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A COMPARISON BETWEEN CORROSION PROTECTION PROPERTIES OF ELECTROCHEMICALLY AND CHEMICALLY PREPARED POLYANILINE

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ABSTRACT

Electrochemical potentiodynamic polarisation supported by SEM morphological examinations have been used to evaluate a range of chemically and electrochemically deposited polyanilines films for use in inhibiting corrosion, in particular 304L stainless steel. It was found that emeraldine salt coatings provided superior protection compared to their base counterparts. This was explained in terms of the more compact morphology and higher conductivity of the former, which allows the film to act as an electronic as well as a physical barrier. With respect to protection against pitting corrosion it appears that conductivity is the most important parameter, whereas for general uniform corrosion the morphological of the physical barrier seems to be dominant. It was also found that emeraldine salt coatings greatly reduced the rate at which active pits propagated, postulated to be due to the restricted ion mass transport through the film. Finally, it had been expected that the higher purity and compact morphology expected from electrochemical deposition would produce the best films. For general uniform corrosion this was indeed the case, however, for pitting corrosion the highly conductive chemically deposited films proved to be provide the best protection. This is an encouraging result, since chemical deposition is likely to prove the more economically viable method of application.

Key words : *Potentiodynamic polarisation, emeraldine salt and pitting corrosion.*

1. INTRODUCTION

One class of materials that has recently attracted attention for possible use in corrosion protection is the conducting polymers, of which the most widely studied is polyaniline [1, 2, 3, 4, 5,6]. The aim of this work was to compare the applicability of a range of chemically and electrochemically deposited polyanilines films, both treated a manner such that either the emeraldine salt (doped) or the emeraldine base (undoped) forms were obtained, for use in inhibiting corrosion [7]. The choice of the two deposition methods was based on the fact that electrochemical techniques usually gives high purity films with good compaction, hence these may be expected to perform better than their chemical counterparts. However, from the viewpoint of industrial application electrochemical deposition is only feasible on small-scale components, whilst on large structures chemical deposition is the more practical alternative.

2. EXPERIMENTAL

Stainless steel was chosen as the substrate in preference to carbon steel as preliminary tests showed that the polyaniline films, particularly the chemically deposited ones, demonstrated poor adhesion to the latter metal. A 6 mm diameter AISI 304L grade stainless steel rod (Advent Research Materials) was cut to suitable lengths (ca. 150 cm) and the sides were covered by epoxy resin. One cut end of the rod was used for the electrical contact whilst the working face of the other end was polished on 1200 grit silicon carbide paper followed by washing with distilled water and then acetone. The polyaniline films were coated onto the specimens either chemically or electrochemically.

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The chemical procedure was based on that outlined by MacDiarmid and Epstein [8] and involved placing the stainless steel specimens in a 100 ml solution of 1M H_2SO_4 containing 2 vol% aniline and then slowly adding drop-wise, with stirring, 10 ml of a solution consisting of 1M H_2SO_4 + 0.5M $(NH_4)_2S_2O_8$. The polymerisation reaction was allowed to continue for a period of 1 hour. On the other hand, the electrochemical procedure was galvanostatic deposition at 1.0 mA cm^{-2} to a total charge density of 3600 mC cm^{-2} from a solution of 1 mol dm^{-3} freshly distilled aniline in 1M H_2SO_4 [9].

After deposition both the chemically and electrochemically deposited polyanilines were rinsed with distilled water and then either washed with 1M H_2SO_4 (to produce the emeraldine salt) or 0.5 M KOH followed by distilled water (to form the emeraldine base). All the samples were dried under vacuum for 24 hours prior to further use. The exact procedure for forming the emeraldine base coatings was washing with the potassium hydroxide until the colour transformation from green to blue was complete (typically about 1 hour) and then leaving to soak in distilled water for 20 minutes prior to the drying. For convenience the chemically deposited emeraldine salt and base are referred to CS and CB respectively, and their electrochemical counterparts as ES and EB. Since it has been reported that the base to salt transition for polyanilines is not completely reversible [10] investigations were conducted into whether the time at which the doping process is performed has any influence on a coatings ability to provide protection against corrosion. That is to say, does an emeraldine base coating that is protonated after it has been applied to a metals surface provide the same degree of protection as a coating that was originally cast in the emeraldine salt form? Therefore some of the chemically produced polyaniline coated specimens were deprotonated to form the emeraldine base in 0.5M KOH for 24 hours, rinsed with distilled water and then protonated by immersion in 1M H_2SO_4 for a further 24 hours to re-form the emeraldine salt. The samples were finally dried under vacuum for another 24 hours. These specimens are referred to as chemically redoped emeraldine salt or CRS. The electrochemical experiments were carried out in 0.028M NaCl (1000 ppm Cl^-) using a traditional three-electrode cell with a platinum plate counter-electrode and a saturated calomel reference electrode (SCE) at room temperature (25°C ±3). The specimens were allowed to stabilise in the solution for 30 minutes prior to potentiodynamic polarisation, which was conducted over the range -700 mV to 1000 mV vs SCE at a scan rate of 2 mV s^{-1} and controlled by an ACM Field Machine DSP. The scan direction was reversed either after a current limit of 6.5 mA cm^{-2} had been exceeded or at the positive potential limit of 1000 mV vs SCE. Each electrochemical experiment was repeated at least three times, using a fresh coating for each experiment.

In subsequent analysis of the digitally recorded data, the pitting potential (E_p) was defined at a sustained anodic current density of at least 0.1 mA cm^{-2} accompanied by a hysterisis loop on the reverse cycle. The repassivation potential (E_R) was taken as the point at which the reverse scan current crossed that of the forward scan. Tafel extrapolations were used to obtain corrosion current densities, and thus calculate corrosion rates, from the polarisation scans. However, it is recognised that since these were not steady-state measurements and that some of the measured current density may have resulted from oxidation of the polymer coating, rather than from corrosion of the underlying metal, this procedure probably led to the corrosion rates being overestimated. Nevertheless, the values obtained were still useful for comparing the relative performances of the various types of polymer coatings tested. A Philips XL30 FEG Scanning Electronic Microscopy (SEM) operated at between 5 kV and 10 kV (see individual photographs for exact values) was used to observed the morphologies of the conducting polymer coatings before and after the potentiodynamic experiments. Conductivity measurements were made, via a four-point probe, on compressed pellets of the polyaniline films after these had been scrapped of the surface of the respective specimens and dried under vacuum for two hours.

3. RESULTS

3.1 Electrochemical Tests

The range of corrosion potentials (E_{corr}) displayed by specimens coated by the four types of polyaniline and bare 304L stainless steel after being immersed in 0.028M NaCl for 30 minutes are tabulated in Table 1.

	E_{corr} (mV vs SCE)	I_{corr} (μA cm^{-2})	Corrosion Rate (μm year^{-1})
Bare 304L stainless steel	-290 to -310	1.39 (0.5)	15.7 (0.7)
Chemical Base (CB)	-235 to -245	0.90 (0.6)	9.89 (0.4)
Chemical Salt (CS)	-185 to -205	0.37 (1.2)	4.10 (1.5)
Chemical Redoped Salt (CRS)	-200 to -220	0.38 (1.0)	4.32 (1.5)
Electrochemical Base (EB)	-140 to -160	0.70 (1.5)	7.98 (0.5)
Electrochemical Salt (ES)	-340 to -370	0.33 (0.8)	3.66 (0.1)

Table 1 : Corrosion potentials (E_{corr}), measured 30 minutes after immersion along with the estimated corrosion currents (I_{corr}) and corrosion rates extrapolated from the potentiodynamic polarisation curves. Standard deviations are shown in brackets.

It can be seen that all the coatings caused a positive displacement in the corrosion potential, relatively to the value of the bare 304L stainless steel, except for the electrochemically grown emeraldine salt coating (ES), which caused a negative shift. The reason for unusual behaviour of the electrochemical salt film can be see from the cathodic regions of the polarisation diagrams (Figures 1 & 2).

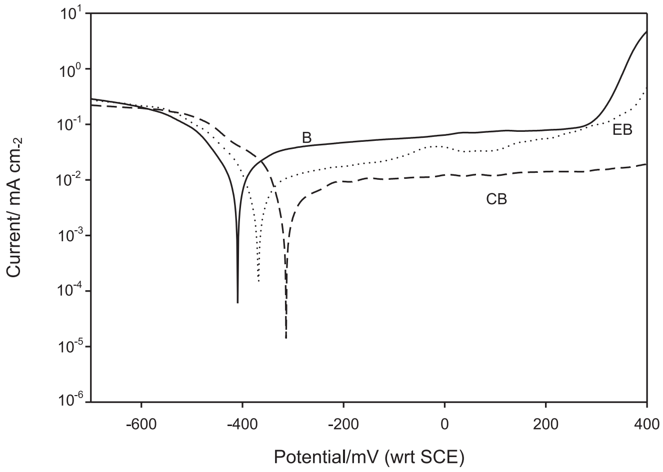


Figure 1 : Potentiodynamic polarisation curves of 304L stainless steel with and without emeraldine base coatings in 0.028M NaCl. (B) Bare 304L, (EB) electrochemically coated and (CB) chemically coated.

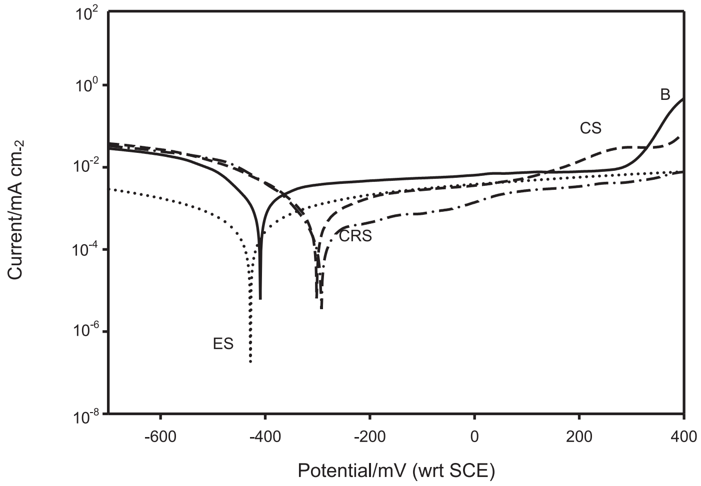


Figure 2 : **Potentiodynamic polarisation curves of 304L stainless steel with and without emeraldine salt coatings in 0.028M NaCl. (B) Bare 304L, (ES) electrochemically coated, (CS) chemically coated and (CRS) a chemically redoped coating.**

These reveal that the kinetics of the supporting cathodic reaction are at least an order of magnitude slower on this coating than on any of the other specimens. For all the other polyaniline coatings the kinetics of the supporting cathodic reaction were slightly faster (less than a factor of 2) than on the bare stainless steel. Figures 1 and 2 show potentiodynamic polarisation scans for specimens coated with emeraldine base or emeraldine salt and exposed to solutions of 0.028M NaCl respectively. A curve for bare 304L stainless steel in the same solution has also been presented in each of these figures for comparative purposes. The average corrosion current densities (I_{corr}) (with standard deviations given in brackets) for the various types of specimen, as determined from Tafel extrapolations of the polarisation plots, are shown in Table 1. Whilst the average pitting (E_p) and repassivation (E_R) potentials abstracted from the polarisation curves, along with the approximate charge density passed from the onset of pitting to repassivation are shown in Table 2.

	E_P (mV vs SCE)	E_R (mV vs SCE)	Charge passed (C cm^{-2})
Bare 304L stainless steel	364 (7)	94 (11)	2.4
Chemical Base (CB)	411 (5)	76 (9)	1.1
Chemical Salt (CS)	No pitting	-	-
Chemical Redoped Salt (CRS)	490 (4)	-11 (5)	1.7
Electrochemical Base (EB)	426 (4)	-95 (2)	1.8
Electrochemical Salt (ES)	839 (2)	6 (3)	1.3
Bare 316 L [21]	550	-	-

Table 2 : **Pitting potentials (E_p), repassivation potentials (E_R) and the charge passed due to pit growth. Standard deviations in brackets.**

It can be seen from Table 1 that relative to the bare stainless steel all the coatings caused the corrosion current density to decrease, by amounts that varied between 35% and 75%. The best protection was provided by the electrochemically deposited emeraldine salt (ES), consistent with the slower kinetics of the supporting cathodic reaction as noted above, closely followed by the chemically cast emeraldine salt (CS) and its redoped counterpart (CRS). Finally, the two emeraldine base coatings both performed relatively poorly. Although general corrosion rates were calculated from the corrosion current density values it needs to be recognised that some of the corrosion current was probably due to the conductive nature of the polymer coatings such that the values displayed in Table 1 are likely to overestimate the true penetration rates [1, 2]. With regards to the pitting corrosion, the polarisation curves revealed that the specimen chemically coated by the emeraldine salt (CS) did not pit within the potential limits of the experiment. Extending the anodic limit resulted in an oxygen evolution that caused the 6.5 mA cm^{-2} current limit to be exceeded prior to the onset of pitting. It was thus concluded that the pitting potential for the CS films was positive of 1200 mV vs SCE. The next highest pitting potential was displayed by specimens with the electrochemically deposited emeraldine salt (ES) coatings, at ca.840 mV vs SCE this was more than 450 mV positive of the value of ca.365 mV vs SCE determined for bare 304L stainless steel. These huge displacements indicate that the CS and ES coatings were very efficient at inhibiting pitting of the stainless steel. The chemically redoped emeraldine salt (CRS) coating had a pitting potential of ca.490 mV vs SCE, which, although not anywhere near as good as its as cast emeraldine salt film counterpart, still represents good protection to the stainless steel. The pitting potentials recorded from specimens coated by the emeraldine bases were only slightly positive of that recorded on the bare stainless steel (ca. 410 mV ca.425 mV vs SCE for the CB and EB coatings respectively) and thus these films provided only marginal protection. With respect to pit repassivation all the coated specimens had E_R values negative of that recorded on the bare stainless steel (ca. 94 mV vs SCE), indicating that it was harder to repassivate the pits underneath the coatings (Table 2). There was also an unexpectedly large difference in the repassivation potentials of the samples coated by the two emeraldine bases. The value at the chemically deposited film (CB) being almost the same as for the bare stainless steel (ca. 76 mV vs SCE), whilst repassivation at its electrochemical counterpart (EB) did not occur until some 170 mV more negative (ca. -96 mV vs SCE). The difference between the repassivation potentials of the two forms of emeraldine salt that showed pitting was much smaller (ES +6 mV vs SCE: CRS -11 mV vs SCE). Inspection of Table 2 also reveals that amongst the coated specimens there was a correlation between E_R and the approximate charge density passed between the times of pit initiation and pit repassivation. Furthermore careful examination of the current densities flowing during the reverse scans (that is after pit initiation) in the region positive to the repassivation potential revealed that after pit initiation the dissolution rates from the specimen coated by the polyaniline films were usually smaller than that of the bare specimen. This indicates that either fewer pits initiated or the pit growth rates were lower on the coated specimens. The exception was the set of samples coated by the electrochemically deposited emeraldine base (EB), which displayed higher current densities after pit initiation than the bare stainless steel. This suggests higher pit growth rates under this coating. Although Table 2 shows that the total charge density passed during the lifetime of active pitting under the EB coating was smaller than with the bare stainless steel, this probably reflects the fact that the polarisation scans were reversed at lower potentials than for all the other specimens. This was due to the set current limit of 6.5 mA cm^{-2} being reached prior to the anodic potential limit of 1000 mV vs SCE.

3.2 Morphological Examinations

Examination of the various types of coating under the SEM prior to corrosion testing SEM revealed that the electrochemically and chemically deposited films appeared to have very similar structures, with emeraldine salt films having a fibrillar-like structure whilst the emeraldine bases had a more porous granular morphology. These morphologies are consistent with previously published images [1-23]. The various types of coating, as well as a bare stainless steel specimen, were also examined under the SEM immediately after corrosion testing. The bare stainless steel specimens showed a number of pits of various diameters between 1 µm and 20 µm, each of which showed the typical lacy covers that have previously been observed by other authors (Figure 3) [16, 17].

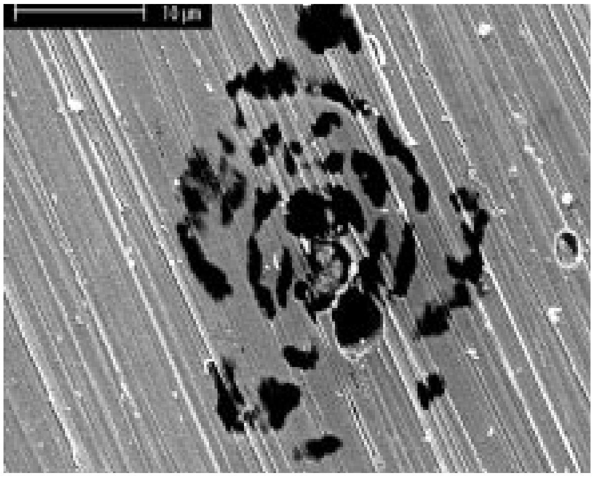
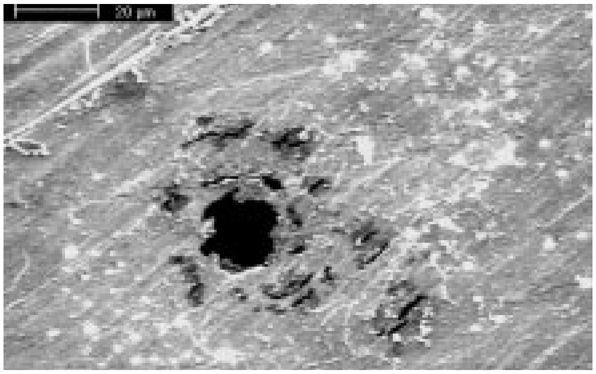
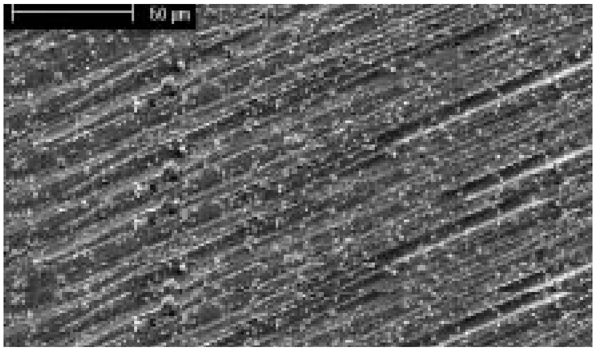


Figure 3 : **SEM micrograph of a bare 304L stainless steel specimen taken immediately after the completion of the polarisation scan.**

The electrochemically deposited emeraldine salt (ES) showed fewer pits than the bare stainless steel, with the majority of the surface being unaffected by the corrosion test, again the pits appeared to have lacy covers (Figure 4a).

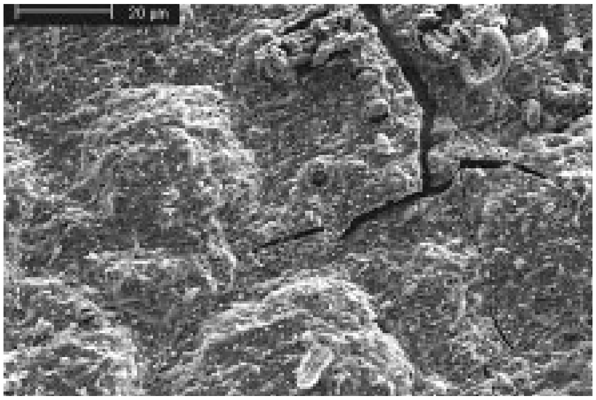


No pits were observed with the chemically deposited emeraldine salt (CS), which is consistent with its polarisation curve (Figure 4b).



However, the chemically redoped emeraldine salt (CRS) had a number of open pits (no lacy covers) on its surface (Figure 4c).

Pits were not visible on either of the two emeraldine base covered specimens, even though the polarisation curves suggested pitting corrosion. Although the electrochemically deposited emeraldine base (EB) was clearly cracked (Figure 4d).



Its chemically deposited counterpart (CB) appeared, on the top surface at least, to be unaffected by the corrosion test (Figure 4e).

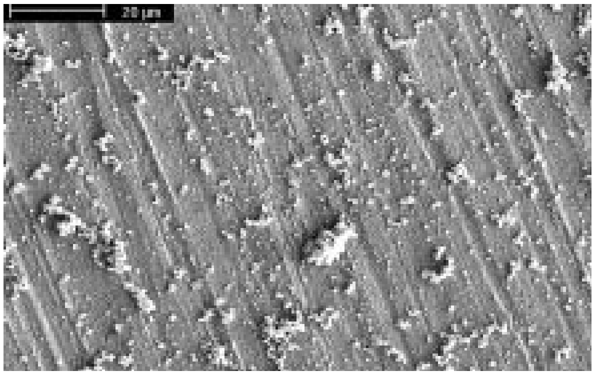
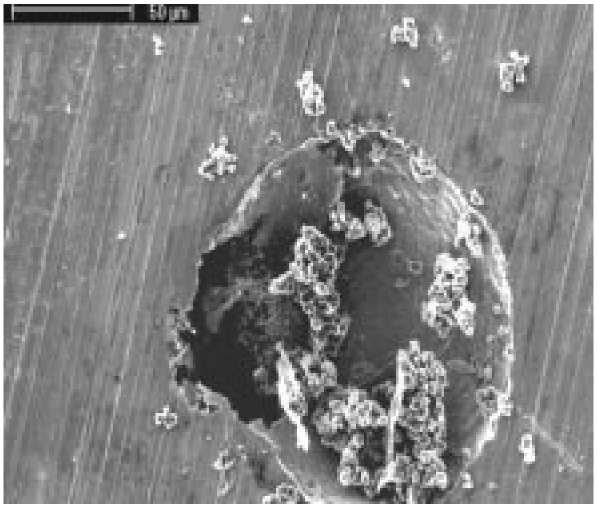
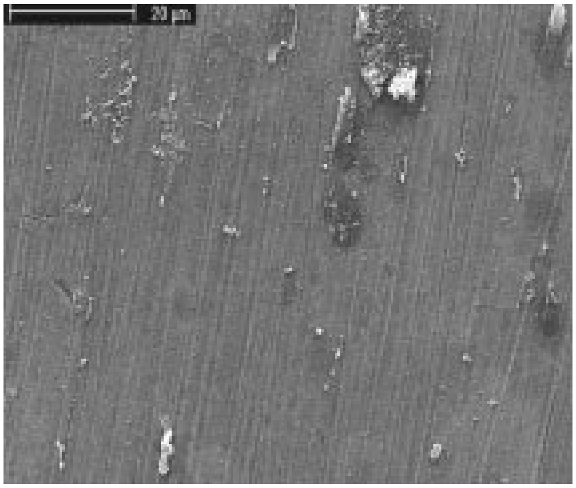


Figure 4 : SEM micrographs of the coatings taken immediately after the corrosion tests: (a) Electrochemically deposited emeraldine salt (ES); (b) Chemically deposited emeraldine salt (CS); (c) Chemically redoped emeraldine salt (CRS); (d) Electrochemically deposited emeraldine base (EB); and (e) Chemically deposited emeraldine base (CB).

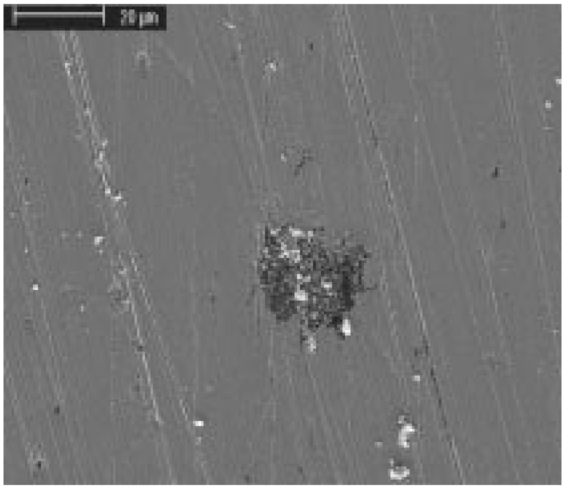
It is worth noting that none of the coatings, bases or salts, showed any signs of peeling from their substrates. The strong adherence of the films was further supported by the fact that polarising in the hydrogen evolution region (-1.0V vs SCE) also did not cause the films to become detached from the stainless steel. Physically scrapping the polyaniline films of the electrodes' surfaces with a spatula did reveal the present of pits on all the specimens except for the ones coated by the CS, entirely consistent with the earlier polarisation scans (Figure 5). The observation of pits on the specimens electrochemically (Figure 5d) and chemically (Figure 5e) coated by the emeraldine base, which had not shown any physical evidence of pitting prior to removal of the coatings, brings the physical evidence in-line with the electrochemical evidence obtained from the polarisation curves. However, in all cases far fewer pits were observed on the coated samples than on the bare stainless steel control specimens. The pits that developed beneath the polyaniline films all had open structures, including those on the samples previously coated by the electrochemically deposited emeraldine salt (ES) that had appeared to have a lacy cover prior to removal of the coating (cf. Figure 4a & 5a). It is also possible to see corrosion products at the base of the pits that developed beneath the coatings, except for the chemically deposited emeraldine base (CB), in the SEM photographs. This suggests that these may be shallower than the pits on the bare stainless steel, the bases of which were sufficiently deep to prevent them from being brought into focus under the SEM (Figure 3). The pits on the specimens with the CB coating (Figure 5e) appeared to be both smaller in diameter (ca. 2 µm) and deeper (as it is difficult to see the base of the pits in their SEM images) than those pits on the other samples (diameters ca. 20 µm to 50 µm). Some salt crystallisation was also observed in the pits on the specimens previously covered by the emeraldine salts (Figure 5a & 5c), which was determined to be predominately an iron chloride by EDX analysis. This contrasts to the material at the base of the pits of samples previously covered by the electrochemical emeraldine base (Figures 5d), that appeared to mainly carbon based, suggesting that it was from degraded polymer.



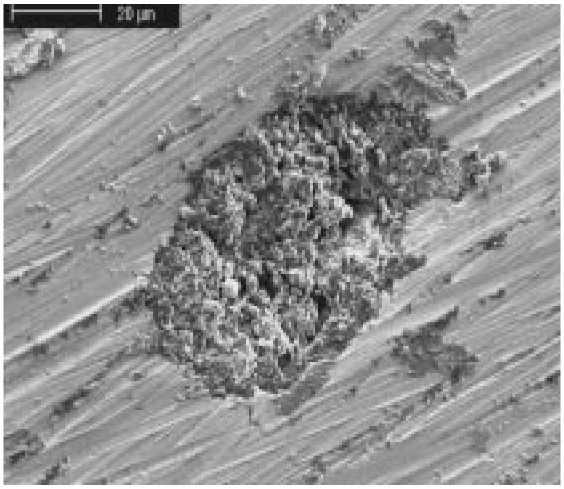
(a)



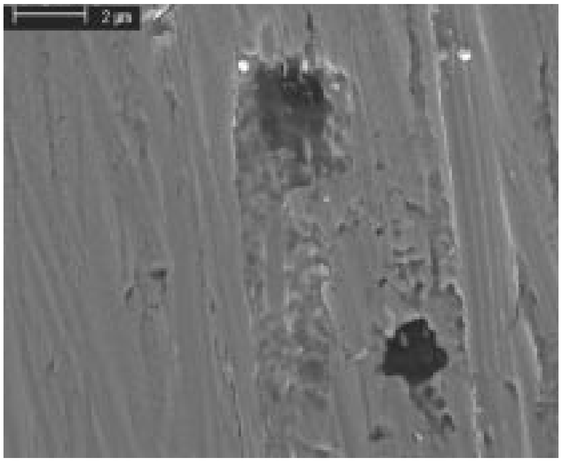
(b)



(c)



(d)



(e)

Figure 5 : SEM micrographs of the stainless steel substrates after the removal of the polymer coatings at the end of the corrosion tests: (a) Electrochemically deposited emeraldine salt (ES); (b) Chemically deposited emeraldine salt (CS); (c) Chemically redoped emeraldine salt (CRS); (d) Electrochemically deposited emeraldine base (EB); and (e) Chemically deposited emeraldine base (CB).

3.3 Electrical Properties

The conductivity measurements on compressed pellets of the various types of polyaniline (Table 3).

	Conductivity (S cm^{-1})
Chemical Base (CB)	0.0023 ±0.0008
Chemical Salt (CS)	20 ±3
Chemical Redoped Salt (CRS)	12 ±3
Electrochemical Base (EB)	0.0023 ±0.0008
Electrochemical Salt (ES)	10 ±2

Table 3 : Conductivities of compressed pellets formed from the various types of polyaniline films deposited.

It revealed that the chemically prepared emeraldine salt (CS) had a conductivity (20 ±3 S cm^{-1}) almost twice is electrochemically deposited counterpart (ES) (10 ±2 S cm^{-1}). The two emeraldine bases had a much lower conductivity than the salts, but were virtually identical with one another (0.0023 ±0.0008 S cm^{-1}). These values are in reasonable agreement with those already published in the literature [14, 1]. However, it is worth noting that the deposited films, or at least the electrochemical salt, were probably anisotropic and hence the their electrical behaviour would be somewhat different to the compressed pellets used in the conductivity measurements [2]. The chemically redoped emeraldine salt (CRS) had an average conductivity of 12 ±3 S cm^{-1}, significantly lower than its as cast emeraldine salt counterpart (but still more conductive than the electrochemically deposited emeraldine salt) reflecting the irreversibility of the doping / dedoping process. The importance of conductivity on the ability of conducting polymers to provide protection against corrosion has previously been addressed by Jain et al. [20].

4. DISCUSSION

4.1 General Uniform Corrosion

The data in Table 1 show that the extent by which the emeraldine bases coatings reduced the general corrosion of the stainless steel was found to be virtually independent of the method of application. However, this was not the case with their more effective salt counterparts, of which the electrochemically deposited coating (ES) gave the best protection. Combining this observation with the data in Table 3 suggests that conductivity is not the most important parameter in regards to reducing general uniform corrosion rates. Table 1 also shows that all the polyaniline coatings reduced the corrosion rate of the bare stainless steel and, with the exception of the ES film, caused positive displacements in corrosion potential. The phenomenon of increasing corrosion potentials coupled to decreased corrosion rates is commonly observed with passive metals, and it is the basis of anodic protection techniques, since a positive shift encourages the passive oxide film to thicken. In the present case this suggests that the polyaniline either acts as an oxidising agent, in a similar manner to an anodic inhibitor, or improves the kinetics of the supporting cathodic reaction (presumably to reduction of dissolved oxygen). Close inspection of Figures 1 & 2 reveals that these coatings did indeed increase the rate of the cathodic reaction, or be it only by about a factor of 2. On the other hand the electrochemically deposited emeraldine salt (ES) coating caused a negative displacement in the corrosion potential, but reduced the general corrosion rate of the stainless steel by a factor of about 5. The reason for both these phenomena can be seen from Figure 2.This shows that the kinetics of the cathodic supporting reaction were at least an order of magnitude slower on the specimens coated with the electrochemically deposited emeraldine salt than on any of the other specimens, including the bare stainless steel. This behaviour is consistent with the dense coating observed under the SEM (Figure 4a), which could at as an efficient barrier between the metal and its environment, and with the high purity expected in coatings deposited electrochemically. It is also worth noting that the data in Table 1 show that all the polyaniline coatings reduced the general I_{corr} values of the stainless steel. Although such an observation are satisfactory as it indicates lower corrosion rates, it contradict some previous published data, for example that of Santos et al. [11] who reported increased corrosion current densities when emeraldine salt films were painted on to carbon steel. This extra current has previously be explained in terms of oxidation of the polymer coating rather than to corrosion of the steel. Since it is not clear why the polymers should oxidise when coated on carbon steel but not on stainless steel, the E_{corr} values being even more oxidising in the latter case, the present results suggest that this explanation for the previously reported addition current may be incorrect.

4.2 Pitting Corrosion

With respect to the prevention of pitting corrosion the performance of the emeraldine salt coatings on 304L stainless steel were better than, or in the case of the CRS films comparable to, the more expensive molybdenum containing 316L stainless steel, which typically pits in 0.028 M NaCl at about 550 mV vs SCE [21]. The two emeraldine base coatings did not give as much protection against pitting corrosion as their salt counterparts, reflecting the more porous morphology and lower conductivity of these films. In addition, as with protection against general corrosion, the ability of the base coatings to protect against pit initiation appeared to be virtually independent of the method of application, possibly reflecting their lack of electrical conductivity. However, once a pit has initiated the electrochemically deposited (EB) films cracked leading to rapid propagation rates (even more rapid than with the bare stainless steel), whilst penetration rates on the chemically coated (CB) specimens were much lower. With respect to the emeraldine salts the polarisation curves and Tables 1 & 2 indicate that the chemically deposited (CS) film displayed a more superior performance than its electrochemical counterpart (ES). However, 304L stainless steel coated by the latter (ES) still resulted in a pitting potential almost 300 mV positive to the value one might expect for the more expensive 316L stainless steel. The superior pitting resistance of chemically deposited emeraldine salt (CS) is consistent with its higher electrical conductivity, which allows it to act as both an electrical as well as a physical barrier as discussed by *Jain et al.* [20]. In contrast the chemically redoped emeraldine salt (CRS) film had a much lower pitting resistance than both its standard chemically deposited (CS) and electrochemically deposited (ES) counterparts. Examination under the SEM suggested that the two types of chemically deposited films (CS & CRS) had very similar morphologies, suggesting that the poor performance of the CRS film relates to its lower electrical conductivity (Table 3). However, the CRS film was still electrically more conductive than its electrochemical (ES) counterpart, yet the pitting resistance of the former was considerably less than the latter. Therefore it is clear that electrical conductivity is not the sole parameter that controls pitting resistance. Generally, electrochemical deposition yields a polymer that is of higher purity as well as more homogenous and adherent than its chemically deposited counterparts. It is likely that it is these factors outweigh the slightly lower conductivity of the ES coating, compared to its CRS counterpart, causing the former to have a higher pitting resistance. The repassivation potentials for all the coatings were more negative than the value on bare stainless steel (Table 2). Furthermore, the charge passed due to pit growth was less with the coatings than on the bare stainless steel, meaning that either fewer pits or shallower pits developed in the former cases. Together these two factors indicate that it would be harder to stop propagation of a pit under a coating than for a similarly sized one in bare substrate. Once a pit has initiated the rate at which it will grow depends on the rate that charge species migrate through the mouth of the pit (i.e. the magnitude of the iR drop) and the level of acidity that develops within its occluded cell [22]. The presence of a polymer coating would separate the pit and bulk solutions and therefore allow greater acidity to develop in the pits, which should favour higher growth rates, but at the same time the coating will restrict the migration of charge species, which should lower the pit growth rate. Which of these two opposes effects dominates in practice will depend on the porosity and adherence of the coating. In practice it was found that the pits under most of the polymer coatings appeared to have lower growth rates (based on lower current densities being recorded after pit initiation) than ones formed on the bare stainless steel, indicating that the restriction in the migration of charge species was dominating process. However, all the coated specimens displayed repassivation potentials that were more negative to that observed on the bare stainless steel, suggesting that the occluded cells in the former were more acidic due to the polymer films preventing mixing with the bulk solution. A similar situation has been previously be presented by Newman et al. who have shown that the addition of inhibitors that stabilise the lacy covers on stainless steel delayed the onset of pitting and slow the pit growth rates, but at the same time stabilised the pits that initiated [16, 23]. The iron chloride crystals observed at the base of the pits below the emeraldine salt coatings (Figure 5a & 5c) are consistent with repassivation resulting from an increase in the pH within the pits occluded cell [16]. The slowest pit growth rates and the most positive repassivation potentials, but also the most negative pitting potential (except for the bare stainless steel), were all displayed by pits beneath the chemically deposited emeraldine base (CB) coating. In addition, after the corrosion tests examination of this film under the SEM revealed no physical evidence of the pits beneath, that is neither cracks nor penetration holes (Figure 4e). Furthermore, Figure 5e shows that once the coating was removed the pits in this case had much smaller diameters (ca. 2 μm) than with any of the other specimens (>10 μm). This behaviour appears to be consistent with the observations of Wen and Kocherginsky [24] who showed that chemically caste emeraldine base films were virtually impermeable to inorganic ions but still selective to protons, whereas emeraldine salt films were found to be permeable to both anions and protons. In contrast to the apparent slow growth rate of pits under the CB coating, the electrochemically deposited emeraldine base (EB) was both the only coating that indicated higher pit growth rates than the bare stainless steel and also had by far the most negative repassivation potential. These two factors are suggest that the environment within the pits below the EB coating was very acidic and that the pit growth rate was not restricted by ion migration. Imaging this EB coating under the SEM revealed that not only did it appear to have the most porous morphology it also cracked during the corrosion tests (Figure 4d), features that may have aided ion migration. Furthermore, on removing the polymer coatings the pits below the electrochemically deposited emeraldine base coating were found to contain a large amount of degraded polymer (or at least carbon based residue). This material may also have helped maintain the acid environment within the pit without impeding ion migration. The possible reasons why the electrochemical base (EB) coating should to much more prone to cracking than its chemical counterpart (CB) is the subject of ongoing investigations.

5. CONCLUSIONS

Although all the forms of polyaniline coatings were able provide some degree of corrosion protection to the 304L stainless steel, it is clear that the performance of the emeraldine salt films were far superior to their base counterparts. This is inline with both the more compact morphology (Figure 4) and the higher conductivity of the former, which allows the film to act as an electronic as well as a physical barrier [20].

With respect to protection against pitting corrosion it appears that conductivity is the most important parameter, whereas for general uniform corrosion it is the morphology of the physical barrier that seems the dominate factor. These influences were particularly clear in the comparison between the two types of chemically deposited emeraldine salt (CS & CRS) films, which had similar morphologies but different conductivities. These two types of films reduced the general uniform corrosion rate by similar amounts, but had vastly different pitting potentials.It was found that not only did the emeraldine salt films provide excellent protection towards 304L stainless steel against pitting initiation (usually superior to that offered by 316L stainless steel), but also greatly reduced the rate at which active pits propagated. This was postulated to be due to the restricted ion mass transport through the film. However, this advantage was partly offset by the more negative repassivation potentials observed with the coated specimens than the bare stainless steel, probably due to the more isolated environment expected for pit beneath a coating, which may make any water treatments designed to re-induce passivation less effective. It had been expected that the higher purity and more compact morphology expected from electrochemical deposition would produce the best films. For general uniform corrosion this was indeed the case, with the ES film causing a dramatic reduction in the kinetics of the supporting cathodic reaction thus leading a lower corrosion rate. However, with respect to pitting corrosion the higher conductivity of the chemically deposited (CS) films led to these giving a higher degree of protection than their electrochemical counterparts. This is an encouraging result, since chemical deposition is likely to prove the more economically viable method of application. However, the difference in performance between the two different types of chemically deposited emeraldine salt films used (CS & CRS) underlines the importance of ensuring that the chosen method of applications results in the coatings having the highest possible conductivity. In practice, since the doping / dedoping process is not completely reversible [10], this is likely to mean that the polyaniline coating should be applied in the conducting emeraldine salt rather than as the emeraldine base form with subsequent protonation to provide the conductivity. However, as yet it is not clear which form of polyaniline is the most suitable for long-term storage prior to application. Although the present results indicate that conducting polymer films can provide excellent protection to stainless steels against pitting corrosion, it is not yet clear how long this protection would last in the field. Long-term exposure to the environment can be expected to lead to leaching of protons from the polymers, which would lead to a drop in conductivity and thus possibility to a loss of protection. In part it may be possible to reduce this phenomenon by the application of a top-coating paint layer. This is currently a topic on ongoing investigation.

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