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Electrochemical monitoring of electrogalvanizing solutions

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The corrosion resistance of steel is vastly improved when a zinc cathodic protective layer is applied. In recent years there has been renewed interest in producing this galvanized coating electrolytically. As with many deposition processes, the control of the operating parameters is very important in order to produce good quality zinc coatings. The homogeneity, ductility and smoothness of the zinc layer are critical. These factors are usually influenced by the electrochemical nature of the solution and organic additives are often used to assist in control.

Studies on the polarization behaviour of solutions for electrogalvanizing electrolytes were made. Cyclic voltammetry techniques were used to develop methods which might be applicable in monitoring the active organic content of liquorice in solution. The morphologies and orientations of the zinc were studied using SEM and X-ray diffraction techniques.

1. Introduction

Corrosion protection is a major concern with the use of steel in commercial applications where there is exposure to the atmosphere. In the wire industry, zinc coating of steel by hot dipping or electrodeposition is used to provide protection because of the favourable technical and economic advantages it affords. Although the hot dip method has dominated the galvanizing industry, electrogalvanizing, which has been used to a limited degree in the past, is gaining more attention in recent years.

A number of electrogalvanizing baths have been used for plating, most often based on sulphate [1] and chloride salts with other chemicals added to supplement and enhance the deposition process. A sulphate electrolyte with some boric acid, chloride and organic additives was used in this research and is similar to that employed by National Standard, Niles, Michigan, in their wire plating process. The zinc-plated wire is usually drawn to a smaller diameter. Because of this mechanical working process, the physical and metallurgical properties of the zinc layer become more critical. Process control is an important aspect of the industrial plating operation, but there are only a limited number of methods available to assist in regulating the deposition. Chemical analysis of the electrolyte is a necessary element in any control scheme, but it is usually not possible to determine the active organic contents of the bath by these means. Since the organic additives usually have a major impact on deposition, a knowledge of the active concentration present in solution would assist in maintaining process uniformity.

The object of this study was to investigate the polarization behaviour of a typical industrial zinc plating bath by means of cyclic voltammetry. The influence of zinc ion concentration, temperature and liquorice content on the system was determined. The results were evaluated from the standpoint of using voltammetry measurements to monitor the organic concentration of the electrolyte.

2. Experimental details

Drawn 1070 steel wire (0.23 cm in diameter) provided by National Standard Company was used as the starting material. The wire was cut to the desired length, straightened by hand and cleaned with trichloroethylene. Electroplaters tape was wrapped around the wire to isolate the area (usually 1 cm^2) to be plated. The wire was then electropolished in 600 $g\,l^{-1}$ H_2SO_4 at 400 $mA\,cm^{-2}$ for about 10–12 min, depending upon the amount of rust on the wire, using a lead (0.75% silver) counter electrode. The wire was cathodically and then anodically cycled for periods of 1 min until no rust remained on the surface of the wire and then rinsed with demineralized water and dried in nitrogen.

The electrolyte contained 90 or 155 $g\,l^{-1}$ zinc (as $ZnSO_4$), 14 $g\,l^{-1}$ Cl (as NH_4Cl), and 14 $g\,l^{-1}$ $B(OH)_3$ with a pH near 5 and was provided by National Standard Company. Various amounts of liquorice, which may have active ingredients of glycyrrhizin [2], were added to the electrolytes as desired.

The steel wire was stationary and the electrolyte was agitated using a magnetic stirrer. A cast zinc bar was used as the counter electrode. The reference electrode was a commercial saturated $Hg–Hg_2SO_4$ electrode (+0.656 V versus SHE), but the potentials reported were converted to the standard hydrogen scale. The cyclic voltammogram was initiated at −0.694 V versus SHE and driven in a negative or cathodic direction at 2 $mV\,s^{-1}$ until the current reached 50 mA, then reversed until the cross-over potential (current shifted from cathodic to anodic) was reached. The effects of liquorice additions on the polarization of zinc deposition from 90 and 155 $g\,l^{-1}$ zinc electrolyte at ambient temperature and 60° C were evaluated. The morphologies of the zinc deposits were observed with a scanning electron microscope.

Zinc coatings were obtained at a current density of 600 $mA\,cm^{-2}$, using the same electrolyte and arrangement described previously but with the reference electrode removed. The wire was rotated at 100 r.p.m. and plated for 5 min to give a theoretical 12 wt % zinc coating on the steel. The influences of temperature, zinc and liquorice concentrations on the orientations and morphologies of the zinc deposits were evaluated by using X-ray diffraction and SEM. Wires of 4 cm length were also plated and drawn in order to test the drawability of the coated wires and the results were reported elsewhere [3].

3. Results and discussion

3.1. *Polarization studies*

Generally, the cyclic voltammograms showed that zinc deposition was polarized by the addition of liquorice, lower zinc concentration and decreased temperature. Four voltammetry curves plotted as log current versus potential are shown in Fig. 1. The curves were generated using a 155 $g\,l^{-1}$ zinc electrolyte: curve A was for 60° C and no liquorice and curve B had 1.0 $g\,l^{-1}$ liquorice; curves C and D were made with electrolyte at 24° C containing 0 and 1.0 $g\,l^{-1}$ liquorice, respectively. The electrode surface area was 1 cm^2 for all tests.

Only the back scans of the curves are shown in Fig. 1 for simplicity. This portion of the scan is more interesting since it approximates steady-state deposition on a zinc surface. The forward scans were similar to the back scans in degree of polarization, but were slightly more complex in shape due to sensitivity to the initial substrate condition and to a dependence on the pretreatment conditions used in preparing the electrode. The curves obtained were generally comparable to those reported previously in the literature [4].

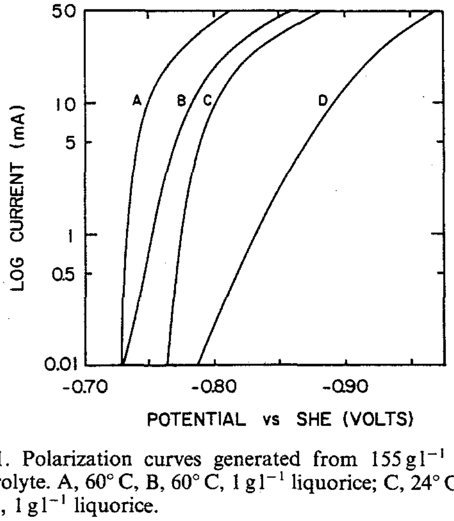

Fig. 1. Polarization curves generated from 155 $g\,l^{-1}$ zinc electrolyte. A, 60° C, B, 60° C, 1 $g\,l^{-1}$ liquorice; C, 24° C; D, 24° C, 1 $g\,l^{-1}$ liquorice.

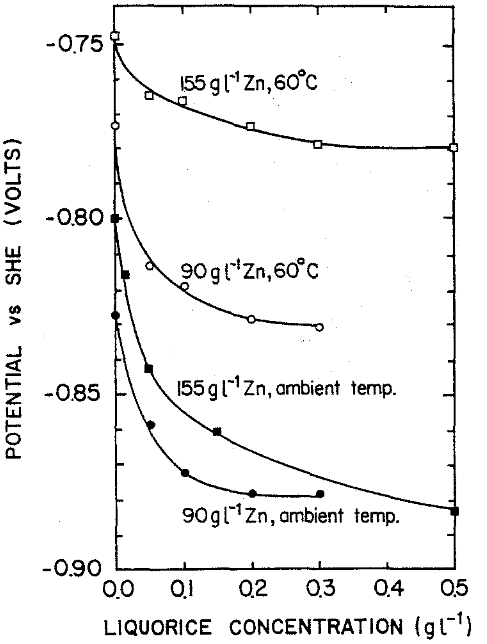

Fig. 2. Changes in polarization potentials measured at 10 mA cm^{-2}.

Some hysteresis between the forward and back scan was noted and tended to decrease with higher zinc concentrations.

The influence of liquorice concentration and temperature on the zinc polarization curves is shown in Fig. 2. The polarization potentials in these plots were taken from the voltammograms at a current density of 10 mA cm^{-2} and corrected for 6 mV increase in the potential of the reference electrode from ambient temperature to 60° C. Potentials at 10 mA cm^{-2} were chosen for comparing polarization behaviour because the curves were relatively parallel and more reproducible in this region. A notable increase in polarization was observed with additions of liquorice as low as 0.05 g l^{-1}. The polarization continued to increase slightly and eventually approached a constant value with increasing addition of liquorice to 1 g l^{-1}. The range of liquorice concentration giving significant changes of polarization varied with the zinc content in the electrolyte, being 0 to 0.5 g l^{-1} for 155 g l^{-1} zinc and 0 to 0.2 g l^{-1} for 90 g l^{-1} zinc. Once these values of liquorice were exceeded, relatively small changes in polarization were detected.

Increasing the temperature from ambient to 60° C caused about a 55mV decrease in polarization for both 90 and 155 g l^{-1} zinc solutions. Increasing the zinc concentration from 90 to 155 g l^{-1} resulted in approximately 25 to 30 mV depolarization at both ambient temperature and 60° C. Liquorice caused an increase in polarization for all electrolytes, as mentioned previously. The polarizing effect of liquorice in electrolyte containing 155 g l^{-1} zinc was greater at ambient temperature than at 60° C. Whereas a 90 mV increase was noted at ambient temperature, similar liquorice concentrations gave only a 30 mV increase at 60° C. In general, the polarizing effect of the liquorice at ambient temperature was very similar regardless of zinc content, but a major difference was noted for the two zinc concentrations when the temperature was increased to 60° C.

SEM micrographs were made of the deposits produced during the cyclic voltammetry tests. It should be mentioned that the morphologies observed may not necessarily be indicative of the actual structure obtained in an industrial operation, since the latter are plated at a much higher current density. However, the variation in morphology during the initial stages of deposition may be more sensitive to the plating parameters and can still be an indication of electrolyte composition, which in turn causes the change in polarization. The addition of liquorice to the 90 g l^{-1} zinc electrolyte changed the nucleation of zinc from scattered clusters (Fig. 3) to a more uniform coverage of zinc consisting of fine

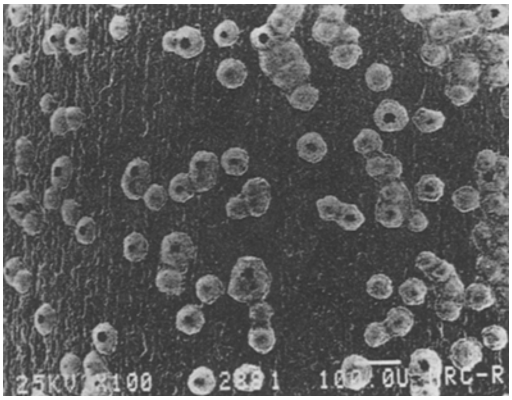

Fig. 3. Zinc deposits obtained during the cyclic voltammetry test from 90 g l^{-1} zinc electrolyte containing no liquorice at ambient temperature. × 60.

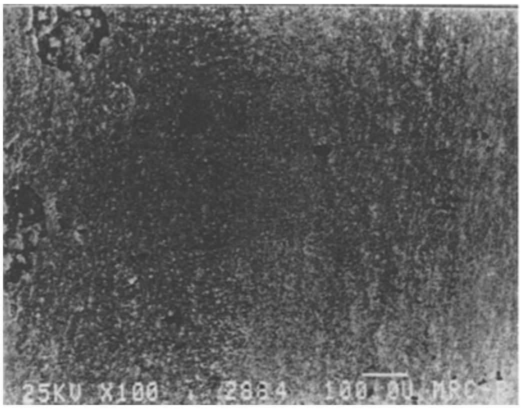

Fig. 4. Zinc deposits obtained during the cyclic voltammetry test from 90 g l^{-1} zinc electrolyte containing 0.2 g l^{-1} liquorice at ambient temperature. × 60.

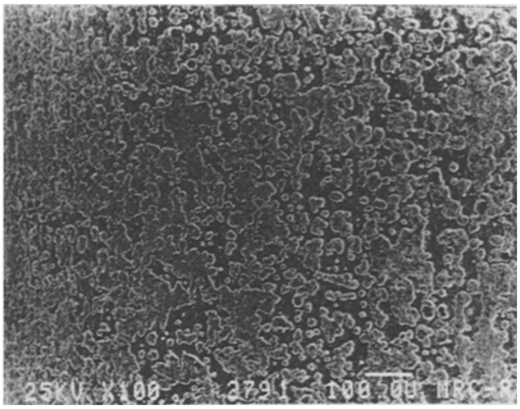

Fig. 5. Zinc deposits obtained during the cyclic voltammetry test from 155 g l^{-1} zinc electrolyte containing no liquorice at ambient temperature. × 60.

contiguous grains (Fig. 4). Additions of liquorice in excess of 0.2 g l^{-1} did not appreciably change the morphology. The deposits obtained at 60°C showed the same nucleation trends as those at ambient temperature, except that the deposits appeared to be less contiguous and had a smaller number of nuclei.

When the zinc concentration was increased to 155 g l^{-1}, the electrode coverage was significantly improved both at ambient temperature and 60° C, even without the presence of liquorice (Fig. 5). As a result, less liquorice was required for 155 g l^{-1} than for 90 g l^{-1} zinc electrolyte to obtain complete coverage of the electrode. Nevertheless, the contiguity of the deposit was not adversely affected by the higher temperature as described for 90 g l^{-1} zinc electrolyte.

3.2. *Orientation and morphology studies*

Zinc deposits were also made at 600 mA cm^{-2} for 5 min, conditions which approximate industrial practice. A relatively thick coating was chosen so that the influence of plating conditions on the orientation, morphology and drawability of the zinc coating would be more pronounced. The major peaks of X-ray diffraction patterns of the zinc deposits are listed in order of decreasing intensity from the top as shown in Table 1. The deposits obtained from electrolytes at ambient

Table 1. Effect of increasing liquorice concentration on the orientations of zinc deposits

Liquorice concentration (g l^{-1})	*0.0*			*0.2*	*0.5*	*1.0*
90 g l^{-1} Zn, ambient temperature	(112)[a] (101)	(101) (110) (112)	(110)	(110)		
155 g l^{-1} Zn, ambient temperature	(112)	(101) (112) (110)			(110)	(110)
155 g l^{-1} Zn, 60° C	(103) (112)	(112)	(101) (112) (110) (103)		(101) (112) (110)	(110) (112) (101)

[a] Relative peak intensity decreases from the top of a given column.

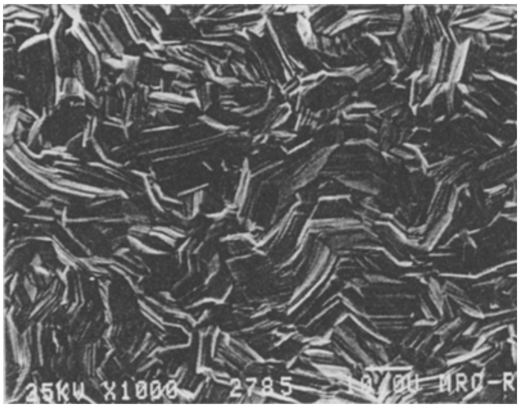

Fig. 6. Zinc deposits obtained at 600 mA cm^{-2} for 5 min from electrolyte containing 155 g l^{-1} zinc at ambient temperature. × 600.

temperature without the presence of liquorice had a predominant (1 1 2) orientation. The SEM micrograph shown in Fig. 6 is typical of a deposit with this orientation, with sharp-edged zinc facets being the dominant feature. The orientation shifted to (1 0 1) as liquorice was added to the electrolyte and changed to (1 1 0) when the liquorice concentration was about 0.2 g l^{-1} for 90 g l^{-1} zinc, and 0.5 g l^{-1} for 155 g l^{-1} zinc electrolyte. The deposits made in the presence of liquorice had smaller, more rounded and less sharply faceted grains, as shown in Fig. 7. Some porosity was noticed in the structure and appeared to be more pronounced as the concentration of liquorice increased. A (1 1 0) preferred orientation was found as the liquorice concentration in the electrolyte increased further. These results were in agreement with the polarization studies where the overpotential did not change significantly after the liquorice concentration reached a particular level.

At 60° C the deposits obtained in 155 g l^{-1} zinc electrolyte had a mixed (1 0 3) and (1 1 2) orientation with a larger grain size and much less edge type growth (Fig. 8). On increasing the liquorice content, the orientation shifted to a (1 1 2), (1 0 1) and finally to a dominant (1 1 0) type. However, a deposit showing only a (1 1 0) orientation was not obtained even with 1 g l^{-1} liquorice present. This might be expected since the polarization curves showed that the polarizing effect of liquorice in 155 g l^{-1} zinc electrolyte was much less at 60° C than at ambient temperature. The deposits obtained from 90 g l^{-1} zinc electrolyte were more dendritic than those made with 155 g l^{-1} zinc, which made X-ray diffraction analysis difficult. However, the dendrites were diminished after the addition of a wetting agent, triethanolamine. This indicated that the formation of the dendrites was probably associated with the surface tension and physical nature of the hydrogen gas evolved during deposition. Additional research would be needed to clarify further the role of the various additives on the amount and nature of the gas co-deposited during plating.

In general, the results indicated that the orientation of the deposits could be correlated with the polarization data obtained by cyclic voltammetry. The general trend noted in

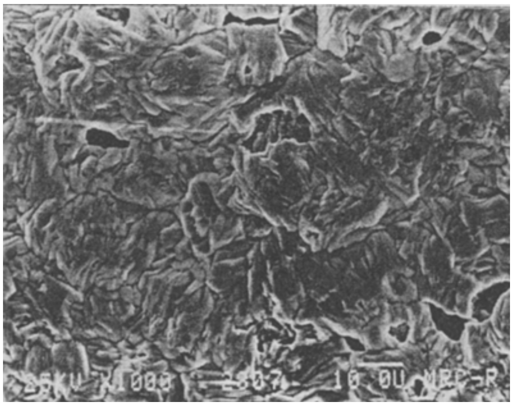

Fig. 7. Zinc deposits obtained at 600 mA cm^{-2} for 5 min from electrolyte containing 155 g l^{-1} zinc and 0.5 g l^{-1} liquorice at ambient temprature. × 600.

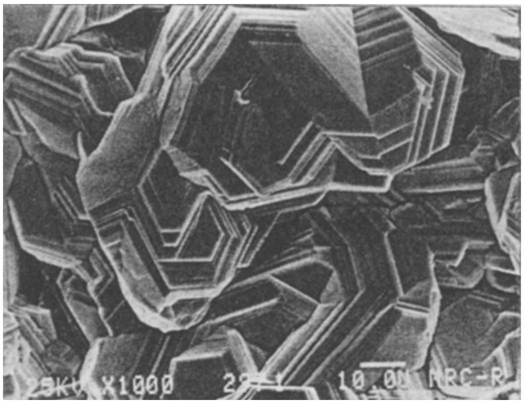

Fig. 8. Zinc deposits obtained at 600 mA cm^{-2} for 5 min from electrolyte containing 155 g l^{-1} zinc at 60° C. × 600.

orientation was a shift to (1 1 0), or the basal plane perpendicular to the substrate, as the polarization increased. The exact point at which this occurred was dependent on the process variables such as zinc content and temperature. Current density was not investigated in this study, but it would be expected to be of influence also.

3.3. *Application to plant practice*

As previously mentioned, both increasing temperature and zinc concentration resulted in depolarizing the zinc deposition, whereas liquorice caused an increase in polarization. The morphology of the zinc could not be predicted strictly from the polarization value, however, since these two effects cannot be differentiated from a single polarization curve. Thus, it would be necessary to generate a series of polarization curves for a fixed zinc concentration and temperature while varying the liquorice concentration. The standard curves could then be used to indicate the concentration of liquorice in a desired electrolyte. The optimum plating conditions could be determined by evaluating the influence of the coating characteristics on such desired properties as ease of drawing and corrosion resistance.

A typical cyclic voltammogram made using industrial electrolyte containing $155\,g\,l^{-1}$ zinc, $19\,g\,l^{-1}$ $B(OH)_3$, and $12\,g\,l^{-1}$ Cl is shown as curve 'h' in Fig. 9 and is compared with synthetic electrolytes containing known concentrations of liquorice. Additions of liquorice had been made to the plant electrolyte over a period of time during use, so that the actual concentration at the time of testing was unknown. By comparing the curve made from the plant electrolyte with the standard curves made from solutions with known liquorice contents, the plant electrolyte appeared to have a liquorice content of about $1.0\,g\,l^{-1}$. The micrograph (Fig. 10) of the deposit made from the plant electrolyte at $600\,mA\,cm^{-2}$ for 5 min was also similar to that obtained from the $155\,g\,l^{-1}$ zinc electrolyte known to contain $1.0\,g\,l^{-1}$ liquorice which was made synthetically in the laboratory. The results indicated that the active liquorice concentration of an electrolyte may be estimated by evaluating the polarization behaviour and comparing the value with known standard curves.

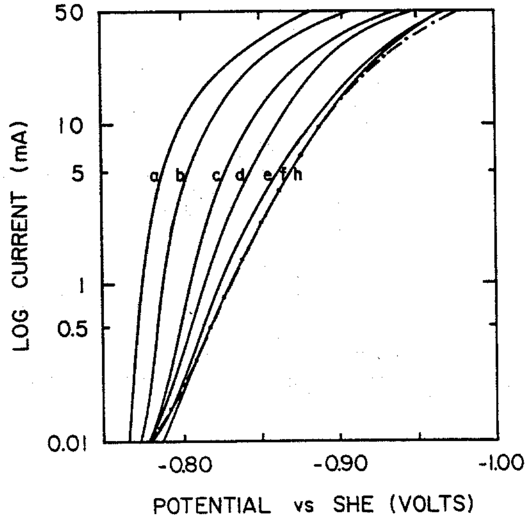

Fig. 9. Polarization curves for $155\,g\,l^{-1}$ zinc electrolyte with different concentrations of liquorice at ambient temperature. Concentration of liquorice ($g\,l^{-1}$): a, zero; b, 0.015; c, 0.045; d, 0.15; e, 0.50; f, 1.0; h, plant electrolyte.

4. Conclusions

The studies have shown that the polarization behaviour and deposition characteristics of zinc in neutral zinc sulphate electrogalvanizing electrolytes (pH 5) were affected by the plating parameters, zinc and liquorice concentration and temperature. A significant change of polarization potential and improvement of the contiguity of

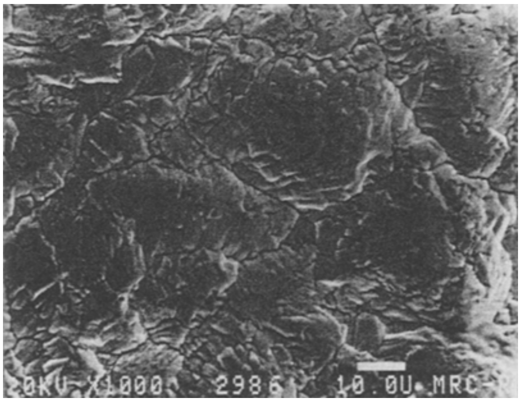

Fig. 10. Zinc deposits obtained at $600\,mA\,cm^{-2}$ for 5 min from plant electrolyte containing $155\,g\,l^{-1}$ zinc and unknown concentration of liquorice at ambient temperature. × 600.

the nucleation was observed for liquorice concentrations of about 0.2 g l and 0.5 $\mathrm{g\,l^{-1}}$ for 90 $\mathrm{g\,l^{-1}}$ and 155 $\mathrm{g\,l^{-1}}$ zinc electrolytes, respectively. The changes were minimal with increased additions of liquorice. Increasing both temperature and zinc concentration caused a depolarization in the zinc deposition reaction. However, the latter improves the coverage and contiguity of the zinc nucleation while the former had a reverse effect.

The orientation and morphology of the zinc deposits obtained at 600 $\mathrm{mA\,cm^{-2}}$ for 5 min were also similarly affected by temperature, zinc and liquorice concentration. The change of orientation of the zinc deposits can be correlated with the polarization data. In general, the predominant orientation shifted to (1 1 0) with increasing polarization.

Overall, it appears that cyclic voltammetry can be used to monitor the active concentration of liquorice, or similar polarizing additives, in zinc electrolyte. By comparing the polarization curve of the unknown plant electrolyte with those generated from electrolytes containing known liquorice concentrations at a fixed temperature and zinc concentration, a good indication of additive content can be obtained.

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