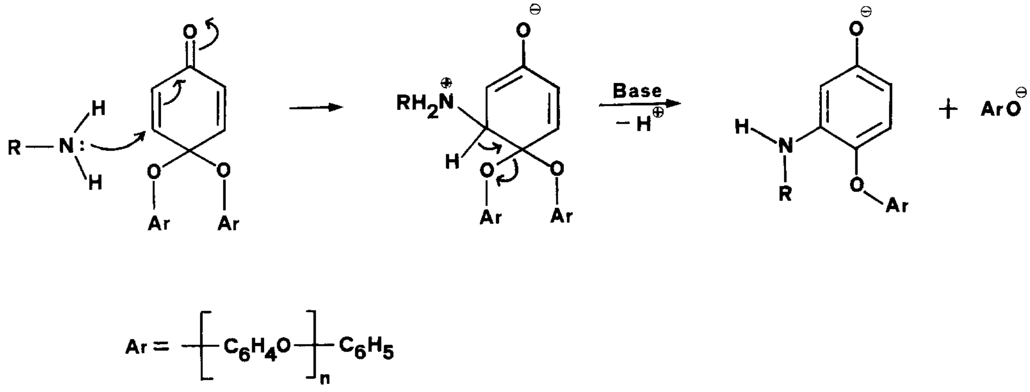
* The nature of these films (polymer mixed with Fe oxides) is supported by their very poor resistance to salt fog and mild acids.

† The 0.5 mol F^{-1} stoichiometry might be maintained by anodic oxidation of the catalyst exhausted after interaction with phenoxide ions.

* Such reaction gives rise initially to aminohydroquinone from quinone and primary and secondary amines, whereas stable zwitter ions are obtained when tertiary amines such as pyridine are used [26].



(4)



(5)

make the nucleophilic attack unfavourable so that the intermediate, I, may dissociate before amine is added. In support of this proposal the polymer obtained from 2-bromophenol (for which an electronwithdrawing effect by Br is expected) has the highest nitrogen content and a large number of amino groups are bound to the polymer obtained from 2,6-dichlorophenol (see Table 3). According to the literature [27] other nucleophilic agents present in the system might add to I, (methanol, cellosolve or OH^-) and indeed elemental analysis of the polymers often shows oxygen contents higher than expected (see Table 3). However the amine, for either concentration or basicity reasons, shows the highest ability to enter into the polymer. In conclusion the coatings prepared from phenol under the conditions described mainly consist of polyoxyphenylene chains modified by a large number of amine moieties grafted on to them.

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