
The application of an electrochemical technique to determine the porosity of electroless nickel coatings produced in hypophosphite baths

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Keywords

Nickel, Coatings, Corrosion prevention

Abstract

An electrochemical polarisation technique was employed to measure the porosity of electroless nickel (EN) coating. The technique is based on the change observed in the electrochemical parameters with varying cathode and/or anode area on a bimetallic corroding surface. The nickel coating test samples were obtained from a hypophosphite plating bath in the presence of different complexing agents. This technique was used to estimate the effect of coating thickness on porosity and the influence of addition of different complexing agents to EN baths on porosity. The results suggest that, unlike other conventional methods, the electrochemical, a non-destructive method, can detect the smallest pore in an EN-coating and quantify its size in terms of pore area fraction.

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Introduction

Electroless nickel (EN) plating is useful for coating certain engineering components because it can sometimes offer satisfactory wear and corrosion resistance and can be applied in situations where conventional electrodeposition is unsuitable or impracticable (Barker, 1993; Weil *et al.*, 1989). EN-coating can provide relatively uniform deposit thickness and are not prone to build-up at sharp corners. EN also requires only relatively simple plating equipment. However, the high cost of chemicals required for EN plating bath may mean the coating relatively expensive and this tends to restrict the thickness of commercial coatings (Fields *et al.*, 1982). In such circumstances, improvements in coating quality are desirable that can help it to withstand corrosive environments. Modifications of pre-treatment processes, bath formulations and operating parameters have been proposed to address this objective (Fields *et al.*, 1982).

The relatively good corrosion resistance of nickel coatings is one reason for their use on engineering components. The good anti-corrosion performance of electroless Ni-P coatings has been attributable to the relatively low porosity of deposit and its phosphorous content. Nickel coatings are non-sacrificial to many common engineering metals/alloys. For example, they are cathodic to carbon steels. Therefore, the presence of any discontinuities or pores in the coating may result in accelerated localised attack (pitting of the base metal, or undercutting of the coating) because of the high cathodic to anodic surface area ratio. The porosity of EN deposits can be affected by pre-treatment processes, surface roughness, bath composition, and other constraints (Das *et al.*, 1997; Kerr *et al.*, 1997). The formation of nodular deposits, as a result of inclusions in the deposit or defects in the substrate surface, debris in the bath, also may be attributable to the presence of pores in the coating (Das *et al.*, 1997). Other investigators have reported that the trapping of hydrogen bubbles during nickel deposition can cause pores in the coating (Kerr *et al.*, 1997; Notter and Gabe, 1992).

In order to achieve the optimal corrosion resistance, the coating should be as pore-free

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as possible. In some circumstances, information on coating porosity can be used to predict the lifetime of components. Thus, while selecting coated components during the design of any equipment / machine in which they may be exposed to corrosion, it is essential to assess the degree of porosity in the coating necessary to determine the minimum service life. Tests, which are typically used to determine coating porosity, are the ferroxyl test, salt fog exposures, and the electrographic test. These tests are widely employed to evaluate the quality of EN-coatings, and the test procedures are described in ASTM B733 and ASTM B117. Besides being destructive in nature, these techniques cannot be used to determine pores size. Moreover, the suitability of the electrographic test for measuring the porosity of EN-coating is yet to be established. Realising the importance of developing a reliable porosity test, some investigators have tried to extend the electrochemical polarisation technique to offer faster and more accurate measurement of porosity (Aroyo and Parisheva, 1992; Das *et al.*, 1997; Kerr *et al.*, 1997; Notter and Gabe, 1990, 1992; Notter *et al.*, 1984). Investigations have been made, so far, on the porosity of tinsplate and brass coatings using this technique, but have rarely been used to study the porosity of EN-coatings.

The current study presents a simple correlation of coating porosity against parameters, obtained from electrochemical techniques, and verified by the conventional ferroxyl test method. The approach was used also to evaluate variations in the porosity and thickness of EN-coatings associated with changes in the concentration and type of complexing agents that had been added to the plating bath.

Basis for electrochemical porosity measurement

The electrochemical porosity test is based on the principle that describes the influence of cathode and anode area on corrosion potential, corrosion current density, and polarisation resistance (Mansfeld, 1971; Stern, 1958). Considering Tafel plots under activation polarisation, the over-voltage equations are:

$$\eta_a = E_a + \beta_a \log i_a / i_{oa} \quad (1)$$

and

$$\eta_c = E_c - \beta_c \log i_c / i_{oc} \quad (2)$$

where η_a and η_c are the anodic and cathodic over-voltages, E_a and E_c are the equilibrium potentials of the anodic and cathodic materials, β_a and β_c are the anodic and cathodic Tafel slopes, i_a and i_c are the anodic and cathodic current densities, and i_{oa} and i_{oc} are the exchange current densities on the anode and cathode materials, respectively.

The exchange current density and Tafel slope properties of individual electrode materials are constant. The exchange current, however, is area specific i.e. it is proportional to the total electrode area. If A_a and A_c are the exposed areas of the anode and cathode materials; and total electrode area $A_a + A_c = 1 \text{ cm}^2$ (as in present study), the above equations may be written in the form:

$$\eta_a = E_a + \beta_a (\log I_a - \log i_{oa} A_a) \quad (3)$$

and

$$\eta_c = E_c - \beta_c (\log I_c - \log i_{oc} A_c) \quad (4)$$

where I_a and I_c are the anodic and cathodic currents.

At the corrosion potential, where the anode and cathode materials are polarised to the same potential, e.g. $\eta_a = \eta_c = E_{\text{corr}}$, the anodic and cathodic currents will be $I_a = I_c = I_{\text{corr}}$. Substituting these values in equations (3) and (4), we obtain:

$$\log I_{\text{corr}} = \frac{E_c}{\beta_c} - \frac{E_{\text{corr}}}{\beta_c} + \log i_{oc} A_c \quad (5)$$

and by combining these two equations in order to eliminate I_{corr} , we get:

$$E_{\text{corr}} = \frac{\beta_a E_c}{\beta_a + \beta_c} + \frac{\beta_c E_a}{\beta_a + \beta_c} + \frac{\beta_a \beta_c}{\beta_a + \beta_c} \log i_{oc} A_c - \frac{\beta_a \beta_c}{\beta_a + \beta_c} \log i_{oa} A_a$$

or

$$E_{\text{corr}} = K - \frac{\beta_a \beta_c}{\beta_a + \beta_c} \log \frac{A_a}{A_c} \quad (6)$$

where "K" represents a constant comprised of the remaining terms.

Similarly by eliminating the term E_{corr} from the equations (5) and (6), we get:

$$\log I_{\text{corr}} = \frac{E_c - E_a}{\beta_a + \beta_c} + \frac{\beta_c}{\beta_a + \beta_c} \log i_{oc} A_c + \frac{\beta_a}{\beta_a + \beta_c} \log i_{oa} A_a \quad (7)$$

In terms of current density,

$$i_{\text{corr}} = \frac{I_{\text{corr}}}{A_a}$$

Therefore:

$$\log i_{\text{corr}} = \frac{E_c - E_a}{\beta_a + \beta_c} + \frac{\beta_c}{\beta_a + \beta_c} \log i_{\text{oc}} \frac{A_c}{A_a} + \frac{\beta_a}{\beta_a + \beta_c} \log i_{\text{oa}}$$

or:

$$\log i_{\text{corr}} = C + \frac{\beta_c}{\beta_a + \beta_c} \log i_{\text{oc}} \frac{A_c}{A_a} \quad (8)$$

where “C” is a constant and represents the other terms in the equation.

Equations (7) and (8) both show the dependence of corrosion potential and corrosion current on the anode and cathode area.

Experimental details

Coupon samples 3 cm × 2 cm and 3 mm in thickness of carbon steel sheet containing 0.32 per cent C were ground and polished to 600 grit emery paper. The samples were weighed before pre-treatment in “Teepol”, a proprietary alkaline soak cleaner. The samples were then rinsed in distilled water and immersed in 10 per cent HCl solution for about a minute. After rinsing again in distilled water, the samples were immersed in the EN plating solutions. One 7 cm × 7 cm coupon, cut from nickel sheet, was also prepared and plated in the same bath, in order to determine the corrosion potential of pure Ni-P alloy.

EN plating and thickness measurement

Plating was carried out in a bath containing 21 g/l NiSO₄, 25 g/l sodium hypophosphite, and 25 ml/l lactic acid and is described as a “reference bath” in the forthcoming discussion. The effects on deposition rate and porosity from the introduction of 6 ml/l acetic acid, 4 g/l citric acid, and 10 g/l sodium acetate that was added separately to the reference bath, also were studied. The pH of the solutions was maintained at 4.5 by adding the requisite amount of sodium hydroxide. Plating was done at a constant temperature of 90 ± 2°C for different periods, in order to obtain the desired coating thickness.

Coating thickness was determined by the weight gain method (ASTM B-659-90) and was calculated by using the density of pure

nickel i.e. 8.9 g/cm³, instead of the deposit. The deposit contains phosphorous and therefore, its density is actually less than that of the pure nickel (Minjer and Brenner, 1957). Hence, the thickness values reported in the paper may be approximately 20 per cent lower than were actual coating thicknesses. This was confirmed, subsequently by sectioning plated specimen and observing it under an Image Analyser equipped with the software supplied by Metal Power, Bombay to determine the coating thickness.

Electrochemical polarisation tests

Cathodic Tafel plots were carried in 0.5 M H₂SO₄ + 0.1 M KSCN solution by means of a Basic Electrochemical Systems Model ECDA-001, (supplied by Con-Serv Enterprises, Mumbai). Thiocyanate ions are very sensitive to the presence of ferrous materials and can easily enter pores to react with the bare metal substrate to expose pore locations (Notter and Gabe, 1990). The samples were polarised away from open circuit potential (OCP) to –250 mV (SCE). A saturated calomel electrode was used as a reference electrode. The plots were analysed to establish the corrosion potentials, E_{corr} , and corrosion currents, I_{corr} of the samples.

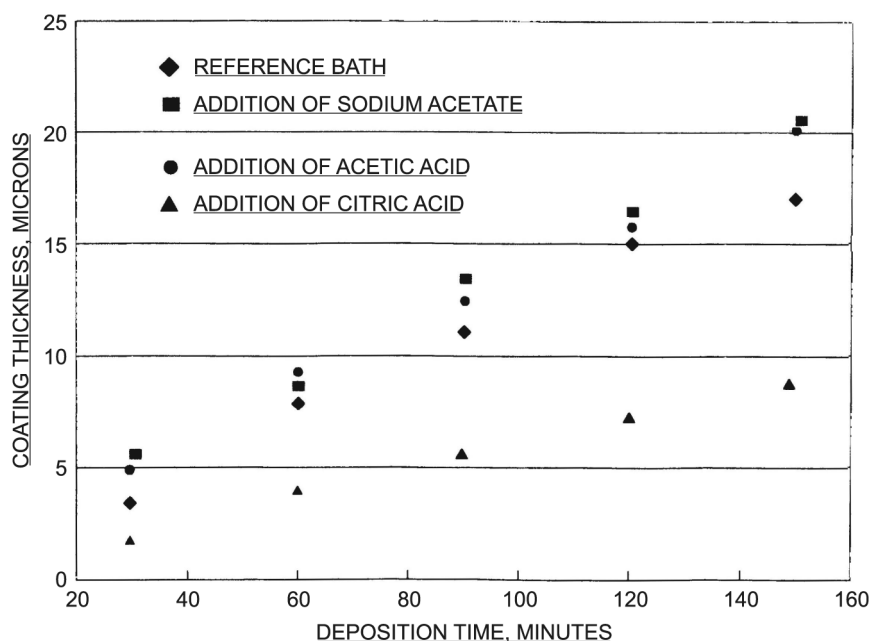
Ferroxyl test

The ferroxyl test was conducted according to ASTM B733 (1998). The experimental solution was prepared by adding 25 g potassium ferricyanide and 15 g sodium chloride to 1 l of distilled water. EN-coated samples were immersed in the test solution for 25 s at room temperature. Samples were rinsed, dried and examined for blue spots, which indicated the location of pores in the EN-coating. The blue spots were counted on the entire surface of the sample. Number of corrosion spots reported are the average of total spots appearing on 6 cm² area of the specimen.

Results

Deposition rate

EN plating was performed in the bath containing lactic acid (a reference bath). Deposit thicknesses from 1 to 17 μm were obtained by increasing the deposition time. The test results are shown in Figure 1. The purpose of the tests was to evaluate

Figure 1 The effect of various complexing agents in a lactic acid EN bath on deposition rate

the variations in porosity with increase in coating thickness. It is evident from figure that the rate of Ni-P deposition increased linearly with time, as is well documented in literature (Barker, 1993; Kerr *et al.*, 1997; Minjer and Brenner, 1957). The coating thicknesses obtained from the reference bath with varying plating time also were determined by the evaluation of sectioned samples using Image Analyser and representative photographs are given in Figure 2. Additions of citric acid, sodium acetate, and acetic acid were made (separately) to the reference bath, to assess their effects on plating rate and on the extent of porosity in the coatings. The addition of sodium acetate in the bath seemed to accelerate the plating rate and showed highest porosity in the EN-coating, while lowest plating rate was observed with the addition of citric acid. The latter additive, suppressed the rate of Ni-P deposition. The presence of acetic acid in the EN bath slightly enhanced the rate of deposition. Changes in the plating rate with varying complexing agents are to be expected, due to the nature of ligand group and ring size of complexed nickel ion (Mallory, 1974).

Electrochemical porosity measurement

The corrosion potentials were calibrated for the couple made by soldering a carbon steel specimen of area 1 cm^2 to the EN plated nickel sheet of 98 cm^2 area. A thick Ni-P

coating of about $25 \mu\text{m}$ was applied on nickel sheet, before soldering, and was assumed to be pore-free, (Kerr *et al.*, 1997). The couple was, then, exposed to $0.5 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M KSCN}$ solution to obtain its corrosion potentials. During the E_{corr} measurement, the soldered area was completely waxed to avoid the exposure of the solder to the experimental solution. The area of the carbon steel, in the bimetallic system, was assumed to be a representative of pores in EN-coatings. In this couple, carbon steel will become anodic and will dissolve preferentially, whereas the EN-coated Ni sheet will act as a cathode. The changes in corrosion potential were then recorded for the corresponding (change in) area of the carbon steels sample. The latter was varied by insulating the undesired surface. The area fractions of carbon steel (anode), $A_a/(A_a + A_c)$, exposed to solution during E_{corr} measurement, were calculated and are plotted against the corresponding corrosion potentials as shown in Figure 3. This was used as a standard reference plot for evaluating the porosity of specimens coated in the similar bath.

The E_{corr} value obtained for uncoated carbon steel was -713 mV , and for Ni-P coating was -252 mV . The redox potential of the couple made of these two alloys should lay in the range -713 mV to -252 mV , as was the case in the present study. This complies with the principle of electrochemical kinetics. It was observed for values of

Figure 2 Representative photographs of sectioned coating of thicknesses 7, 11, and 17 μm

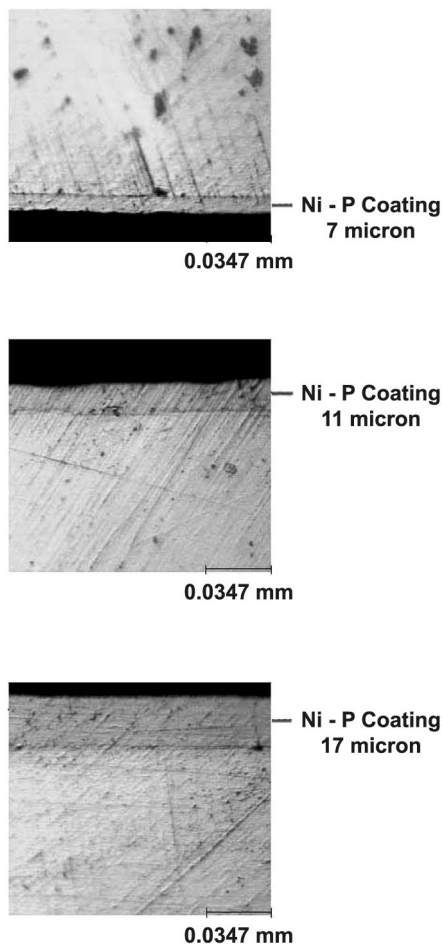
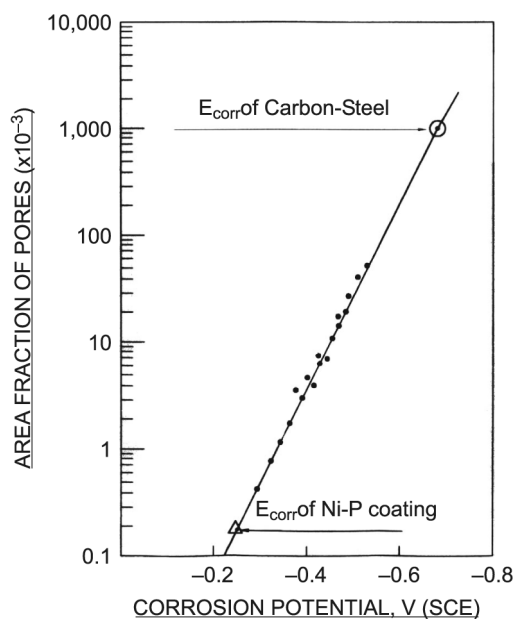


Figure 3 Calibration plot for pore area fraction and corrosion potential for EN-coating produced in baths with various complexants



the anodic area fraction from 0.41×10^{-3} to 86×10^{-3} , the corrosion potential varied from -300 to -565 mV.

The electrochemical technique was used to investigate the variations in porosity due to the change in coating thickness and the quality of coating, produced from the baths added with different complexing agents; this is described in forthcoming discussion.

Variation of porosity with coating thickness

The observed changes in E_{corr} value with increasing deposit thickness are shown in Table I. It can be observed that the corrosion potential became less negative as the thickness of coating was increased. The trend was similar for all the deposited samples, irrespective of complexing agents added to the reference EN bath. The pore area fraction, in the coatings of various thicknesses, can be read off from the calibration plot (Figure 3) for the corrosion potentials observed. These results are given in Table II. The values of E_{corr} , and the corresponding pore area fractions, clearly show that the porosity of the coating decreased as thickness was increased. Microscopic observation of the sectioned coating confirmed that the number of coating holidays decreased, especially near the interface of coating and base metal, for increasing coating thicknesses from 7 to 17 μm (Figure 2). Thus, by measuring the E_{corr} , the thickness of the plated deposit can be optimised to attain the minimum pore-free coating, in order to enhance the service life of the component. Figure 4 showed the observed changes in corrosion current (I_{corr}) with the thickness of EN-coating. This illustrates that I_{corr} was highest for uncoated carbon steel ($56 \mu\text{a}/\text{cm}^2$), and it was lowest for the 17 μm EN-coating ($7 \mu\text{a}/\text{cm}^2$). The latter result could be due to the increased thickness providing better surface coverage to the base alloy as a result of the total pore area (and consequent exposure of the base alloy surface) becoming smaller.

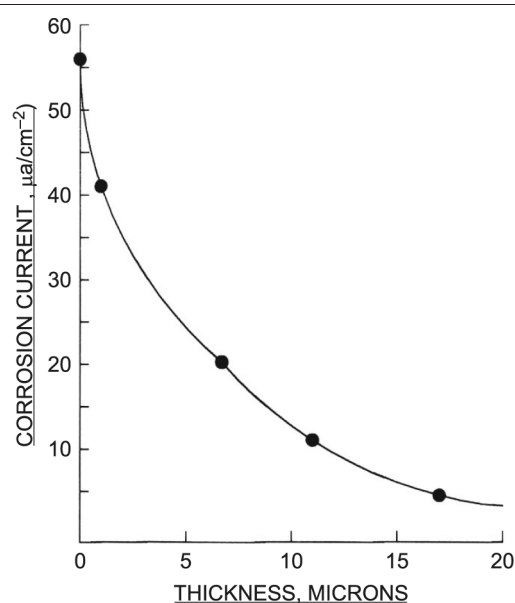
These results show that E_{corr} and I_{corr} may be useful electrochemical parameters in evaluating the porosity, and thereby the corrosion resistance, of coatings. Additionally, unlike conventional test methods, the degree of porosity can be assessed, in terms of anodic area fractions, by means of these electrochemical parameters.

Table I Variation of corrosion potential with thickness of coating for different complexing agents in the reference EN bath

| Coating thickness (μm) | Corrosion potential (mV) | | | |
|-------------------------------------|--------------------------|-------------|----------------|-------------|
| | Reference bath | Citric acid | Sodium acetate | Acetic acid |
| 1 | – 648 | – 601 | – 639 | – 652 |
| 7 | – 472 | – 462 | – 465 | – 470 |
| 11 | – 407 | – 343 | – 413 | – 410 |
| 17 | – 309 | – 209 | – 302 | – 316 |

Table II Variation of pore area fraction with thickness of coating f for different complexing agents in the reference EN bath

| Coating thickness (μm) | Pores area fraction ($\times 10^{-3}$) | | | |
|-------------------------------------|--|-------------|----------------|-------------|
| | Reference bath | Citric acid | Sodium acetate | Acetic acid |
| 1 | 320 | 120 | 260 | 380 |
| 7 | 11 | 8.9 | 9 | 10 |
| 11 | 2.9 | 0.9 | 3.2 | 3 |
| 17 | 0.41 | 0.21 | 0.38 | 0.52 |

Figure 4 Variation of corrosion current with coating thickness obtained from the reference lactic acid bath without complexant**Effect of complexing agents on porosity**

It is apparent from Table I that in the presence of citric acid, the coatings had a less negative E_{corr} . This trend was less pronounced in the case of sodium acetate additions, and less again in the case of baths dosed with acetic acid or the reference baths. Corresponding pore area fractions were derived, as discussed earlier, and are presented in Table II. It can be inferred on the basis of these results that the presence of citric acid and sodium acetate in the bath resulted in lower coating porosity or a smaller total pore area. It would appear that a

slightly greater (negative) shift in E_{corr} occurred when acetic acid was added to the reference bath.

Where components are to be used in severely corrosive environments, it is a common practice for the coating thickness to be increased in order to produce an additional corrosion allowance. This increases the cost of the components. However, if the quality of a coating can be improved by reducing its porosity, a thicker coating may not be required. Complexing agents seem to be the important constituent of EN baths and have a significant effect on coating porosity. The electrochemical results presented in this paper, are preliminary, but may be useful when evaluating changes in porosity due to the addition of organic complexing compounds.

Discussion

The pore size, in an EN-coating system, may be influenced by varying the relative area of the anode/cathode, which then affects the electrochemical process. The latter evolves two important kinetic parameters i.e. corrosion potential and corrosion current which may be useful to indicate the behaviour of a corroding system. These variables, in equations (7) and (8), are shown to be closely related to the area of the anode and cathode in a bimetallic system. The test results suggested that with increased anode area, E_{corr} became more negative or approached the potential

value of the uncoated steel sample (Figure 3). This observation indicates that the pore size affected the corrosion potential in such a way that latter approached the E_{corr} of the base metal with increase in the pore area, as would be expected. By contrast, if an E_{corr} of the plated carbon steel were closer to the corrosion potential of pure Ni-P coating (-252 mV) it would indicate that the coating was pore-free, or had minimal porosity. The corrosion current (Figure 4) found to decrease with increase in coatings' thickness. This also appears to be an indicative of porosity in addition to the corrosion potential.

The porosity of the EN deposits was also evaluated by means of the conventional chemical method (i.e. the ferroxyl tests). Application of the ferroxyl test on coatings produced using the reference bath showed the highest numbers of blue spots per cm^2 (i.e. 60 per cm^2), for a $1 \mu\text{m}$ thick coating, while no such spots were visible on a coating $17 \mu\text{m}$ in thickness. The number of blue spots appeared on $7 \mu\text{m}$ and $11 \mu\text{m}$ thick coatings were 20 and 4 per cm^2 , respectively. Though the ferroxyl test does not give the idea of pore size, the test confirmed the reduction in porosity which occurred with increased deposit thickness, as was predicted by the electrochemical tests.

The electrochemical technique could also be able to distinguish the coatings produced in the baths added with different complexing compounds. This may probably be due to the variations in smoothness of coating, provided by complexing compounds, with regard to their porosity. It seemed that the electrochemical technique might be useful for selecting a bath, amongst different EN baths, for obtaining a coating with least porosity.

Conclusions

- The corrosion potential became less negative, and the corrosion current was smaller with increasing coating thickness.
- It appeared that an empirical relationship might link the pore fraction area with changes in the observed corrosion potential for coatings produced under similar plating conditions. This behaviour indicated that thicker coatings were less porous, and this was verified by ferroxyl test results.

- The addition of citric acid and sodium acetate to the reference bath were observed to reduce coating porosity, whereas porosity tended to increase slightly in the presence of acetic acid bath additions. The selection of appropriate complexing agents when formulating EN bath constituents may result in the production of better quality coatings.
- The test results demonstrated that the electrochemical parameters i.e. corrosion potential (E_{corr}) and corrosion current (I_{corr}) could be used to obtain a qualitative indication of the area of the exposed pores. Use of the electrochemical parameters provides a faster, non-destructive method of evaluating EN-coatings on carbon steel.
- The electrochemical technique can provide a higher sensitivity of detection and relative quantification of coating porosity, and hence its probable corrosion resistance, than can conventional tests for comparing similar EN-coatings.

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