

The role of amines as complexing agents in film growth during electropolymerization of ester substituted phenols onto mild steel

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Received 19 February 1985; revised 12 June 1985

Electrolytic scouring required prior to the electrodeposition of non-polymerizable phenols onto an iron oxide layer at low potentials can be accelerated by the addition of polyamines as iron complexing agents. The scouring ability of $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$ diamines increases as n increases. Monoamines display a general tendency to delay electropolymerization.

1. Introduction

In seeking to prepare polyphenylene oxide films displaying good corrosion protection properties for steel, we recently conducted a previously described [1] electropolymerization of phenols with an ester functional group substituent and deduced from the voltammetric study of these phenols that film growth falls into two categories. A more in-depth potentiostatic study of these film growth processes, described herein, indicates that for certain phenols film formation can occur directly on the oxide layer, whereas for other phenols it can occur on the metal electrode surface only after removal of the oxide layer by electrolytic scouring.

The presence of a complexing agent that can prevent iron in the form of insoluble hydroxide from redepositing onto a surface is known to greatly enhance the efficiency of an alkaline electrolytic scouring bath. It would seem to follow, by analogy, that the addition of complexing agents such as amines to electrolytic solutions might accelerate the destruction of the oxide layer hindering the electropolymerization of certain phenols such as methyl salicylate and thereby quicken the formation of very adherent films at moderate potentials.

Unlike strong complexing agents such as gluconates, widely used in the industrial treatment of metal surfaces, amines dissolve easily in water. Herein, particular attention is paid to polyamines that can form very stable chelate complexes; other families of amines are compared to polyamines to highlight the effects of Fe(III) ion complexation on phenol electropolymerization.

Mengoli *et al.* [2-4] have also used amines in their work on the electrodeposition of phenol-derived polymers in aqueous media, but unlike the present work they have used them as thickening agents at much higher potentials. From the wide variety of amines studied, they have found allylamine ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_2$), benzylamine and propylamine to be the best suited for the formation of thick uniform films.

2. Experimental details

All the amines were Aldrich products except for the N_3 and N_4 oligoamines which were BASF products. Phenol derivatives were commercial products.

The potential of the working electrode was imposed by a PAR 173 potentiostat piloted by a PAR 175 signal generator. The current was

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measured versus time or potential with a Sefram T2Y recorder. The working electrode was a 5 mm ϕ cylinder embedded in Teflon. For ESCA analysis, the working electrodes were steel plates of different sizes. Both cylinder and plate electrodes were XC 10 (0.1% C) mild steel. The counter electrode was a platinum grid or a layer of platinum sputtered onto a glass plate with a Balzers Sputron II apparatus. The reference electrode was a saturated calomel electrode (SCE) which could be filled with methanol.

2.1. Film formation

Polyphenylene oxide film formation in a 0.3 M NaOH–MeOH solution with phenols (0.2 M) occurs either by electrolysis at a constant potential over a given period of time or by a series of potential scans between 0 V (SCE) and a variable upper limit depending on the monomer.

The NaOH–methanol solution was prepared from Prolabo R.P. normapur sodium hydroxide and Baker analysis quality methanol. The solution was filtered before use. Mild steel surfaces were polished with No. 500 emery paper before being washed with pure methanol by ultrasonic stirring. This rinsing was repeated after film formation.

2.2. ESCA analysis

Films were identified by ESCA analysis using a Vacuum Generators Escalab MK1 instrument with unmonochromated $MgK\alpha$ X-rays (1253.6 eV) with a beam width of ~ 1 eV. When possible, multiple peaks were separated by means of a simple computer simulation program.

2.3. Measurement of the Fe(III) ion concentration

The concentration of Fe(III) ions in solution was measured by absorptiometry with red ferrothiocyanate complexes. Mild steel plates were polarized in different media over a period of time long enough to obtain significant concentrations of Fe(III) ions. Spectra were recorded with a Varian Cary 210 double beam spectrometer in a reference solution of 0.3 M NaOH–MeOH

containing 0.2 M of one of the phenols under study.

A 20 ml solution of 0.3 M NaOH–MeOH with 0.2 M phenol was prepared; 5 ml of concentrated hydrochloric acid and 12 ml of a 15% solution of initial solution. The resulting mixture was adjusted to 50 ml and the Fe(III) ion content was measured immediately thereafter at 580 nm by comparing the visible spectrum to a reference spectrum.

3. Results

3.1. Potentiostatic curves recorded during electrolysis of phenol–ester solutions

The shape of the potentiostatic curves varies considerably from one monomer to another.

3.1.1. Phenyl salicylate. When the potentiostatic curves of phenyl salicylate are expressed as a $\log i$ versus $\log t$ relationship (as in Fig. 1) straight lines with slopes (α) of about -0.8 are obtained throughout the range of potential used. This holds true for other phenols such as *o*-cresol or 2,6-dimethylphenol. With these monomers the electrolysis phenomena on mild steel are independent of the potential and fit the simple law $i = kt^\alpha$, thereby indicating that the kinetics are controlled by monomer diffusion.

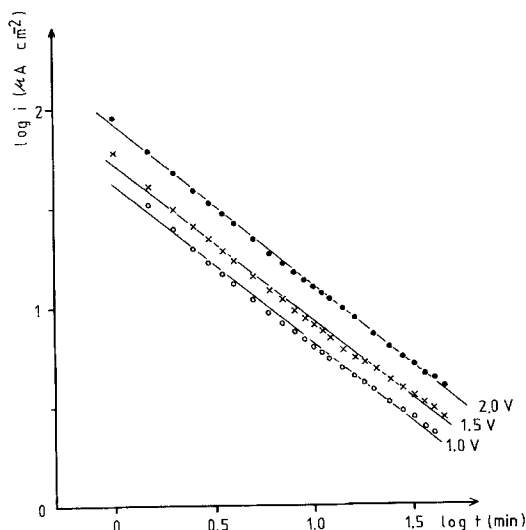


Fig. 1. Potentiostatic curves recorded by polarizing a mild steel electrode in 0.3 M NaOH–MeOH with 0.2 M phenyl salicylate at 1.0, 1.5 and 2.0 V (SCE).

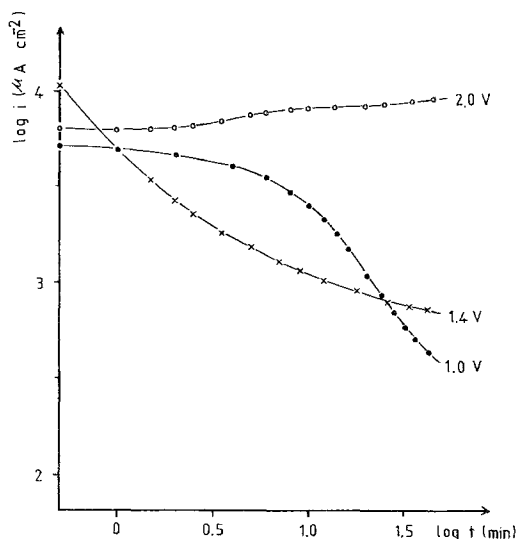


Fig. 2. Potentiostatic curves obtained by polarizing a mild steel electrode in 0.3 M NaOH-MeOH with 0.2 M methyl salicylate at 1.0, 1.4 and 2.0 V (SCE).

3.1.2. Methyl salicylate. Unlike the potentiostatic curves for phenyl salicylate, the potentiostatic curves for methyl salicylate expressed in $\log i$ versus $\log t$ (as in Fig. 2) do not produce straight lines, thereby indicating that, aside from monomer diffusion, there are other phenomena involved in polyphenylene oxide film growth. The shape of these curves, and hence the nature of the phenomena occurring at the electrode, are voltage-controlled. It can also be seen that the intensities measured for methyl salicylate are higher than those for phenyl salicylate, thereby indicating, in the case of methyl salicylate, the prevalence of reactions competing with electropolymerization.

3.1.2.1. At low potentials [+1.0 V (SCE)]. Two types of time-dependent intensity variation are observed. In an initial phase there is a very slow drop in current and a dark yellow colour gradually diffuses from the electrode towards the solution (the source of colouring is dealt with in section 3.2.2). This slow drop is followed by a faster drop in current caused by the formation of a film on the electrode surface. During this faster drop in current, the above-mentioned dark yellow colouring in the vicinity of the electrode becomes much lighter.

3.1.2.2. At intermediate potentials [+1.4 V (SCE)]. The slope of the curve of $\log i$ versus

$\log t$ departs from a value of ~ 1 and drops below 0.25 (Fig. 2). The yellow colour is visible in the vicinity of the electrode all along the $i-t$ curve.

3.1.2.3. At high potentials [+2.0 V (SCE)]. The rise in electrolysis current is slightly time-dependent. The yellow colouring is visible in the vicinity of the electrode throughout the $i-t$ curve.

In all three cases film formation is observed; however, film thickness is not uniform at high potentials.

3.2. Dissolution of the oxide layer during electrolysis

3.2.1. Detection of Fe(III) ions in the electrolysis solution. When a mild steel electrode is polarized beyond the OH^- ion discharge potential in 0.3 M NaOH-MeOH with or without phenols such as methyl salicylate, dissolution of the oxide layer is observed. The red colouring characteristic of ferrithiocyanate complexes appears as soon as sodium thiocyanate is added to the acidified solution [5]. This would seem to indicate that the very basic methanol solution acts as an electrolytic scouring bath for the anode; such behaviour would be in keeping with the well-known scouring effect that oxygen can exert on metal surfaces [6, 7] resulting in the destruction of the oxide layer and in the dissolution of impurities.

The Fe(III) ions which pass into the solution could be complexed by the phenol; this could account for the yellow colouring detected in the vicinity of the electrode. Although the appearance of a blue, violet or red colouring upon the addition of ferric chloride to dilute solutions of phenols is a well-known reaction which has long been accepted as a qualitative test for the phenol group, the formation of Fe(III)-phenol complexes has also been known to occur in neutral and basic media [8-12]. In basic media, these complexes are generally yellow.

3.2.2. The source of the yellow colouring produced during electrolysis. To analyse further the source of colouring produced during the electrolysis of methyl salicylate solutions, and thereby gain further knowledge concerning the phenomena involved in polyphenylene oxide film growth at

Table 1. Iron dissolution rate

Solution	Iron dissolution rate ($\mu\text{g cm}^{-2} \text{h}^{-1}$)
MeOH-NaOH 0.3 M	3.6
MeOH-NaOH 0.3 M + hexylamine 0.1 M	1.0
MeOH-NaOH 0.3 M + allylamine 0.1 M	3.9
MeOH-NaOH 0.3 M + hexanediamine 10^{-2} M	43
MeOH-NaOH 0.3 M + methyl salicylate 0.2 M	1.9

the electrode, colorimetry was used to determine the rate of dissolution of iron in alkaline methanol solutions.

Colorimetric analysis was effected by using red ferrithiocyanate complexes according to a procedure described in the experimental section. The spectra for phenol solutions in which bulk plates of mild steel were polarized at +1.0 V (SCE) display a shoulder in the low wavelength zone of the ferrithiocyanate absorption band, thereby indicating that ferrithiocyanate complexes are not the sole source behind the yellow colouring. To minimize the influence that any product other than ferrithiocyanate complexes might have on this yellow colouring, the concentration of Fe(III) ions in solution was measured at 580 nm. The rates of dissolution measured for iron by colorimetry are given in Table 1.

3.3. Interpretation of the different film growth modes

The study described above indicates that polyphenylene oxide film growth is determined by the state of the electrode surface and by the nature of the phenol monomer.

3.3.1. Phenyl salicylate. 3.3.1.1. Film formation on the oxide layer. During the electropolymerization of phenyl salicylate, the yellow colour in the vicinity of the electrode is barely perceptible and the drop in electrolysis current occurs as soon as polarization is applied. This indicates that this phenol can be easily oxidized onto polyphenylene oxide and that it oxidizes directly onto the oxide layer coating the metal. The fast formation of a film all along the electrode plane prevents the oxide layer from dis-

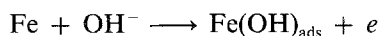
solving at the metal surface, thereby indicating the permanence of this oxide layer. As the shape of the potentiostatic curve of a metal surface subjected to electrolytic scouring at +1.0 V (SCE) for 20 min in 0.3 M NaOH-MeOH before introduction of the phenol is the same as for an unscoured metal surface before introduction of the phenol, it can be deduced that the presence or absence of an oxide layer on the electrode surface barely affects the electropolymerization of phenyl salicylate.

3.3.1.2. Interpretation of potentiostatic curves. The potentiostatic curves recorded for phenyl salicylate which are expressed by $it^\alpha = k$ are analogous to the theoretical curves calculated by assuming that the current is limited by the diffusion of the phenol monomer within the film [13]. By applying electrochemical diffusion laws to the polymer film and by replacing the diffusion layer by the thickness of the film, it can be shown that $i = kt^{-1/2}$.

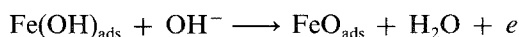
3.3.2. Methyl salicylate. At potentials in the vicinity of +1.0 V (SCE), the first part of the potentiostatic curve, where only a very slow drop in current occurs, indicates that film formation is not instantaneous and, in all likelihood, is delayed by the presence of the oxide layer on the metal surface (Fig. 2). During this phase the active surface for the propagation stage of the electropolymerization is very small and the formation of soluble non-polymer quinoid products is enhanced.

The first part of the potentiostatic curve might correspond to electrochemical scouring of the surface which would dissolve the oxide layer and activate the electrode surface. As oxide formation is expected during oxidation, the occurrence of scouring might come as a surprise. However, scouring during oxidation [9] is a common technique in the industrial treatment of metal surfaces (e.g. in preparing stainless steel before chroming) which, via the mechanical action of oxygen in very basic solutions, results in the elimination of impurities (particularly oxides) at the electrode surface. Moreover, scouring during oxidation is generally preferred over scouring during reduction because the latter technique heightens metal fragility through the inclusion of hydrogen.

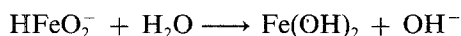
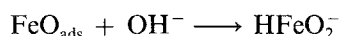
Scouring during oxidation might occur via the generally accepted multistep mechanism involved in the electrochemical dissolution of iron in aqueous alkaline media [15], whereby the formation of the transient surface compound $\text{Fe(OH)}_{\text{ads}}$ via a single electron transfer



is followed by a slow step



and by two fast reactions resulting in the formation of the final product



This mechanism would result in dissolution of the iron as HFeO_2^- rather than in formation of an oxide film. Aside from the fact that Fe(OH)_2 is, by nature, poorly adherent to a metal surface, the mechanical action of the oxygen in a basic medium would hinder oxide formation on an electrode surface.

After dissolution of the oxide layer, polymer film formation is accompanied by a sharp drop in current caused by a sharp drop in the hydrox-

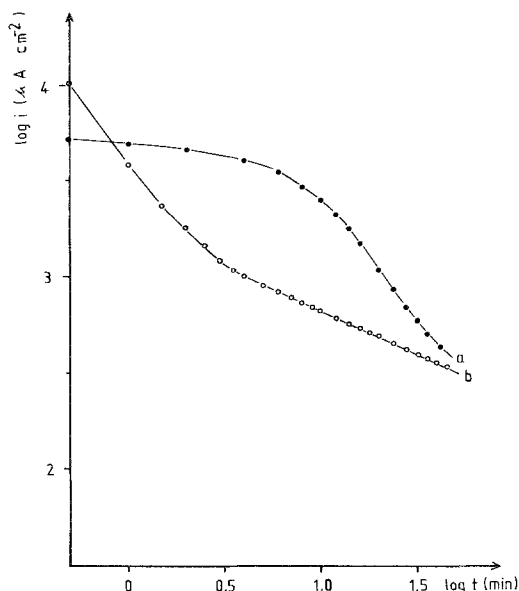


Fig. 3. Potentiostatic curves obtained by polarizing a mild steel electrode in 0.3 M NaOH–MeOH with 0.2 M methyl salicylate at +1.0 V (SCE). (a) Electrode mechanically polished with N° 500 emery paper; (b) with same mechanically polished electrode previously subjected to 1.0 V (SCE) polarization for 20 min in 0.3 M NaOH–MeOH.

ide ion discharge current and by the mechanical action of the oxygen. By subjecting the electrode surface to electrolytic scouring for 20 min at +1.0 V (SCE) in the 0.3 M NaOH–MeOH solution before introduction of the phenol, the influence of the dissolution of the oxide layer on polyphenylene oxide film growth can be measured at this potential. Fig. 3 shows that electrode passivation accelerates markedly after the scouring treatment and stems from the fast formation of an insulating film.

At a higher potential, the formation of quinoid products accounts for a significant part of the current measured throughout the recording of the $i-t$ curve. The physical properties of the resulting films are not conducive to insulation and prevent complete electrode passivation.

4.1. Amine effects on $i-E$ curves of methyl salicylate

4.1.1. General appearance of $i-E$ curves. A wide variety of amines (0.1 M) were added to the electrolytic solution containing methyl salicylate and the corresponding $i-E$ curves were recorded.

Figs 4 and 5 show the $i-E$ curves resulting from the addition of hexamethylenediamine and hexylamine, respectively. During the first scan, at low potentials, the current density drops slightly with hexamethylenediamine but rises

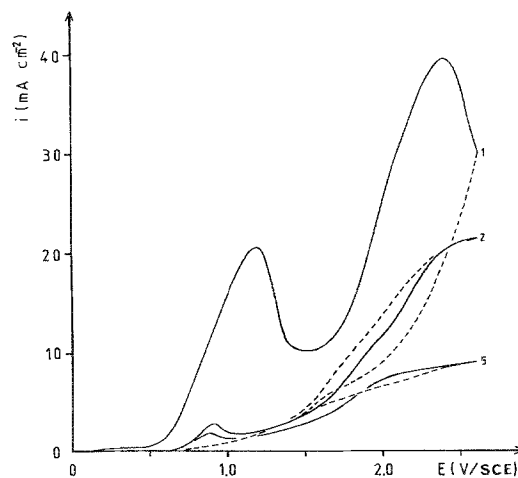


Fig. 4. $i-E$ curves for methyl salicylate with hexamethylenediamine (0.1 M) in 0.3 M NaOH–MeOH with 0.2 M phenol at 50 mV s⁻¹. 1, first scan; 2, second scan; 5, fifth scan.

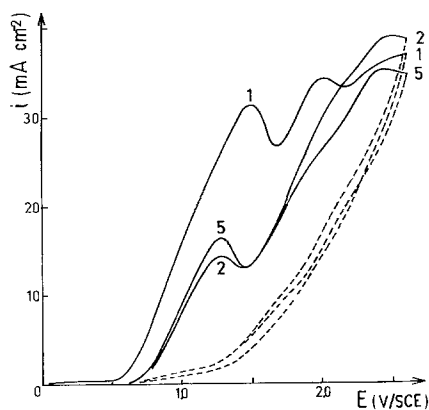


Fig. 5. i - E curves for methyl salicylate with hexylamine (0.1 M) in 0.3 M NaOH-MeOH with 0.2 M phenol at 50 mV s^{-1} . 1, first scan; 2, second scan; 5, fifth scan.

with hexylamine. At high potentials the current density rises considerably whatever the amine. The amines used are not electroactive so instead of ascribing the second peak in Figs 4 and 5 to their oxidation, it must be ascribed to reoxidation of the phenol through the film which, at high potentials, displays physical properties altered by the presence of amines.

Hexamethylenediamine and hexylamine produce markedly different effects during subsequent scans at low potentials: (a) electrode passivation is much stronger with hexamethylenediamine than with the phenol alone ($P_2 = 86\%$ versus $P_2 = 58\%$)*; (b) electrode passivation is less with hexylamine than with the phenol alone ($P_2 = 55\%$ versus $P_2 = 58\%$; $P_5 = 47\%$ versus $P_5 = 93\%$)*. However, in both cases passivation is little affected by the number of scans and stabilizes at a low value, thereby indicating that the resulting film is fairly porous.

4.1.2. Physical properties of resulting films. Films obtained with hexamethylenediamine or with hexylamine after five potential scans between 0 and +2.5 V (SCE) are poorly adherent. However, adherence is poorer for films formed with hexylamine which display holes after ultrasonic stirring. The loss of adherence following thickening is a general phenomenon in films formed

* The passivation at the n th sweep can be expressed by $P_n = (i_1 - i_n)/i_1$ where i_1 and i_n designate the peak intensity at the first and n th sweep, respectively.

with an amine at high potentials. Hereafter, the discussion of amine effects is restricted to what occurs at low potentials on i - t curves. In all likelihood, the loss of adherence arises from OH^- ion discharge through the film via polymer chains which grow perpendicularly to the electrode surface in the presence of an amine at high potentials.

4.1.3. Different amine effects on passivation at low potentials. To summarize the effects of the various amines used, only polyamines with a linear structure ($\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ diamines and N_3 and N_4 oligoamines) or with a single-ringed structure (piperazine) noticeably improve electrode passivation; triethylamine and allylamine improve it slightly; diethanolamine and hexamethylene-tetramine have practically no effect whereas primary amines (propyl-, hexyl-, dodecyl- and isopropylamine) delay passivation.

A comparison of the i - E curves for methyl salicylate with those for phenyl salicylate shows that the latter are barely affected by the presence of an amine in the electrolysis solution; only a slight rise in current density is detected, whatever the amine.

Broadly speaking, for films able to form directly on the oxide layer, film growth is practically unaffected by amines at low potentials.

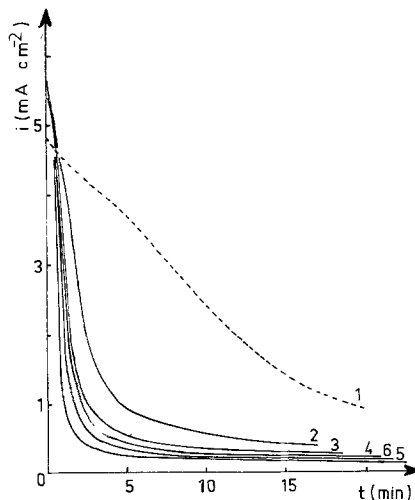


Fig. 6. Potentiostatic curves during electropolymerization of methyl salicylate (0.2 M) at +1.0 V (SCE) in 0.3 M NaOH-MeOH devoid of amine and with an amine (0.1 M). 1, without amine; 2, with ethylenediamine; 3, with propane-diamine; 4, with hexamethylenediamine; 5, with dodecane-diamine; 6, with N_3 or N_4 oligoamine.

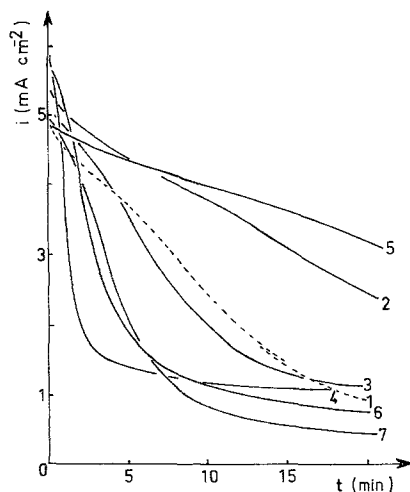


Fig. 7. Potentiostatic curves during electropolymerization of methyl salicylate (0.2M) at +1.0V (SCE) in 0.3M NaOH-MeOH devoid of amine and with an amine (0.1M). 1, without amine; 2, with phenethylamine; 3, with diethanolamine; 4, with piperazine; 5, with hexylamine; 6, with allylamine; 7, with triethylamine.

4.2. Amine effects on polymethylsalicylate film growth under potentiostatic conditions

Amine effects on polymethylsalicylate film growth were studied under potentiostatic conditions by polarizing a mild steel electrode at +1.0V (SCE). Figs 6 and 7 show the $i-t$ curves obtained by adding different amines to the electrolytic solution. Potentiostatic results on electrode passivation are consistent with potentiodynamic results.

4.2.1. Effect of complexing polyamines. The best passivation occurs with N_3 and N_4 oligoamines and with $H_2N(CH_2)_nNH_2$ diamines. The efficiency of the latter in promoting film insulation increases as n increases.

The presence of these amines yields uniform adherent films either yellow or blue in colour. Films obtained in the absence of polyamines are thin to the point of being practically invisible. Even at very low concentrations (10^{-3} - 10^{-4} M for hexamethylenediamine and dodecylamine) these amines can improve electrode passivation (Fig. 8).

The $i-t$ curves recorded for *p*-cresol (Fig. 9) display the same characteristics as those recorded under the same conditions for methyl salicylate.

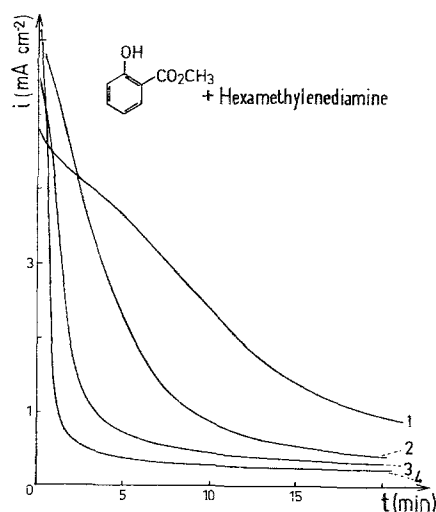


Fig. 8. Potentiostatic curves during electropolymerization of methyl salicylate (0.2M) with hexamethylenediamine at +1.0V (SCE) in 0.3M NaOH-MeOH. Hexamethylenediamine concentration: 1, zero; 2, 10^{-4} M; 3, 10^{-3} M; 4, 10^{-2} M.

4.2.2. Monoamine effects. Unlike polyamines, monoamines (propyl-, hexyl-, phenethyl-, etc.) hinder the formation of an insulating film. With these monoamines, as with methyl salicylate alone, a yellow colouring is detected in the vicinity of the electrode, but it is darker and longer lasting with the monoamines than with the phenol alone. With the monoamines this yellow colouring is emitted at the electrode throughout the recording of the $i-t$ curve, whereas with the

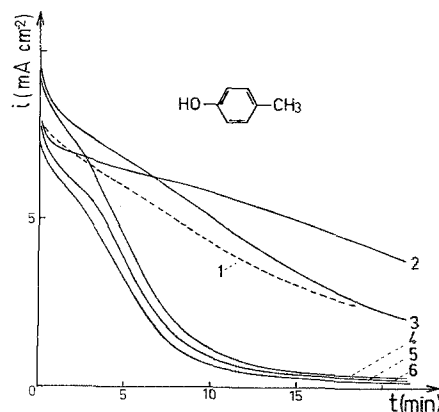


Fig. 9. Potentiostatic curves during electropolymerization of *p*-cresol (0.2M) at +1.0V (SCE) in 0.3M NaOH-MeOH devoid of amine and with an amine. 1, without amine; 2, with hexylamine; 3, with allylamine; 4, with ethylenediamine; 5, with propane diamine; 6, with hexamethylenediamine.

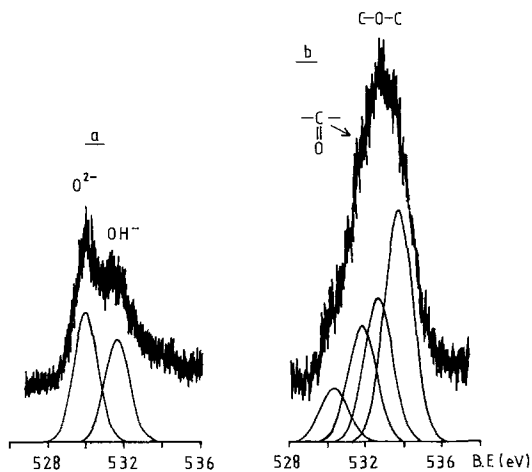


Fig. 10. ESCA spectra with O_{1s} signals recorded with mild steel surfaces for 10 min at +1.0 V (SCE) in a methyl salicylate solution (0.2 M). Medium: 0.3 M NaOH–MeOH. (a) Devoid of amine: O^{2-} , 529.9 eV; OH^- , 531.5 eV. (b) With dodecanediamine (10^{-2} M): $-C(=O)-$, 532 eV; $C-O-C$, 533.5 eV.

phenol alone it bleaches considerably after the scouring phase. This indicates that these monoamines are adsorbed and delay scouring of the electrode surface while protecting the oxide layer, thereby hindering electropolymerization propagation while enhancing quinone formation.

4.2.3. ESCA analysis of polymethylsalicylate films formed in the presence of amines. To determine the role played by amines in the electropolymerization of methyl salicylate, the chemical composition of the various films was studied by ESCA analysis. All films were formed by a 10 min electrolysis at +1.0 V (SCE), then stirred ultrasonically in methanol and quickly placed under vacuum in the ESCA apparatus.

Fig. 10a shows the O_{1s} signals from the ESCA spectrum of a steel surface polarized for 10 min at +1.0 V (SCE) in a methyl salicylate solution devoid of amine. The surface is essentially composed of an oxide layer characterized by signals at 530.0 and 531.6 eV corresponding to O^{2-} and OH^- , respectively [16]. This indicates that this electrolysis does not last long enough for complete destruction of the oxide layer to occur and thereby prevents electropolymerization propagation.

In contrast, when a complexing amine is

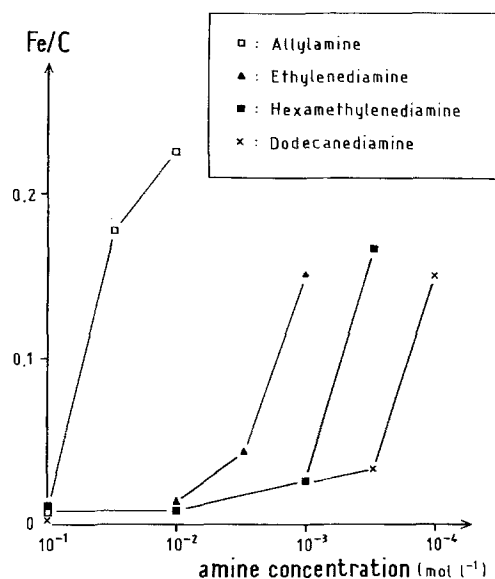


Fig. 11. Fe/C ratio determined from ESCA analysis of a mild steel surface polarized for 10 min at +1.0 V (SCE) in a methyl salicylate solution (0.2 M) for different amine concentrations.

added to the electrolysis solution, electropolymerization of the phenol can occur after scouring of the electrode surface. Fig. 10b shows the O_{1s} signals from the ESCA spectrum of a steel surface polarized at +1.0 V (SCE) for 10 min in a methyl salicylate solution with a low concentration (10^{-2} M) of dodecyldiamine. There are signals at 532.7 and 533.8 eV for two new types of oxygen corresponding to $-C(=O)-$ and

$C-O-C$ bonding of the polymer, respectively [17]. The intensity of the oxygen atoms from the oxide layer decreases at the same time, thereby indicating the start of polymer film formation.

$H_2N(CH_2)_nNH_2$ diamines and N_3 and N_4 oligoamines efficiently trigger film formation, even at very low concentrations in comparison to the phenol concentration. Fig. 11 shows the oxidized Fe/C atomic ratio calculated from ESCA analysis for different amine concentrations in the electrolytic solution. $H_2N(CH_2)_nNH_2$ diamines with $n = 2, 6$ and 12 were tested and their effects on film formation were compared to the effects of allylamine for which $i-t$ curves were recorded. This comparison shows that of all the amines mentioned

Table 2. Weight percentage of amine in polymethylsalicylate films

Amine (10^{-1} M)	N_{1s} binding energy (eV)	Weight percentage
Dodecanediamine	399.9	4.8
Hexamethylenediamine	399.8	2.8
Allylamine	399.6	1.0

herein, allylamine is the least conducive to the rapid formation of an insulating film. It can be seen (Fig. 11) that for diamines with $n > 6$ the amount of oxide detected remains low down to amine concentrations of $\sim 10^{-3}$ M, whereas allylamine loses its complexing ability at concentrations below 10^{-1} M. However, it should be noted that the addition of amines to the medium gives rise to an inclusion effect in the film, as can be seen from the ESCA analyses reported in Table 2.

4.2.4. Interpretation. Amines which facilitate polymethylsalicylate film formation are essentially polyamines that are able to form stable chelate complexes with Fe(III) ions [18–22] and can thereby accelerate destruction of the oxide layer. Only hexamethylene–tetramine does not enhance film formation; sterically, it cannot form chelate complexes and the complexes it can form are bridged [23, 24].

The rate at which the oxide layer dissolves in the presence of certain amines was measured by determining the amount of iron dissolved in 0.3 M NaOH–MeOH in which the electrode was polarized at +1.0 V (SCE). A comparison of the results obtained in the presence of amines with results obtained in the presence of methyl salicylate confirms that the formation of a polymethylsalicylate film is indeed related to the scouring of the oxide layer by the electrolysis medium (Table 1).

The above study of polyamine effects indicates that there is a tie between the length of the carbon chain of α,ω polymethylenediamines and their ability to dissolve the oxide layer. This relationship might be ascribed to stability in the Fe(III)–amine complexes which can grow as the ligand donor character grows. The extent of that character can be estimated from amine basicity. As can be seen in Table 3, the acidity constants

Table 3. Acidity constants of α,ω polydiamines

n	pK_1	pK_{1-2}	Reference
2	9.93–9.87	6.85–6.80	[26]
3	10.30–10.72	8.29–8.98	[26]
4	10.19–10.82	8.78–9.61	[26]
5	10.25	9.13	[26]
6	10.93	9.83	[26]
8	11.0	10.1	[26]
10	11.2	10.7	[27]

of these diamines increase with the length of the carbon chain.

The complexing ability of long-chained diamines can be explained in part by a lower solubility than in short-chained diamines which thereby increases their affinity for the metal surface. Moreover, as the hydrophobic part of the molecule grows with the length of the chain, these diamines acquire surfactant properties as soon as $n > 6$ [25]. A drop in interfacial tension during electrolytic scouring in the presence of these amines can enhance the release of oxygen bubbles formed on the surface and thereby accelerate destruction of the oxide layer.

5. Conclusion

For electropolymerized polyphenylene oxide film growth requiring prior removal of the oxide layer from the electrode surface by electrolytic scouring, initial testing of amines as complexing agents indicates that amines can act in one of two ways, i.e. as scouring accelerators or as scouring delayers.

Among the polyamines studied, only polyamines able to form chelate complexes with Fe(III) ions can accelerate scouring, thereby making possible the electrodeposition of certain non-polymerizable phenols onto an oxide layer (methyl salicylate, *p*-cresol). Even in concentrations as low as 10^{-3} M, $NH_2(CH_2)_nNH_2$ diamines with $n > 6$ are efficient scouring agents. In contrast, the monoamines studied are adsorbed onto the electrode surface and protect the oxide layer, thereby delaying scouring and hindering electropolymerization propagation. The ability of polyamines to dissolve the oxide layer seems related to the length of the carbon chain and to their complexing ability with

Fe(III) ions. Because polyamines as complexing agents require little energy consumption, their use on an industrial scale would seem to warrant further attention.

References

- [1] P. Mourcel, M. C. Pham, P. C. Lacaze and J. E. Dubois, *J. Electroanal. Chem.* **145** (1983) 467.
- [2] G. Mengoli, *Adv. Polymer Sci.* **33** (1979) 1.
- [3] G. Mengoli, S. Daolio, U. Giulio and C. Folonari, *J. Appl. Electrochem.* **9** (1979) 483.
- [4] G. Mengoli, S. Daolio and M. M. Musiani, *ibid.* **10** (1980) 459.
- [5] G. Charlot, 'Chimie Analytique Quantitative', Masson et Cie., Editeurs, Paris (1974) p. 413.
- [6] G. Baquias, Galvano-organo-traitements de surface, Sarl Galvano, Editeurs, Paris, N° 530, Novembre 1982, p. 942.
- [7] G. David, 'Techniques de l'ingénieur'; M 1492, Editeurs, Paris (1976) p. 29.
- [8] R. T. Foley and R. C. Anderson, *J. Amer. Chem. Soc.* **70** (1948) 1195.
- [9] C. V. Banks and J. H. Patterson, *ibid.* **73** (1951) 3062.
- [10] H. Broumand and J. H. Smith, *ibid.* **74** (1952) 1037.
- [11] Z. L. Ernst and P. G. Herring, *Trans. Faraday Soc.* **61** (1965) 454.
- [12] P. H. Gore and P. J. Newman, *Analyt. Chim. Acta* **31** (1964) 111.
- [13] M. Delamar, M. C. Pham, P. C. Lacaze and J. E. Dubois, *J. Electroanal. Chem.* **108** (1980) 1.
- [14] P. C. Lacaze, M. C. Pham, M. Delamar and J. E. Dubois, *ibid.* **108** (1980) 9.
- [15] B. G. Ershov, *Upsekli Khim.* **50** (1981) 2137.
- [16] N. S. McIntyre and D. G. Zetaruk, *Analyt. Chem.* **49** (11) (1977) 1521.
- [17] U. Gelius, P. F. Haden, J. Hedman, B. J. Lindberg, R. Manne, R. Nordberg, C. Nordling and K. Siegbahn, *Physica Scripta* **2** (1970) 70.
- [18] F. P. Dwyer and D. P. Mellor, 'Chelating Agents and Metal Chelates', Academic Press, London (1964) p. 107.
- [19] H. B. Jonassen, A. Schaafsma and L. Westerman, *J. Phys. Chem.* **62** (1958) 1022.
- [20] J. W. Wang, *J. Amer. Chem. Soc.* **77** (1955) 4715.
- [21] R. C. Jaragin and J. H. Wang, *ibid.* **80** (1958) 786.
- [22] G. Wada, T. Nakamura, K. Turauchi and T. Nakai, *Bull. Soc. Chim. Japan* **37**(4) (1964) 447.
- [23] J. R. Allan, D. H. Brown and M. Lappin, *Inorg. Nucl. Chem.* **32** (1970) 2287.
- [24] M. A. Buhannic and J. E. Guerchais, *Rev. Chim. Minérale* **8**(1) (1971) 111.
- [25] A. D. Finch and E. A. Peterson, British Patent 658 422 (1951).
- [26] D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution, Butterworths, London (1965) p. 226.
- [27] G. Schill, *Acta Pharm. Suecica* **2** (1965) 99.