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Anodic formation of thick polyoxyphenylene coatings onto Fe plates from phenol-ethylenediamine systems

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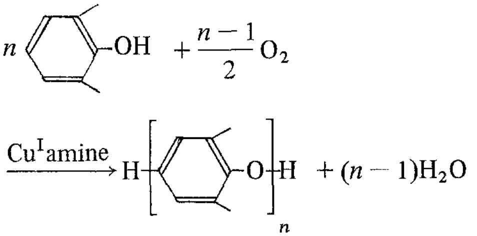
The electrolysis at an iron anode of water–methanol (20–30 vol%) solutions containing phenol as the main monomer and small amounts of a substituted phenol (generally *o*-chlorophenol) and ethylenediamine leads to thick and adhesive polyoxyphenylene coatings on the electrode surface. The yield of polymer indicates that 2F mol^{-1} of phenol are transferred in the polymerization: the thickness of the deposit depending on both the applied potential and the composition of the solution. Thus in such systems it is possible in a single-step to attain preparation of the polymer and its deposition as a cross-linked highly insoluble protective film onto Fe articles.

1. Introduction

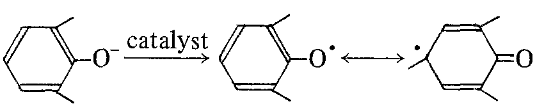
The polymerization of phenolic compounds is generally carried out with oxygen in the presence of a metallic catalyst [1–4], according to the scheme



(1)

The process takes place through two fundamental steps [3–5]:

(a) oxidation of phenolate anions to free radical intermediates



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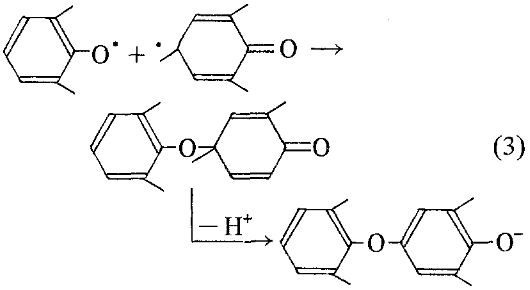
(b) Coupling of phenoxy radicals,



(3)

both oxidation and coupling† being repeated at each monomer addition.

The oxidative coupling polymerization of phenols has also been performed electrochemically [6, 7] (by replacement of the catalytic oxidation with anodic oxidation) but this route has no advantages over the chemical synthesis which is considered quite satisfactory.

The electrochemical method may, however, become favoured when the polymerization develops on the anode surface with the formation of protective films: polyoxyphenylenes have very good properties [8] but their application to a sub-

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† Coupling reactions other than head-to-tail addition can occur [4, 5].

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strate as protective cross-linked films is difficult by the traditional coating techniques.

The formation of passivating films has been observed by several authors during the investigation of the anodic oxidation of phenol compounds [9–11] and the phenomenon is of interest for practical utilization. Thus the synthesis of polyoxyphenylene coatings onto anodes of several metals was studied using a molten phenol in the presence of alkaline hydroxides [12] or organic bases [13] as media. The resulting films were very thin, $\sim 10^2$ nm, but had good dielectric properties and thermal stability. The current efficiency was, however, very low as the electropolymerization of 1 mol of phenol required 50–70 F, and the toxicity and resistivity of the medium made the development of the process difficult. In this second respect the electropolymerization of the phenol–NaOH system in water claimed by a patent assigned to Grace company [14], appears more advantageous but the current efficiency was low and the throwing power of the coating must be negligible since the deposition process performed at constant potential is not coupled to any significant current decrease.

The most interesting results have recently been obtained by electrolysis of substituted phenols in methanol–OH^- [15, 16]: this medium favours polyoxyphenylene precipitation on the anode surface with the consequent formation of compact insulating films of good throwing power. However, since the fast deposition process is paralleled by a complete passivation of the anode, coatings having a thickness over $\sim 10^2$ nm cannot be obtained. Films of this type are likely to have only very limited applications (e.g. in electronics).

Recently, however, we have shown [17] that some water-based phenol–ethylenediamine compositions lead, on electrolysis at Fe anodes, to coatings reaching 15–20 μm in thickness.

Such deposits might have a wide range of possible applications and in the present paper the details of the process are described and an interpretation of the results is attempted.

2. Experimental

2.1. *Chemicals*

All compounds used in this work were commercially available reagent grade chemicals and were used as supplied.

2.2. *Preparation of the Fe plates*

The Fe samples to be utilized for the coating process were cut from sheets of both hardened steel and soft steel of dimensions 23·5 cm x 2·5 cm x 0·05 cm; the total surface utilized for coating was $\simeq 25$ cm^2.

To obtain reproducible results it was necessary to carefully clean the Fe plates. The cleaning procedure conformed to the metal anti-rust treatment practised by the manufacturers. After degreasing with acetone, the soft steel plates were washed by alkaline soaps and acid solutions (HCl 10%) and were adopted for the hardened steel plates; they were then rinsed again with acetone and finally dried at room temperature. Generally the plates could be utilized for the coating process even some days after such treatment.

2.3. *Electrochemical runs*

The coating was performed at 25° C in a single compartment cell by applying a constant potential difference between two electrodes; the cell consisted of a glass cylinder, in which a platinum coil fastened to the cell wall was the cathode and the Fe plate to be coated was the anode placed vertically along the axis of the cylindrical cell.

This very simple electrolyser could be adopted since with water-based systems the cathode reaction was the discharge of water which did not affect the polymerization at the anode surface.

Formation of coatings was also investigated on a microscale by steady state potentiostatic technique, linear sweep voltammetry and potential step: a two compartment cell equipped with a SCE reference electrode which was separated from the working anode by a Luggin capillary and a tap was used. Fe anodes having a surface area in the range 0·5–0·2 cm^2 were used for these measurements.

2.4. *Characterization of the coatings*

Having been coated for a prefixed electrolysis time and withdrawn from the cell, the Fe plate was left for some minutes to allow excess solution to drip onto blotting paper and then dried in an oven at 100–120° C for 15 mins. Afterwards, the amount of polymer formed in the run was calculated from the difference in weight of the plate before and after the coating process and was normalized in mg cm^{-2}. The thickness of the films was measured by a magnetic gauge supplied by Amico: it showed that 1 mg cm^{-2} corresponds to $\sim 9 \mu m$ thickness.

Cross cut adhesion tests were performed by making a series of parallel cuts in one direction and a second series at right angles to the first, applying adhesive tap and stripping.

Conical mandrel tests were performed with the apparatus described in ASTM method D 522. Salt fog resistance was tested by ASTM method B 117 for times from 24–48 h. The hardness, relative to a glass standard, was metered using a pendulum hardness rocker. Chemical composition of the coatings was analysed by i.r. spectrometry and elemental analysis.

3. Results

3.1. *Preliminary runs*

Water was chosen as the main solvent because of its obvious practical advantages. The complete solubilization of high concentrations of phenol (1–2 M) could be obtained by adding some methanol (20–30 vol%).

When such solutions are electrolysed at an Fe plate anode, two main results may be observed according to whether phenol is partially neutralized with an alkaline hydroxide or an organic base.

In the first case the results do not differ much from those reported for alcoholic solutions [15, 16]. With low potential differences applied the Fe plates are rapidly (a few minutes) passivated by a very thin film whose presence may be deduced only because the surface becomes hydrorepellent. For high potential differences the films are broken and for long electrolysis times a powdery or spongy deposit is formed.

With an aliphatic amine as the base, however, a fast passivation of the Fe anode is not observed and on prolonged electrolysis polymeric oils gather at the bottom of the cell.

The results do not substantially change on electrolysing phenol, substituted phenols or their mixtures.

Quite remarkably when phenol is neutralized with ethylenediamine an intermediate behaviour is observed; the passivation is considerably slowed down and polymeric material is visibly formed onto the Fe anode.

However compact, adherent networks build up only when minor amounts of a mono- or di-substituted phenol are present in the solution: *o*-chlorophenol proved to be particularly suitable.

Thus, the system which will be discussed below generally comprised phenol, *o*-chlorophenol (ratio of *o*-chlorophenol to phenol from $\simeq 0{\cdot}1$ to $\sim 0{\cdot}2$) and ethylenediamine. The systems may also contain from 1–3% of cellosolve, which gives a better gloss to the coatings.

3.2. *Variables of the process*

The coating process was performed in the cell described above using potential differences in the range 3–6 V and this leads to initial currents in the range 5–15 mA cm^{-2}.

When the electrolysis was carried out at 3 V with a hardened steel plate in an aqueous solution of CH_3OH (25 vol%), phenol (1·42 M), *o*-chlorophenol (0·16 M), ethylenediamine (0·45 M) and having a pH of 9·6 the current decreases with time according to the plot (curve a) of Fig. 1. The cur-

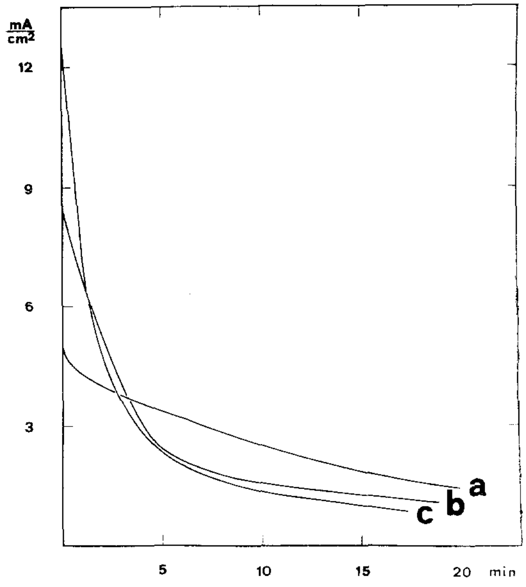

Fig. 1. Plots of the current versus time for various applied potentials: (a) 3 V; (b) 4·5 V; (c) 5·5 V. Electrolysis system: H_2O–CH_3OH (25 vol%), phenol (1·42 M), *o*-chlorophenol (0·16 M), ethylenediamine (0·45 M).

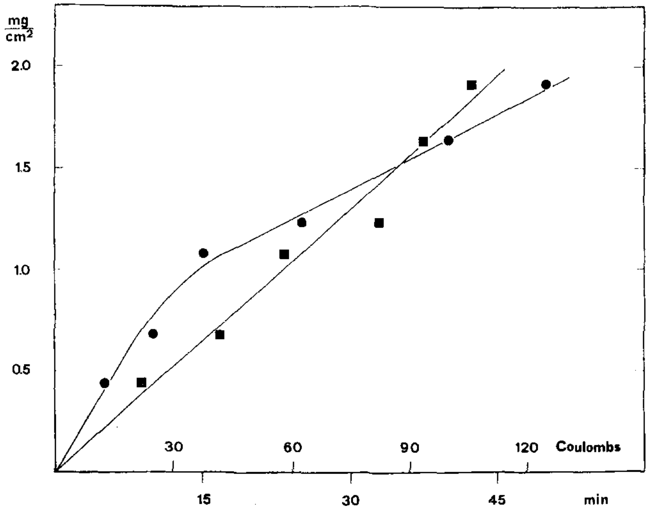

Fig. 2. Polymer yield obtained from the system of Fig. 1 as a function of: ● electrolysis time; ■ coulombs passed through the solution (potential applied, 3 V).

rent drop is paralleled by the formation of a homogeneous coating which grows for different electrolysis times according to the data reported in Fig. 2 (circles).

The growth rate slows down with time since there is a linear proportionality between the weight of the polymer formed on the plate and coulombs passed. When the applied potential difference is increased, the coating process becomes faster and results in the sharper drop in the current (curves b and c of Fig. 1). The same proportionality between yield of polymer and charge passed is maintained until the cell potential is 8–9 V. On increasing the potential further the current yield of polymer drops and eventually the coating is no longer formed.

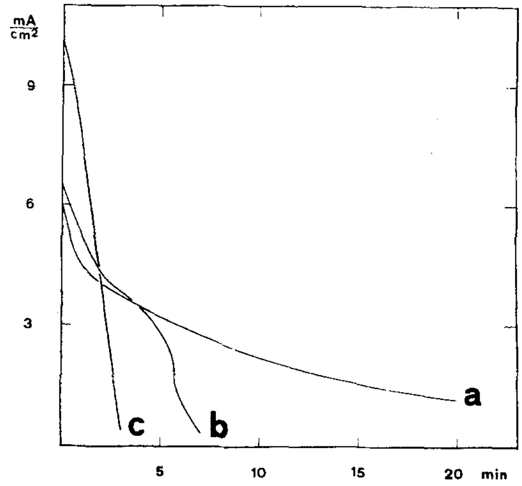

Fig. 3. Plots of the current versus time for systems having the same monomer composition as in Fig. 1 but different ethylenediamine concentrations. Curve a: ethylenediamine 0·75 M, 3 V applied; Curve b: ethylenediamine 1·35 M, 3 V applied; Curve c: ethylenediamine as for curve a but 4·5 V applied.

In quantitative terms, this behaviour is strongly dependent on the relative amounts of the active components in the solution. Thus, if the concentrations of phenol and *o*-chlorophenol are kept constant and the concentration of ethylenediamine is increased, the passivation of the Fe anode tends to be faster (Fig. 3 curves a and b). With these concentrations of ethylenediamine the system becomes much more sensitive to an increase of the applied potential and the passivation becomes even faster. Thus in Fig. 3 for the same conditions of curve a, a 1 V increase in potential leads to the sharp current drop shown by curve c.

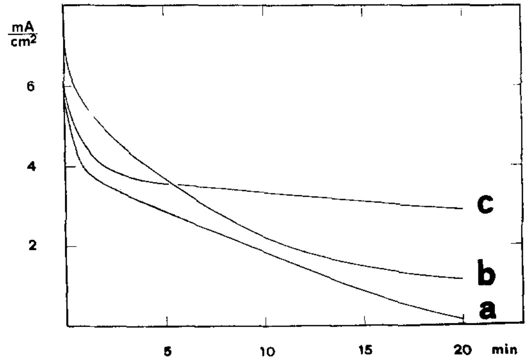

Fig. 4. Plots of the current versus the electrolysis time for systems having the same composition: H_2O–CH_3OH (25 vol%) *o*-chlorophenol (0·19 M) and ethylenediamine (0·75 M), but different phenol concentrations: (a) 0·8 M; (b) 1·06 M; (c) 1·6 M.

Table 1. Polymer coating yields from different phenol/o-chlorophenol/ethylenediamine systems [solvent H_2O/CH_3OH (25 vol%); $T = 25°$ C; cellosolve = 2·5 vol%]

Phenol (M)	o-*Chlorophenol* (M)	*Ethylenediamine* (M)	*Potential difference* (V)	*Electrolysis** *time* (min)	*Yield*	
					(mg cm^{-2})	(g F^{-1})
0·80	0·19	0·75	3·0	18	0·80	40
0·80	0·19	0·75	4·0	2	0·20	39
1·06	0·08	0·75	2·7	19	0·80	42
1·06	0·08	0·75	3·0	15	0·84	43
1·06	0·08	0·75	4·0	5	0·40	38
1·06	0·08	0·75	4·5	2	0·16	39
1·06	0·10	0·75	3·0	25	1·20	42
1·06	0·19	0·75	3·0	45	2·00	45
1·06	0·19	0·75	3·0	30	1·50	38
1·42	0·16	0·45	3·0	30	1·10	37
1·42	0·16	0·90	3·0	30	1·50	45
1·42	0·16	0·90	4·0	5	0·30	35
1·42	0·16	1·35	2·5	36	1·10	46
1·42	0·16	1·35	3·0	6	0·40	42
1·60	0·19	0·75	3·0	50	3·10	46
1·60	0·19	0·75	4·0	30	1·80	42

* Time necessary to reduce the initial current by > 90%.

If the ethylenediamine concentration is kept constant and phenol (or *o*-chlorophenol) concentration is varied, at high monomer concentrations the current shows a slower decrease with electrolysis time, whereas the passivation is faster at low concentration. These observations are illustrated in Fig. 4. Table 1 reports the electrolysis times for the current to be reduced (at hardened steel plates) to a negligible value ($\leqslant 0{\cdot}2$ mA cm^{-2}, less than 10% of the initial value) and the polymer yields obtained for different phenol/*o*-chlorophenol/ethylenediamine compositions.

If the rate of current drop is a good test for the completeness of the coating, then high ratio of ethylenediamine/phenol and high potentials lead, as a rule, to a faster coating of the Fe substrate, but the deposit is thinner since the coatings are formed with a well-defined stoichiometry (40–45 g per faraday). Conversely one may programme the conditions to control the thickness of the finished film.

3.3. *Electrochemical measurements*

The formation of passivating films and the effects of phenol concentration on Fe passivation rate are also shown by the current–potential curves reported in Fig. 5. These curves were plotted by recording at each potential the current after either 3 min (squares and triangles) or 30 s (circles) of potentiostatic electrolysis.

At high ethylenediamine–phenol ratios (squares) the Fe anode becomes almost completely passivated for the whole range of potentials. On increasing the concentration of phenol an electrode reaction is observed at ~ + 1 V and at short times higher currents are obtained at each potential (circles) but after 3 min the same irreversible passivation of the electrode is seen.

The linear sweep voltammetry runs are illustrated by the two curves of Fig. 6; one was obtained at a hardened steel and the other at a soft steel anode of the same area.

Two oxidation processes seem to take place with current plateaux at + 0·75 V and + 1·15 V respectively. The first process, which gives the same current at both the electrodes, probably involves the one electron oxidation of phenolate anion [15] while the second may be related to Fe oxidation. These reactions are followed by an irreversible passivation and successive sweeps show a totally passivated surface unless the anode is scratched and cleaned between cycles.

The lower current at + 1·15 V attained at a

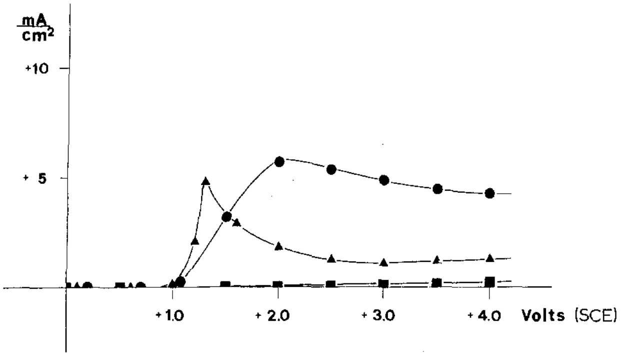

Fig. 5. (Pseudo) steady state current–potential curves for the systems: ■ H_2O–CH_3OH (25 vol%), phenol (0·53 M), *o*-chlorophenol (0·05 M), ethylenediamine (0·75 M), 3 min of electrolysis at each point. ▲ H_2O–CH_3OH (25 vol%), phenol (1·42 M), *o*-chlorophenol (0·13 M), ethylenediamine (0·75 M), 3 min of electrolysis; ● same composition but 30 s of electrolysis.

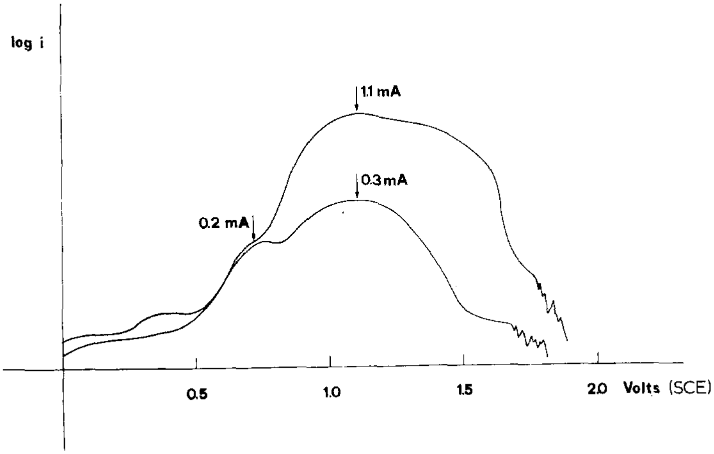

Fig. 6. Current–potential curves recorded by linear sweep voltammetry (200 mV min^{-1}) from the system: phenol (1·06 M), *o*-chlorophenol (0·15 M), ethylenediamine (0·75 M). The lower current was obtained at a hardened steel anode, the higher at a soft steel anode.

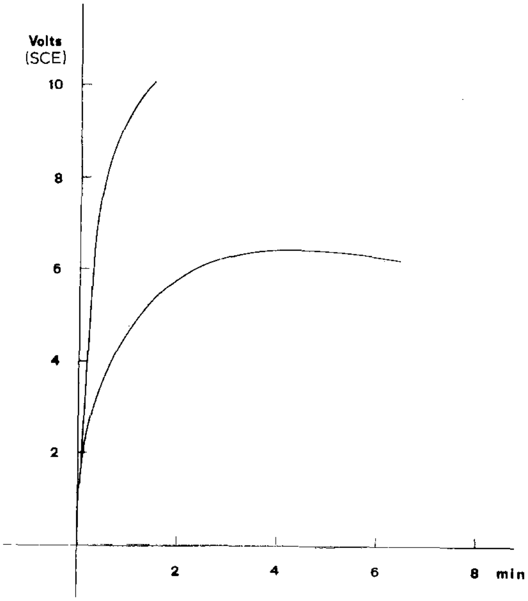

Fig. 7. Variation of the potential with time following an amperostatic pulse (6 mA cm^{-2}). The sharper curve was recorded at hardened steel, the other at soft steel.

hardened steel anode probably does not involve a slower oxidation rate of Fe but the faster formation of a homogeneous and insulating film. This fact is confirmed by a galvanostatic experiment (see Fig. 7), where, following a 6 mA cm^{-2} current pulse, a far steeper potential increase is recorded at hardened steel than at a soft steel anode.

3.4. *Physical properties*

The coatings are tightly bound to the Fe substrate and very hydrorepellent so that they may be easily rinsed by water or alcohol without removing any solid material. Once dried in an oven they show a homogeneous aspect and a good gloss, the colour varying from green–yellow to dark yellow or red depending on the thickness of the deposit and the composition of the electrolytic bath in which they were prepared. When observed under an electron microscope (x 5000) the surface of the coating appears homogeneous with some very small lumps or holes. If the thickness exceeds ~ 10 μm, how-

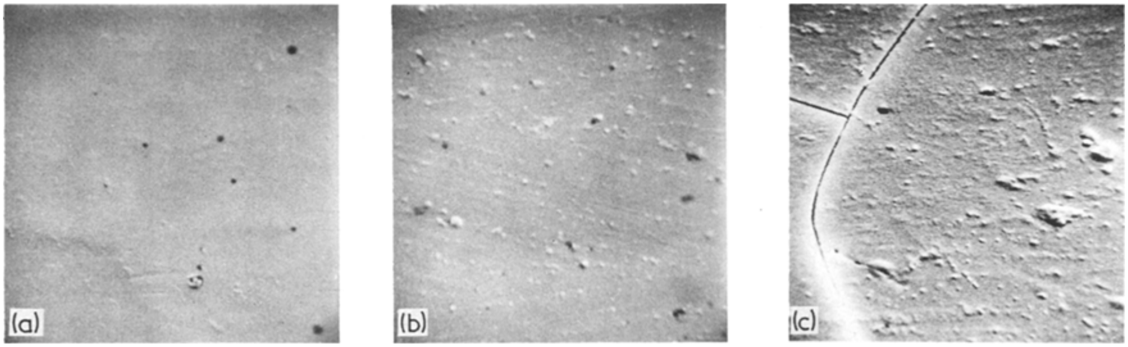

Fig. 8. Micrographs of coating samples taken by an electron microscope (X 5000). (a) Homogeneous coating, thickness = 9 μm; (b) coating showing some lumps and holes; (c) coating showing cracks, thickness = 15 μm.

ever, cracks are formed during the drying procedure. Electron micrographs of typical samples are shown in Fig. 8.

The adhesion and hardness of the coatings is good, as is their resistance to solvents and dilute mineral acids and bases. There is some lack of elasticity probably due to the intrinsic rigidity of polyoxyphenylene chains with cross-linking.

The salt fog resistance may be considered sufficient to good for the samples described in Table 1. These samples were withdrawn from the electrolytic cell when the current had fallen to a low value. When the coating process was stopped before reaching this low current (as for the coatings of Fig. 2) the films generally have a higher microporosity and consequently a higher rate of corrosion.

3.5. *Experiments with substituted phenols other than* o*-chlorophenol*

Not every mono- or di-substituted* phenol is suitable for replacing *o*-chlorophenol in these systems; homogeneous adherent polymer networks on Fe anodes were, however, obtained from the systems reported in Table 2. Although these data substantially fit with those obtained using *o*-chlorophenol, the coating process often exhibits some differences with respect to the current–time behaviour and the

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* With the para position free.

Table 2. Polymer coating yields from various phenol/substituted phenol/ethylenediamine systems [solvent, H_2O/CH_3OH (20–25 vol%); concentration of phenol = 1·06 M; cellosolve = 2·5%; applied voltage = 3 V; T = 25° C]

Substituted phenol	*Concentration* (M)	*Ethylenediamine* (M)	*Electrolysis time* (min)	*Yield*	
				(mg cm^{-2})	(g F^{-1})
2·6 dimethyl-	0·08	1·50	7	0·52	46
2·6 dimethyl-	0·08	1·50	15	0·76	46
2·6 dimethyl-	0·08	1·50	25	1·08	46
2·6 dimethyl-	0·08	1·50	45	1·80	47
3·5 dimethyl-	0·08	0·75	7	0·48	47
3·5 dimethyl-	0·08	0·75	15	0·80	39
3·5 dimethyl-	0·08	0·75	45	1·12	37
3·5 dimethyl-	0·08	1·50	15	0·76	33
o-methoxy-	0·18	0·75	7	0·64	43
o-methoxy-	0·18	0·75	15	1·08	41
o-methoxy-	0·18	0·75	25	1·52	41
o-methoxy-	0·18	0·75	30	1·84	42
o-methyl-	0·18	1·50	15	0·85	42
o-methyl-	0·18	1·50	20	1·25	41
o-methyl-	0·18	1·50	30	1·60	42
o-methyl-	0·18	1·50	45	2·50	46

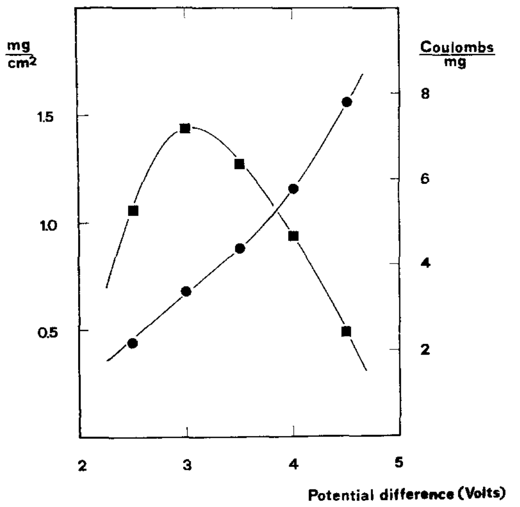

Fig. 9. System: H_2O–CH_3OH (20 vol%), phenol (1·04 M), *o*-cresol (0·19 M), ethylenediamine (1·35 M). ■ polymer yield after 25 min of electrolysis versus the applied potential. ● Coulombs necessary for the deposition of 1 mg of polymer versus the applied potential.

influence of the potential. For example, using *o*-cresol instead of *o*-chlorophenol results in coating which are less insulating; i.e.:

(a) With a low applied potential (2.8–3 V), the electrolytic current after an initial drop decreases very slowly. Thick coatings may consequently be obtained as the current yield is in the range 40–45 g F^{-1}. The microporosity of the film may, however, be high after prolonged electrolysis.

(b) No passivation of the Fe plates occurs at higher potentials and, since the current attains some relatively high stationary value, there is a sharp drop in the current yield of the coating. These facts are illustrated in Fig. 9.

As a consequence of this behaviour the resulting polymer films may give a lower protection against corrosion as seen in Table 3 which shows the influence of some substituted phenols on the physical properties of the products.

3.6. *Composition of the coatings*

As previously mentioned the coatings are practically insoluble in every solvent. Consequently molecular weight determinations were not possible and the polymer constitution could not easily be investigated. However, when a film was analysed by i.r. the spectrum reported in Fig. 10 was obtained. It is typical of polyoxymethylene structures, the broadened adsorption in the 3500–3000 cm^{-1} region being attributable to hydroxyl groups and amino groups (from ethylenediamine).

The presence of large amounts of amine in the coatings was confirmed by elemental analysis, the N content generally varying from ~ 2·5 to ~ 5·5%.

In an experiment of polymer degradation, some powdery material scratched from the plates was stirred with a boiling solution of HCl (10 M). After 3 h of reaction about 33% of the polymer had dissolved. The insoluble material had the following composition: N = 2·6%, C = 64·7%, H = 4·5%. However, mass spectroscopic analysis of the acid solution showed phenols and ethylenediamine as the main products of the hydrolysis.

Although ethylenediamine seems unlikely to enter directly in the polymer chains,* it has, however, a specific function in the formation of the coatings as emphasized by the following data:

(a) The coatings obtained from solutions having a low concentration of ethylenediamine have a high content of this compound in their composition (Fig. 11).

Table 3. Characteristics of coatings obtained from various phenol/substituted phenol/ethylenediamine systems

T_g(K)	*Hardness*	*Aspect*	*Thickness*	*Elasticity*	*Adhesion*	*Salt fog resistance*	*Substituted phenol*
312	good	v. good	15	poor	good	good	*o*-chloro-
310	good	v. good	12–15	poor	good	poor	2·6 dimethyl-
312	good	good	6–15	poor	poor	poor	3·5 dimethyl-
309	good	good	10–11	fair	poor	poor	*o*-methoxy-
310	good	good	15–25	poor	poor	poor	*o*-methyl-

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* Ethylenediamine probably grafts onto polyoxyphenylene chains.

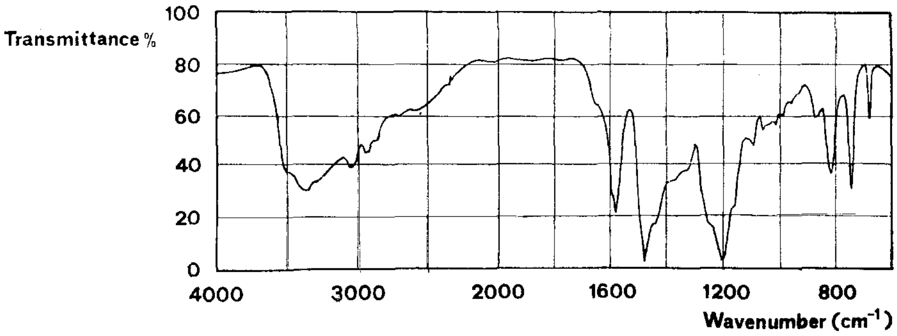

Fig. 10. i.r. spectrum of a typical coating.

(b) A H_2O–methanol (25 vol%) solution was prepared containing phenol (1·06 M) and *o*-chlorophenol (0·13 M) which were partially neutralized with NaOH (0·23 M) so that a pH of 10·5 was attained. When this system was electrolysed with an applied potential in the range 2·5–10 V, less than 0·1 mg cm^{-2} of spongy deposits could be obtained on an Fe plate anode after 30 min electrolysis. Conversely, the step-wise addition of ethylenediamine caused polymer formation even at the first addition; the optimum ethylenediamine concentration was 0·75 M, as is shown in Table 4. It must be noted that during the experiment the pH of the solution did not change from the initial value of 10·5.

3.7. *Stability of the systems and reproducibility of the results*

Obtaining good coatings is not sufficient to assess the utility of a coating process. The process must also give reproducible results and the bath must be stable and allow repeated coating operations.

The phenol/*o*-chlorophenol/ethylenediamine system fulfills such reproducibility and stability requirements as can be seen from the following experiment.

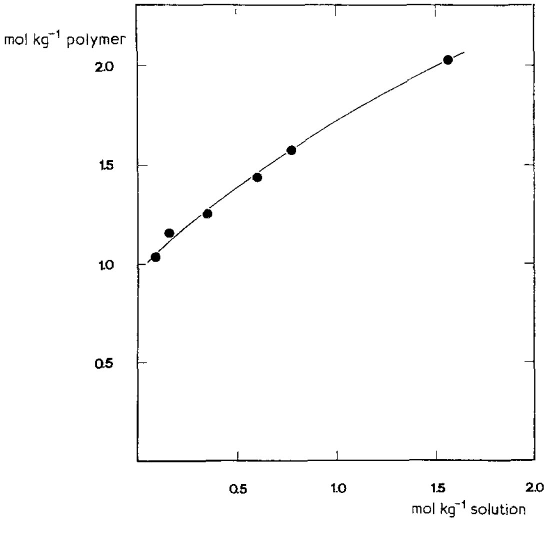

Fig. 11. Ethylenediamine in the polymer as a function of its concentration in the electrolysed system.

Table 4. Polymer yield obtained after electrolysing for 30 min a water–methanol (25 vol%) solution containing phenol (1·06 M) o-chlorophenol (0·13 M) and NaOH (0·23 M) for various additions of ethylenediamine

Ethylenediamine (M)	*Polymer yield* (mg cm^{-2})
0·00	$\leqslant$ 0·10
0·22	1·28
0·37	1·56
0·45	1·76
0·75	1·88

After introducing into the cell 100 cm^3 of a water–methanol (25 vol%) solution containing phenol (1·06 M), *o*-chlorophenol (0·15 M) and ethylenediamine (0·75 M), 95 Fe plates were anodized by applying 3 V for 30 min. When the last plate was withdrawn from the cell ~ 8000 C had been passed through the system. The solution during the coating operations lost about 26% of its initial volume. Furthermore, on analysis by gas chromatography the solution was found to contain phenol (72·5% of the initial amount) and *o*-chlorophenol (83%). The total polymeric material coated onto the plates was 3·3 g, corresponding to ~ 26% of the initial monomer content. Only traces of Fe ions were present in solution ($< 10^{-5}$ M), and and the pH had the initial value of 10·02.

The efficiency of the process does not decrease as can be seen from Fig. 12 where the polymer yield on each plate is plotted as a function of the progressive number of the plate. Also the appearance and the physical properties of the coatings are independent of the progressive number of the plate.

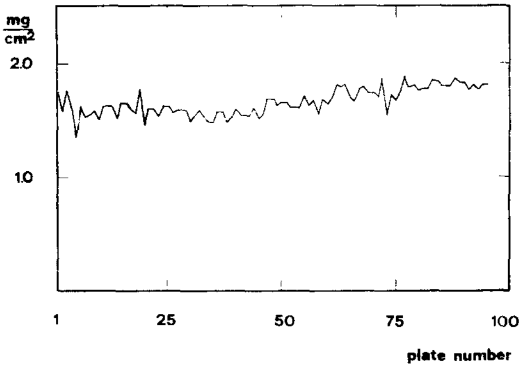

Fig. 12. Polymer yield obtained after 30 min of electrolysis with 3 V, versus the number of the coated plate. System: H_2O–CH_3OH (25 vol%), phenol (1·04 M), *o*-chlorophenol (0·15 M), ethylenediamine (0·75 M).

4. Discussion

The results presented above allow some sound deductions about the mechanism for the anodic formation of polyoxyphenylenes, but other aspects of the process must remain only speculation.

There are good reasons to think that the polymerization takes place by the oxidative coupling mechanism suggested for the related chemical process. It can be calculated from the current yields reported in Tables 1 and 2 that the polymerization of each phenol molecule involves the transfer of ~two electrons to the Fe anode. This is in agreement with the mechanism of Reactions 2 and 3 whereby each monomer addition step requires, independent of the polymer chain length, the oxidation of two anionic ends to the corresponding radicals.

It seems more difficult to explain why thick coatings are obtained under the conditions of this work, whereas only very thin films are possible with systems based on phenols neutralized with metal hydroxides. When a Fe plate is anodically polarized in a solution containing some phenolic compounds partially neutralized with an inorganic base, phenolate anions are present at the metal–solution interface. These anions are very likely to assume:

(a) a planar position towards the electrode surface [18] owing to the interaction of aromatic nucleous π-bonds with the ions of the anode lattice.

(b) A well-defined orientation with respect to each other (for instance head-to-tail) due to the lateral interaction of the negative ends.

Thus, once the charge transfer with the anode metal commences, the coupling reaction is highly likely to develop along the plane of the electrode which becomes rapidly coated by a polymer layer. At this point the charge transfer between phenolate anions and metal may still take place through either the chain interstices or the π-systems of polyoxyphenylene molecules, but the initial metal/phenolate anion interactions are fading. Consequently if the solvent causes the precipitation of the chains which are subsequently formed (as methanol [15, 16]) in a short time the anode will be passivated by a compact thin film; otherwise the charge transfers taking place through the first polymer layers are unlikely to be fruitful for further polymerization *in situ*.

On the other hand, if phenol is neutralized with an amine, the accumulation and orientation of phenolate anions at the Fe anode surface will be different owing to the competitive adsorption of the amine, which also interacts with Fe ions of the anode lattice. When the charge transfer occurs, the amine molecules break the coupling reactions along the electrode plane and the polymerization will propagate towards the bulk of the solution: this is the situation with most of the amines.

What about ethylenediamine? An experiment shows the accumulation of ethylenediamine at the metal–solution interface (see Fig. 11); but why are homogeneous thick coatings formed with high current yields from solutions of this amine?

Some speculation is necessary here. Probably much of this behaviour is due to the presence of two functional groups whereby ethylenediamine might both interact with the Fe anode and interact with the phenolic compounds at the interface (perhaps through ionization). Thus the polymerization would mainly occur flat, close to the electrode surface. The fast passivation of the electrode by thin hydrophobic polyoxyphenylene layers would be overcome by ethylenediamine solvation, which would allow the charge transfers to take place through relatively thick coatings.

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