

# Effects of 2-picoline on zinc electrowinning from acidic sulfate electrolyte

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The behaviour of 2-picoline with and without antimony during electrowinning of zinc from acidic sulfate solutions was studied and was compared with that of gum arabic which is commonly used in industry as a levelling agent. The effects of these additives on current efficiency, power consumption, deposit quality, polarization behaviour, crystallographic orientation and surface morphology were determined. The addition of 2-picoline reduced current efficiency, increased power consumption and lowered the surface quality of electrowon zinc. Addition of antimony increased current efficiency, reduced power consumption and produced improved surface morphology and crystal orientations, (101) (112) (102) (103) (114) over a wide range of their combinations.

## 1. Introduction

The major problems encountered in the electrowinning of zinc from acidic sulfate electrolytes are (i) achieving high current efficiency, (ii) operating at high current density, and (iii) producing a levelled deposit. These problems arise mainly from the contamination of the zinc electrolyte by metallic impurities. In spite of rigorous and costly purification steps, these impurities enter the zinc cell house at either ppm or ppb levels. This lowers current efficiency by increasing the rate of hydrogen evolution and also lowers the quality of the cathode deposit. These effects are enhanced at higher current densities. Organic additives, in particular glues, are used to promote deposit growth and to minimize the adverse effects due to these metallic impurities. Nevertheless the operating current density in the zinc industry is normally limited to about 300–600 A m<sup>-2</sup>. A considerable saving of capital investment together with reductions in operating costs would result if the operating current density could be increased whilst maintaining high current efficiency and cathode quality.

At present, 80% of the total energy requirement in zinc production is consumed in the cell house. This suggests it is useful to investigate alternative additives which may permit higher impurity levels in the electrolyte and higher current density whilst maintaining current efficiency and deposit quality.

A number of organic compounds [1–11] appear to give better performance than the traditional glues. Piron *et al.* [11] have studied the effect of 2-butyne-1, 4-diol and shown its beneficial effect on improving current efficiency. MacKinnon and coworkers have tested [12–14] a number of organic compounds and

reported that tetrabutylammonium chloride (TBACl) improved surface morphology and current efficiency. Fray and Thomas [15] claimed they could operate at a current density of 2000 A m<sup>-2</sup> using TBACl. Recently, Honsy [16] investigated the use of nonyl-phenol oxyethylene as a surfactant. Karavastev *et al.* [17, 18] suggested a combination of surfactants: nonyl-phenolpolyethyleneglycol, dinaphthylmethane-4,4'-disulfonic acid and polyethylene glycol with which they could operate at 1000 A m<sup>-2</sup> using a zinc electrolyte containing impurities at higher level than usual.

Pyridine and its derivatives act as corrosion inhibitors [19, 20] and as levelling agents in metal plating [21, 22]. These compounds are protonated (cationic) in acid solution [23] and are adsorbed on active sites of the metal surface [20]. The introduction of a methyl group (–CH<sub>3</sub>) onto the pyridine ring (picolines) has a marked effect on the inhibition efficiency of pyridine. The present study was undertaken to obtain basic information on the effects of 2-picoline on the current efficiency, power consumption, surface deposit quality and morphology, and polarization behaviour for zinc deposition from an acidic sulfate electrolyte. The results were compared with data for gum arabic which is widely used in the zinc industry as a levelling agent.

## 2. Experimental details

### 2.1. Apparatus and material

The electrolysis cell used for the galvanostatic experiments was of 250 cm<sup>3</sup> capacity of conventional design with a polypropylene lid provided with slots to accommodate the electrodes. 99.9% pure aluminium and

platinum sheets were used as the cathode and anode, respectively. The working cathode area was  $10\text{ cm}^2$ .

The zinc electrolyte was prepared from reagent grade  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (AR, Ajax, Australia) and  $\text{H}_2\text{SO}_4$  (AR, Sigma, USA). 2-picoline and potassium antimony tartrate used were also of reagent grade. Gum arabic was procured from Hindustan Zinc Ltd, Udaipur, India. All the solutions were prepared with distilled Millipore Milli-Q water.

## 2.2. Electrolysis

All the electrowinning experiments were conducted for 2 h at a current density of  $400\text{ A m}^{-2}$  and at  $25 \pm 1^\circ\text{C}$ . The electrolyte solution contained  $55\text{ g dm}^{-3}$  zinc and  $150\text{ g dm}^{-3}$  sulfuric acid. The additives and antimony additions were made as aliquots from their respective stock solutions. After electrolysis, the cathode was removed from the cell, thoroughly washed with water and acetone and finally dried in an oven at  $60^\circ\text{C}$  under nitrogen atmosphere. The cathodic current efficiency was calculated from the cathode weight. Occasional duplicates indicated that the experimental reproducibility was  $\pm 0.5\%$  (absolute) of the current efficiency.

## 2.3. Deposit examination

Photographs of the deposit surface were taken using a stereomicroscope to examine their quality and appearance. A Philips PW 1050 X-ray diffractometer was used to examine sections of the deposits by X-ray diffraction (XRD) to determine their orientation relative to the ASTM standard for zinc powder. The surface morphology of the deposit was examined by scanning electron microscopy (SEM) and scanning tunnelling microscopy (STM). The SEMs were obtained by using a Philips SE 101B microscope and the STMs were obtained through a Park Scientific universal model scanning tunnelling microscope.

## 2.4. Cyclic voltammetry

Cyclic voltammetry experiments were conducted at  $25^\circ\text{C}$  to determine the polarization characteristics of zinc deposition in the presence of additives and their combinations with Sb. A rotating disc apparatus and cell of standard design were used for these experiments. The polarization experiments were carried out using various substrates like Al (3 mm dia.), Au (3 mm dia.), Pt (5 mm dia.) and glassy carbon (3 mm dia.) as cathodes, a Pt counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

The working electrodes were prepared by wet polishing (at 150 rpm): Al on 4000 carbide paper, Au on 1200 carbide paper, Pt on 2400 carbide paper and glassy carbon on 800 carbide paper. The electrodes were then washed thoroughly with deionized water, acetone, distilled water and finally dried with filter paper. The freshly prepared electrode was then

transferred into the cell containing zinc electrolyte, under pure nitrogen sparging. The electrode was kept immersed for 10 min before the cycle started.

A PAR (Princeton Applied Research, NJ) 175 universal programmer was used to drive a PAR 173 potentiostat. The cathodic potentials were cycled between  $-0.7$  and  $-1.3\text{ V vs SCE}$  for Al,  $-0.5$  and  $-1.3\text{ V vs SCE}$  for Au,  $-0.2$  and  $-1.3\text{ V vs SCE}$  for Pt and  $-0.5$  and  $-1.2\text{ V vs SCE}$  for glassy carbon electrodes at a potential sweep rate of  $50\text{ mV s}^{-1}$  and at 2000 rpm. The cyclic voltammograms were recorded as I vs E plots on a Bryans X-Y recorder. All the cyclic voltammetry tests were conducted with  $200\text{ cm}^3$  of zinc electrolyte containing  $\text{Zn } 55\text{ g dm}^{-3}$  and  $\text{H}_2\text{SO}_4 150\text{ g dm}^{-3}$ .

## 3. Results and discussion

### 3.1. Current efficiency

The effect of 2-picoline on current efficiency and power consumption during zinc deposition was studied in the concentration range  $0\text{--}40\text{ mg dm}^{-3}$  (Table 1). Also shown for comparison in Table 1 are the results for gum arabic. At low concentrations of 2-picoline ( $\leq 5\text{ mg dm}^{-3}$ ) the current efficiency decreased by about 6%. At higher concentrations (10 or  $20\text{ mg dm}^{-3}$ ), the current efficiency increased by about 3% but fell drastically at  $40\text{ mg dm}^{-3}$ . For gum arabic, the current efficiency dropped by only 2–3% up to  $10\text{ mg dm}^{-3}$  but it decreased drastically at  $20\text{ mg dm}^{-3}$ . Drops in current efficiency during zinc deposition on addition of surface active agents like glue [24, 25], gelatin [26], tetraalkylammonium salts [26] and nonyl-phenol oxyethylene [16] are well documented and have been attributed [19] to surface coverage by a strongly adsorbed layer of these additives. As 2-picoline is protonated (cationic) in acid solution [23] it is likely to be strongly adsorbed at the cathode surface. It has been suggested [16] that such adsorption increases the interfacial viscosity which leads to a decrease in the diffusivity of zinc ions and hence, the mass transfer and zinc deposition rate. As the evolution of hydrogen, the major side reaction during zinc deposition from acidic sulfate solutions, is chemically controlled, it is unlikely to be affected to

Table 1. Effect of additives on current efficiency and power consumption

Concentration / $\text{mg dm}^{-3}$	Additives			
	2-picoline		Gum arabic	
	CE/%	Power/ $\text{kWh t}^{-1}$	CE/%	Power/ $\text{kWh t}^{-1}$
0	89.6	2891	89.6	2891
1.0	83.7	3150	—	—
2.5	83.8	3142	87.9	3046
5.0	82.5	3211	86.1	3043
10.0	86.4	3031	86.2	3104
20.0	85.3	3059	72.7	3615
40.0	78.4	3411	74.5	3537
40 + 0.04 Sb	90.7	2928	67.8	3870

the same extent and thus there is a decrease in the current efficiency with respect to zinc deposition.

There have been numerous studies [27–33] on the effects of antimony ions in zinc electrowinning. Antimony has long been recognized [34, 35] as one of the most deleterious solution impurities with respect to coulombic efficiency. However, it is also well known [25, 32, 36] that its addition in combination with glue gives rise to optimum coulombic efficiency and the preferred morphology. We investigated this effect for 2-picoline and compared the results with gum arabic (Table 1). When  $0.04 \text{ mg dm}^{-3}$  of Sb was added to zinc electrolyte containing  $40 \text{ mg dm}^{-3}$  each of 2-picoline or gum arabic, the current efficiency, in the case of 2-picoline increased from 78 to 90%, with a fall in power consumption from 3411 to  $2928 \text{ kWh t}^{-1}$  of Zn. On the other hand, for gum arabic the current efficiency fell from 74 to 67% causing an increase in power consumption from 3537 to  $3870 \text{ kWh t}^{-1}$  of Zn (Table 1). The unexpected decrease in current efficiency in the presence of gum arabic is probably due to gum arabic/Sb concentrations not being optimized. The increase in the current efficiency for the 2-picoline case may be explained as follows. During zinc electrowinning from acidic sulfate solutions there is a strong interaction between  $\text{H}^+$  and  $\text{Zn}^{2+}$ . Wiart [37] explained this in terms of a model based on a competition between the autocatalytic production of adsorbed intermediate,  $\text{Zn}_{\text{ads}}^+$  ( $\text{Zn}^{2+} + \text{Zn}_{\text{ads}}^+ + \text{e}^- = 2\text{Zn}_{\text{ads}}^+$ ) and the adsorption of  $\text{H}_{\text{ads}}$ , which acts primarily as an inhibitor. When Sb is present, it interferes with the hydrogen adsorption by forming a volatile hydride in the double layer [28, 38] thus, preventing  $\text{H}_{\text{ads}}$  from acting as an inhibitor for zinc deposition. Since combination of 2-picoline and Sb yielded encouraging results, a detailed investigation on their combination was made (Table 2). The results indicate that the current efficiency was maximum and the power consumption was minimum with  $0.04 \text{ mg dm}^{-3}$  Sb. Table 2 also shows that at an Sb concentration of  $0.04 \text{ mg dm}^{-3}$  the maximum current efficiency and minimum power consumption were obtained with  $20 \text{ mg dm}^{-3}$  of 2-picoline.

### 3.2. Surface quality

Surface active agents not only affect the current

Table 2. Effect of different combinations of 2-picoline and Sb on current efficiency and power consumption

(A) Variation of [Sb] at $40 \text{ mg dm}^{-3}$ 2-picoline			(B) Variation of [2-picoline] at $0.04 \text{ mg dm}^{-3}$ Sb		
[Sb] / $\text{mg dm}^{-3}$	CE /%	Power / $\text{kW g t}^{-1}$	[2-picoline] / $\text{mg dm}^{-3}$	CE /%	Power / $\text{kW h t}^{-1}$
0	78.4	3411	0	89.6	2891
0.02	87.6	3020	10	89.3	2913
0.04	90.7	2928	20	91.1	2877
0.08	81.1	3978	40	90.7	2928

efficiency but also cause significant changes in surface quality. The zinc deposits obtained with varying concentrations of 2-picoline and gum arabic showed marked changes in the surface quality. It was found that the smoothness of the zinc deposit increased up to  $10 \text{ mg dm}^{-3}$  2-picoline but decreased at higher concentrations. Addition of up to  $5 \text{ mg dm}^{-3}$  gum arabic resulted in smoother deposits compared with that from addition-free electrolyte but at  $10 \text{ mg dm}^{-3}$  and above, the surface roughened progressively, becoming nodular above  $20 \text{ mg dm}^{-3}$ . The combination of Sb with 2-picoline caused significant improvement in surface levelling. Very flat zinc deposits could be obtained with  $0.04\text{--}0.08 \text{ mg dm}^{-3}$  Sb and  $20\text{--}40 \text{ mg dm}^{-3}$  of 2-picoline. Addition of  $0.04 \text{ mg dm}^{-3}$  of Sb to  $40 \text{ mg dm}^{-3}$  of gum arabic, on the other hand, caused the surface to be more nodular. Some typical photographs of zinc deposits obtained from addition-free electrolyte, as well as electrolyte containing additive alone and in combination with Sb, are shown in Fig. 1.

### 3.3. Polarization behaviour

Polarization curves are very sensitive to the experimental conditions, especially to trace electrolyte constituents [39]. In the present investigation, the polarization behaviour of zinc electrolyte containing 2-picoline was examined using different substrate cathodes and compared with gum arabic. The results are given in Figs 2 and 3.

3.3.1. Aluminium substrates. Figure 2(a) shows the effects of 2-picoline and 2-picoline together with Sb on the cyclic voltammograms of zinc. The cyclic voltammetric scans on the aluminium electrode were initiated at  $-0.7 \text{ V}$  vs SCE (point 'A' in Fig. 2(a)) and first swept in the cathodic direction. Negligible current flowed through the circuit until the point 'B' ( $-1.2 \text{ V}$  vs SCE), known as the decomposition potential, where the current increased sharply due to the zinc electrodeposition. The potential scan was reversed at 'C' ( $-1.3 \text{ V}$  vs SCE). The crossover from cathodic to anodic current corresponding to zinc dissolution occurred at the potential shown as 'D' (crossover potential) in Fig. 2(a). The potential difference between the points B and D is a measure of the activation overpotential for zinc deposition on the aluminium substrate. Addition of 20 or  $40 \text{ mg dm}^{-3}$  of 2-picoline did not change the activation overpotential (i.e., B–D) but there was a decrease in the cathodic and anodic peak currents on addition of 2-picoline (Fig. 2(a)). The current on the descending branch of the loop (C–D) was higher than on the ascending branch (B–C). The cathodic overpotential in this region is associated essentially with the zinc deposition on to freshly deposited zinc and is termed the plating overpotential [40]. It appears from Fig. 2(a) that the plating overpotential was not sensitive to the presence of 2-picoline. Further, the cross-over potential (Fig. 2(a)) was also

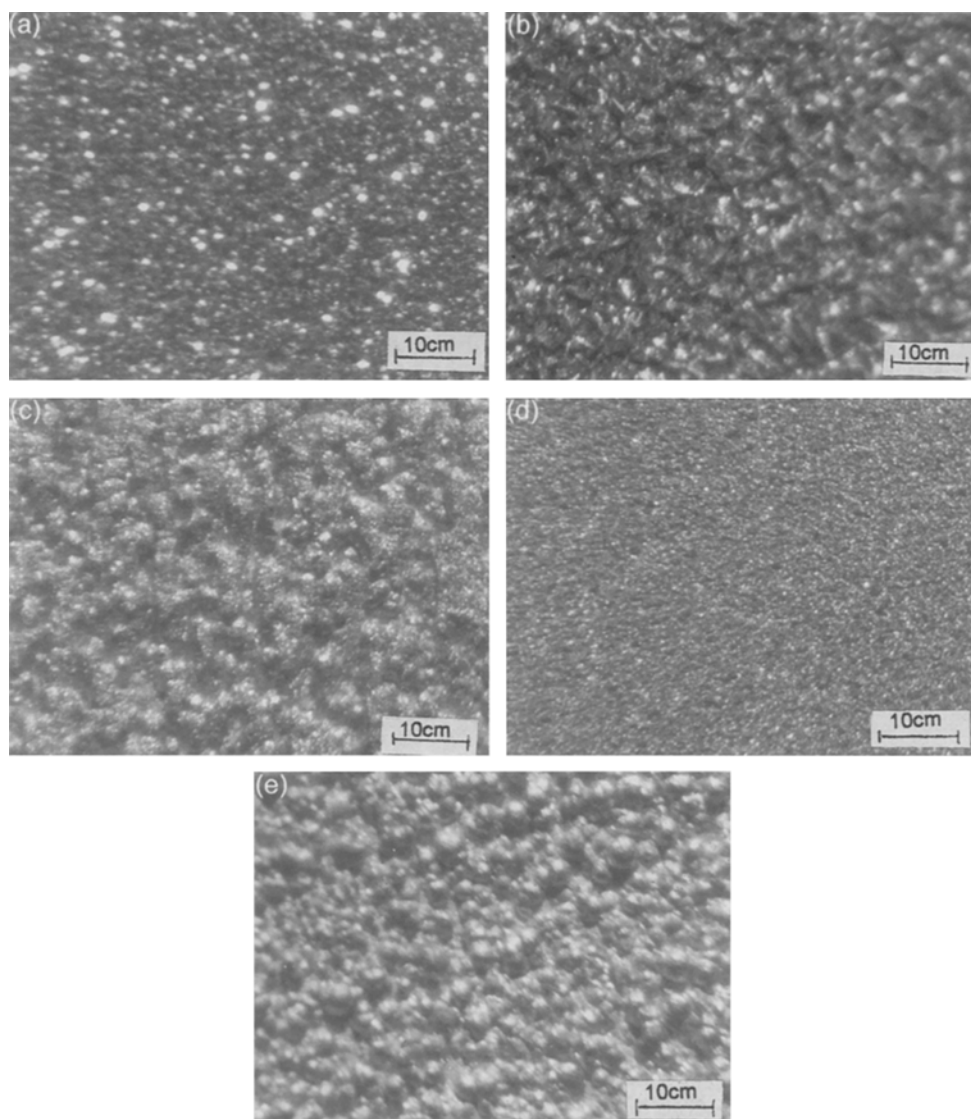


Fig. 1. Photograph of zinc deposits from solutions containing different additives in the presence and absence of Sb. (a) No addition, (b) 2-picoline  $40 \text{ mg dm}^{-3}$ , (c) gum arabic  $40 \text{ mg dm}^{-3}$ , (d) 2-picoline  $40 \text{ mg dm}^{-3} + \text{Sb } 0.04 \text{ mg dm}^{-3}$ , and (e) gum arabic  $40 \text{ mg dm}^{-3} + \text{Sb } 0.04 \text{ mg dm}^{-3}$ .

unaffected by the presence of 2-picoline which is consistent with that observed by MacKinnon *et al.* [12].

It can be seen in Fig. 2(a) that the addition of  $0.04 \text{ mg dm}^{-3}$  of Sb along with 2-picoline strongly influences the cyclic voltammograms. A broad peak at 'F' appears in the cathodic portion of the curve. This may be due to a difference in the course of the zinc deposition reaction on the aluminium substrate. Initially zinc may deposit simultaneously with Sb and hydrogen evolution. After surface coverage by Sb is completed the reaction path is altered because of the interference of Sb with the hydrogen evolution reaction [28, 38]. Increased peak current (voltammogram 3) and higher current efficiency is observed in the presence of Sb than with 2-picoline alone (Tables 1 and 2). Addition of Sb also caused a significant decrease in the activation overpotential, as can be seen from the Fig. 2(a). Figure 2(b) shows the effects of gum arabic and gum arabic together with Sb on the cyclic voltammograms. The voltammograms 1 and 2 in Fig. 2(b) were similar to those of 1 and 2 in

Fig. 2(a). However, voltammogram 3, with added Sb, differed significantly from the corresponding one in Fig. 2(a) with the portion F–C missing.

**3.3.2. Gold substrates.** The effects of 2-picoline and gum arabic on the cyclic voltammograms of zinc were also investigated using gold substrates (Fig. 3(a)). Since the overpotential of hydrogen evolution on gold is low, a peak corresponding to  $\text{H}^+$  reduction (shown as 1, 2, 3 and 4) appears prior to the zinc electrodeposition at more negative potentials (shown as 1a and 2a–4a in Fig. 3(a)). Once zinc deposition started, the voltammogram looked similar to that with the aluminium substrate (Fig. 2). Similar observations have been made by Biegler [41]. At a 2-picoline concentration of  $10 \text{ mg dm}^{-3}$  both peaks shifted towards more –ve potentials and the peak currents decreased (Fig. 3(a)). Similar results were obtained for solution containing  $10\text{--}40 \text{ mg dm}^{-3}$  of 2-picoline. This finding suggests that 2-picoline affects both the hydrogen evolution and zinc deposition reactions. The results on the polarization

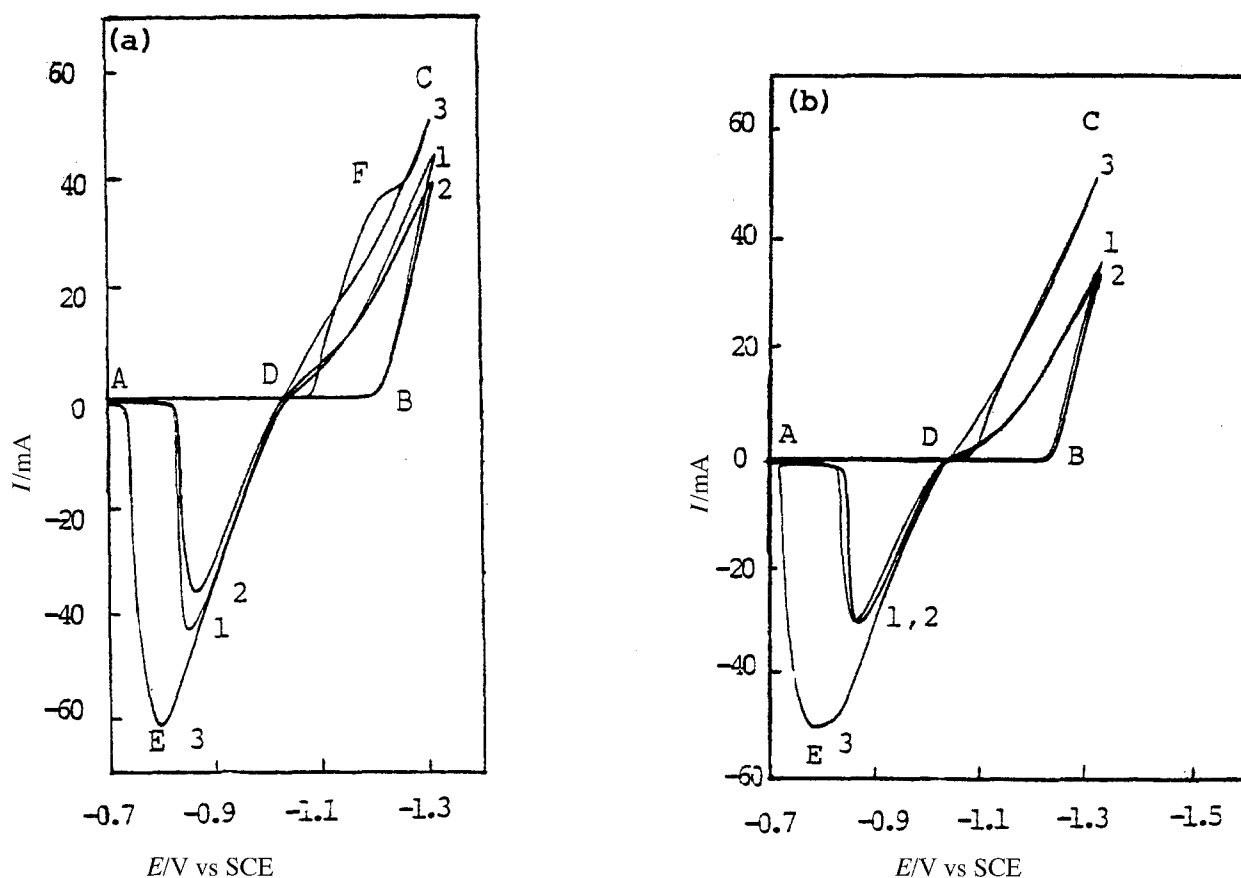


Fig. 2. Voltammograms on aluminium electrode for zinc electrolyte. (a) (1) No addition, (2) 2-picoline  $40 \text{ mg dm}^{-3}$ , and (3) 2-picoline  $40 \text{ mg dm}^{-3} + \text{Sb } 0.04 \text{ mg dm}^{-3}$ . (b) (1) No addition, (2) gum arabic  $40 \text{ mg dm}^{-3}$  and (3) gum arabic  $40 \text{ mg dm}^{-3} + \text{Sb } 0.04 \text{ mg dm}^{-3}$ .

behaviour of zinc in the presence of gum arabic were similar with 2-picoline although the changes were somewhat smaller.

**3.3.3. Platinum substrates.** The cyclic voltammograms on platinum substrates in the pure electrolyte were similar to those on gold with two current 'peaks'. However, the behaviour in the presence of  $40 \text{ mg dm}^{-3}$  2-picoline was completely different, showing an increase in the peak currents for both hydrogen and zinc discharges. Virtually identical results were obtained at the other 2-picoline concentrations and also for gum arabic over the same concentration range, although there was a reduction in peak current and a negative shift in cathode potential.

**3.3.4. Glassy carbon substrate.** Glassy carbon has been reported [41] to be a good material for studying zinc deposition because of its higher hydrogen overvoltage and its reproducibility. Cyclic voltammograms in the presence of 2-picoline and gum arabic are similar to those obtained on aluminium (Fig. 2). On increasing the 2-picoline concentration to  $10 \text{ mg dm}^{-3}$  the peak currents decreased steadily but when the concentration was raised to  $20 \text{ mg dm}^{-3}$  or above, it slowly increased. These changes were reflected in the surface quality of the zinc deposit which improved up to  $10 \text{ mg dm}^{-3}$  of 2-picoline and thereafter deteriorated. Broadly, similar results were found in the presence of gum arabic.

The effect of electrode rotation in the presence of  $40 \text{ mg dm}^{-3}$  of 2-picoline was studied. The relationship between the peak current  $i_p$  and the square root of the rotation speed  $\omega$  is shown in Fig. 3(b). The plot of  $i_p$  against  $\omega^{1/2}$  is a straight line indicating the  $\text{Zn}^{2+}$  reduction is diffusion controlled, but does not go through zero on the current axis. This is consistent with the electrodeposition of zinc being accompanied by the coreduction of  $\text{H}^+$  which is well known to be a chemical controlled electrode reaction. The intercept of the y-axis is a measure of the rate of  $\text{H}^+$  reduction which accompanies the zinc deposition. The important result of this experiment, however, is that the presence of 2-picoline does not prevent the zinc electrodeposition from being diffusion controlled (since  $i_p \propto \omega^{1/2}$ ). This effect is similar to that reported by Palacios *et al.* [42] for TBAC1, and is consistent with the adsorptive nature of the process.

#### 3.4. Deposit morphology and orientation

The morphologies and crystallographic orientations of the zinc deposits were determined by scanning electron microscopy, scanning tunnelling microscopy and X-ray diffraction. The SEM photographs are shown in Figs 4 and 5 and X-ray results are given in Tables 3 and 4, respectively.

Figure 4(a) shows the typical morphology of a zinc deposit obtained from the addition-free electrolyte. The hexagonal platelets had moderate size and were randomly oriented. The morphology corresponded

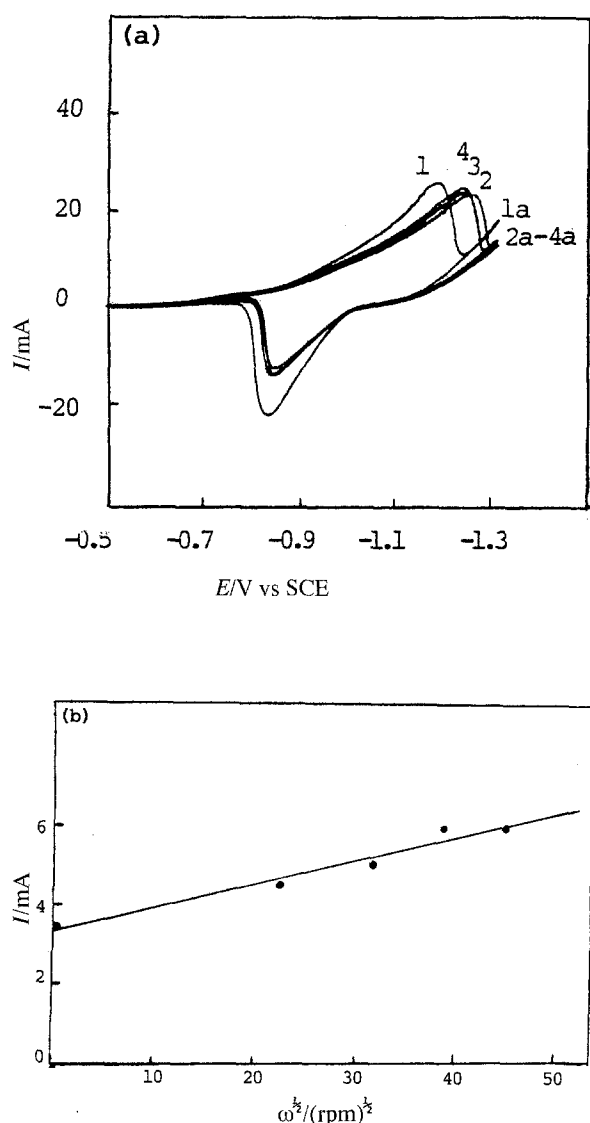


Fig. 3. (a) Voltammograms on gold electrode for zinc electrolyte. (1) No addition, (2) 2-picoline 10 mg dm<sup>-3</sup>, (3) 2-picoline 20 mg dm<sup>-3</sup> and (4) 2-picoline 40 mg dm<sup>-3</sup>. (b) Effect of electrode (glassy carbon) rotation on peak current  $i_p$  in the presence of 40 mg dm<sup>-3</sup> 2-picoline.

to the preferred crystal planes in the order (103) (102) (114) (101) (112). Sato [43] reported the preferred plane to be (114) in the absence of organic additives except where H<sub>2</sub>SO<sub>4</sub>/Zn ratio is 5 or 10. In such cases (101) orientation was obtained. The order of preferred crystal planes reported by Mackinnon and Brannen

[32] for addition-free electrolyte was (102) (112) (114) (101) (103) and for a synthetic electrolyte (114) (112) (102) (103) (101). They also reported a similar morphology to that of O'Keefe *et al.* [25], who observed the preferred planes as (101) (102) (103) for addition-free, as well as balanced, electrolyte.

The addition of 5 mg dm<sup>-3</sup> of 2-picoline abruptly changed the crystallographic orientations of zinc deposit with the growth of all crystal planes being promoted except (002). This change was also marked by a decrease in current efficiency, an improvement in surface quality and a reduction in peak current. Increase in 2-picoline concentration to 10 mg dm<sup>-3</sup> favoured the growth of (103) and (002) planes and the order of preferred planes was (103) (002) (102) (101) (100). This produced a deposit morphology where zinc platelets were basal (002) and perpendicular (100) to the aluminium substrate. When the 2-picoline concentration was further raised to 40 mg dm<sup>-3</sup> the degree of (101) and (100) growth increased and resulted in an entirely different morphology (Fig. 4(b)). The zinc platelet size remained almost unchanged unlike the case of excess glue [30]. The zinc platelets were either inclined to the aluminium substrate or perpendicular, corresponding to preferred crystal planes (101) (100) (103) (112) (102). These changes in surface morphology and crystallographic orientation were reflected in a significant fall in current efficiency and a deterioration of surface quality.

The effects of the addition of 2.5, 10 and 40 mg dm<sup>-3</sup> of gum arabic to the zinc electrolyte on surface morphology of cathode zinc were studied. The crystallographic orientations are given in Table 3. Addition of 2.5 mg dm<sup>-3</sup> gum arabic resulted in reduction in crystallite size similar to that reported by Fosnacht and O'Keefe [30]. The zinc platelets were close packed and produced a cluster type morphology. The order of preferred planes changed from (103) (102) (114) (101) (112) to (101) (102) (103) (112) (114) at low gum arabic concentrations. An increase in the gum arabic concentration further decreased the crystallite size (Fig. 4(c)) but the order of preferred crystal planes remained almost unchanged. Preferred orientations (101) (102) (103) were also obtained by O'Keefe *et al.* [25] with addition-free and balanced zinc electrolyte.

Table 3. Crystallographic orientations of cathode zinc with different additives

Additive	[Additive] mg dm <sup>-3</sup>	Crystallographic orientations, peak heights/cm						
		(101)	(102)	(103)	(002)	(100)	(112)	(114)
2-picoline	0	3.6	6.0	10.7	2.1	nil	2.8	4.6
	5	24.5	14.2	15.2	1.9	8.4	7.0	6.3
	10	7.6	7.7	17.8	9.0	7.6	3.0	7.2
	20	22.7	-	10.8	2.5	10.5	6.4	4.3
	40	28.0	3.1	7.6	nil	17.4	7.0	1.7
Gum arabic	5	19.5	13.4	11.7	1.7	2.7	10.0	6.7
	10	14.3	8.4	8.4	1.2	3.1	7.1	4.7
	20	35.0	13.2	10.1	10.0	4.4	5.9	3.5
	40	15.2	6.4	6.1	4.7	2.2	4.2	2.6

Table 4. Crystallographic orientations of cathode zinc with different 2-picoline and Sb combinations

[2-picoline] /mg dm <sup>-3</sup>	[Sb] \mg sm <sup>-3</sup>	Crystallographic orientations peak heights/cm						
		(101)	(102)	(103)	(002)	(100)	(112)	(114)
0	0	3.6	6.0	10.7	2.1	nil	2.8	4.6
10	0	7.6	7.7	17.8	9.0	7.6	3.0	7.2
40	0	28.0	3.1	7.6	nil	17.4	7.0	1.7
10	0.04	13.1	7.0	6.4	nil	1.9	11.5	3.2
40	0.02	14.7	9.4	8.5	5.9	1.9	7.2	nil
40	0.04	14.9	7.8	6.3	nil	1.6	9.6	3.4
40	0.08	14.9	8.8	7.6	nil	2.0	9.9	3.3

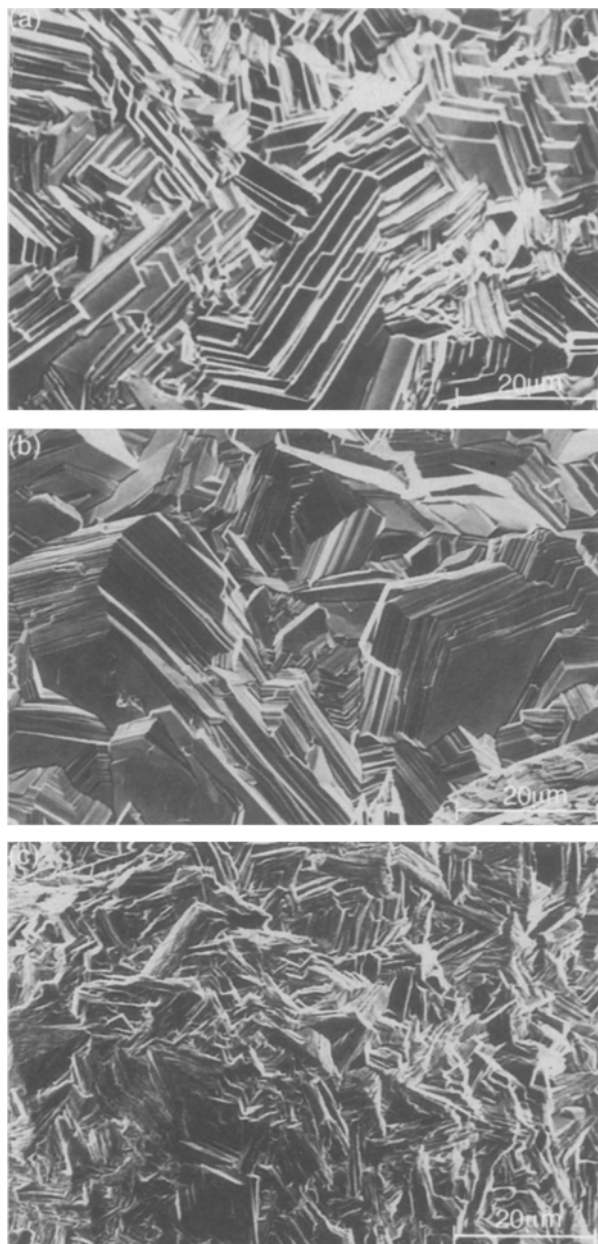


Fig. 4. SEM photograph of zinc deposits from solutions containing different additives. (a) No addition, (b) 2-picoline 40 mg dm<sup>-3</sup> and (c) gum arabic 40 mg dm<sup>-3</sup>.

The effects of various antimony and 2-picoline combinations on surface morphology and crystallographic orientations were investigated. Addition of 0.04 mg dm<sup>-3</sup> of Sb to 10 mg dm<sup>-3</sup> of 2-picoline drastically reduced the zinc platelet size and produced a

random crystallographic orientation (Table 4). The order of the preferred crystal planes changed from (103) (002) (102) (101) (100) (2-picoline alone) to (101) (112) (102) (103) (114) (2-picoline + Sb). Increase in the 2-picoline concentration from 10 to 40 mg dm<sup>-3</sup> (at 0.04 mg dm<sup>-3</sup> Sb) produced similar morphology but with a further reduction in platelet size (Fig. 5(a)). Addition of 0.08 mg dm<sup>-3</sup> of Sb along with 40 mg dm<sup>-3</sup> of 2-picoline resulted in similar morphology but with little increase in zinc platelet size. The order of preferred crystal planes also remained the same. Such changes in deposit morphology and crystallographic orientation on the addition of various combinations of 2-picoline and Sb were reflected in an increase in current efficiency, reduction in power consumption, improvement in surface levelling and a significant change in the cyclic voltammogram as discussed earlier. Figure 5(b) shows the surface morphology of a cathodic zinc obtained on addition of 0.04 mg dm<sup>-3</sup> Sb along with 40 mg dm<sup>-3</sup> of gum arabic to the electrolyte. Addition of Sb caused reduction in platelet size to a fine needle-like structure (Figs 4(c) and 5(b)) corresponding to nodular growth on the surface. This change in morphology was also reflected in surface quality, current efficiency and polarization curves as discussed earlier.

Scanning tunnelling microscopy (STM) was applied to measure the surface levelling effect of 2-picoline. STM images of zinc surface obtained from addition-free electrolyte and electrolyte containing 40 mg dm<sup>-3</sup> of 2-picoline along with 0.04 mg dm<sup>-3</sup> Sb were compared. It was observed that in the former case nucleation and growth of zinc occurred exclusively as the surface imperfections but in the latter case the growth behaviour was markedly altered and lateral spreading of the zinc deposit was favoured. This further confirms 2-picoline as an effective levelling agent in zinc electrowinning.

#### 4. Conclusions

The effects of 2-picoline and gum arabic on the electrowinning of zinc from acidic sulfate electrolyte were as follows:

- (i) Addition of 2-picoline caused a reduction in current efficiency, increase in power consumption, and

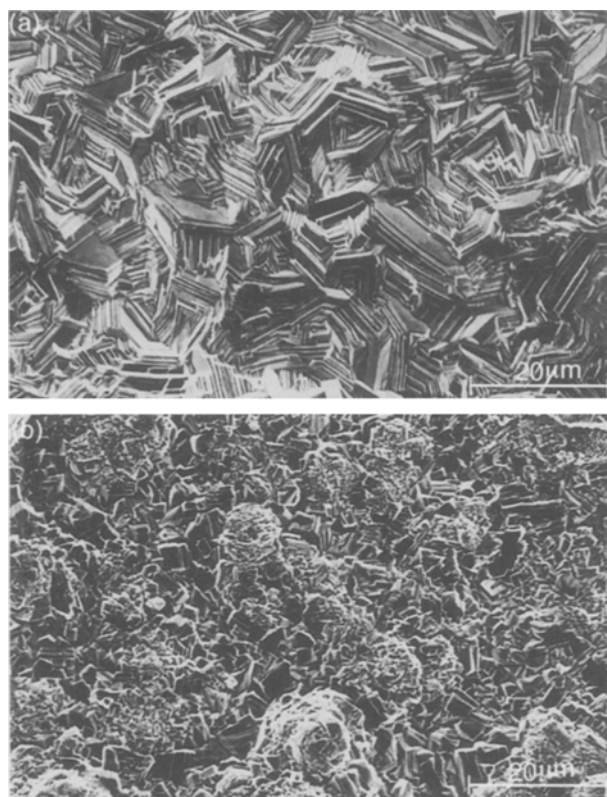


Fig. 5. SEM photograph of zinc deposits from solutions containing different additives with antimony. (a) 2-picoline  $40 \text{ mg dm}^{-3}$  + Sb  $0.04 \text{ mg dm}^{-3}$ . (b) gum arabic  $40 \text{ mg dm}^{-3}$  + Sb  $0.04 \text{ mg dm}^{-3}$ .

modified the surface morphology of the electrodeposited zinc.

(ii) On combination with antimony, 2-picoline produced a smooth surface with increased current efficiency and reduced power consumption (cf. the additive-free electrolyte).

(iii) The polarization behaviour with different substrate cathodes of 2-picoline alone or in combination with antimony were similar to that for gum arabic.

(iv) The 2-picoline and antimony combination produced characteristic zinc morphology with preferred crystal orientations (101) (112) (102) (103) (114).

(v) STM of the zinc surface proved the levelling action of 2-picoline and antimony combinations.

Overall, it may be concluded that 2-picoline in combination with antimony may act as an effective levelling agent for the electrowinning of zinc from acidic sulfate electrolytes.

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