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Evaluation of organic additives as levelling agents for zinc electrowinning from chloride electrolytes

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The effects of various organic additives: Pearl glue, Separan NP10, Percol 140 and tetraalkylammonium chlorides, on zinc deposit morphology and orientation and on the current efficiency and energy requirement for zinc electrowinning from chloride electrolyte have been determined and compared. Tetrabutylammonium chloride (TBACl) was more effective than Pearl glue, Separan NP10 or Percol 140 in smoothing the deposit, refining the grain size and eliminating dendritic growth. TBACl was also the most effective of the tetraalkylammonium chlorides studied. Tetraethylammonium chloride (TEACl) had little effect on the deposit grain size even at concentrations as high as 60 mg dm^{-3}. Tetrapropylammonium chloride (TPrACl) was more effective than TEACl but less effective than TBACl. Small additions (10 mg dm^{-3}) of tetrapentylammonium chloride (TPACl) produced a very fine-grained deposit, but the deposit edges were rougher than in the presence of TBACl.

1. Introduction

Chloride metallurgy using chloride solutions or chlorine gas is currently receiving strong consideration for treating the lower grade, more complex ores from which valuable metals cannot be recovered by conventional processes. One of the drawbacks to the chloride route has been the need for an efficient method for yielding smooth, compact metal deposits from chloride solutions during the electrolysis operation. However, this problem has now been overcome, at least at the laboratory level, and a technique for electrowinning smooth, compact zinc deposits from chloride electrolyte has been described [1]. The solution to the problem, in part, involved finding a suitable additive to aid the levelling of the electrowon zinc deposits.

Organic additives, in particular animal glues, are used in zinc electrowinning from acid sulphate electrolyte to control cathode deposit growth to provide smooth deposits, to control the adverse effects that impurities such as antimony and cobalt have on the current efficiency of zinc deposition, and to assist in acid mist control over the cells [2–5]. The organic additives control deposit growth by inhibiting the formation of dendrites and by producing fine-grained, smoother deposits. Although the precise mechanism by which this is achieved is not known, the following facts have been established:

(a) the additives assume a net positive charge and migrate to the cathode where they are adsorbed;

(b) their actual presence in the deposit is exceedingly small and is difficult to confirm analytically;

(c) columnar deposit growth is eliminated by their presence in the electrolyte;

(d) the composition of the electrolyte tends to alter the electrochemistry of the organic additive.

Reports in the literature indicate that the influence of colloids and surface-active substances on the electrolysis of zinc chloride solutions is less effective than in the sulphate system [6]. Ralston [7] reported that although glue addition to zinc chloride electrolyte produced a smoother deposit, it was not as successful in improving the condition of the cathodes as it was in the sulphate system. Recently, Bressan and Wiart [8] have shown that tetrabutylammonium bromide (NBu_4Br) is effective in inhibiting dendrite formation during zinc deposition from the Leclanché cell electrolyte: 2.67 M NH_4Cl, 0.72 M $ZnCl_2$, pH adjusted to 5.2 with NH_4OH. Previously, Dingle and Damjanovic

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[9] showed that NBu_4Br was effective in supressing dendritic growth and producing compact zinc deposits from alkaline zincate solutions.

An earlier study on the structure of one-hour zinc deposits electrowon from synthetic zinc chloride electrolyte [10] showed that the deposits were characterized by a morphology which featured clusters of large platelets with rounded edges and by a preferred orientation, [002], [103], [105]. The addition of animal glue or tetrabutylammonium chloride (TBACl) resulted in smooth, compact deposits with a [110] preferred orientation. Jaguar C-13 gave a [112] orientation, but Gum Arabic and tetraethylammonium chloride (TEACl) affected only the grain size. The various deposit morphologies and orientations showed some correspondence to changes occurring in the zinc deposition polarization voltages.

The present work was undertaken to evaluate these and other additives on 24-hour zinc deposits electrowon from zinc chloride electrolyte. In addition to glue, TBACl and TEACl, Percol 140, Separan NP10, tetrapropylammonium chloride (TPrACl) and tetrapentylammonium chloride (TPACl) were evaluated.

2. Experimental

2.1. *Electrolysis cell*

Details of the cell design and construction were given in a previous publication [1]. Briefly, the cell consisted of three compartments: two anode compartments which were separated from a central cathode compartment by Dynel cloth diaphragms. The anode compartments were sealed to the atmosphere and the chlorine gas and spent anolyte were withdrawn via glass tubes inserted through the anode seals (Fig. 1). The cathode compartment was open to the atmosphere so that the cathode could be easily removed from the cell to strip the zinc deposit. Vigorous agitation of the electrolyte at the cathode surface was achieved by sparging moist air from the bottom of the cell. Cathodes were cut from 0.4 cm commercial aluminium. An area of 25.3 cm^2 was masked off on each side of the cathode, using electroplating tape (total surface area 50.6 cm^2). The tape also covered the sides of the cathode to minimize edge build-up and to facilitate stripping of the zinc deposit. The dimensionally stable anodes (DSA) were 0.1 cm thick. These anodes extended through a slot in the anode seal and electrical contacts were bolted to the exposed tops of the anodes. Current to the cell was provided by a d.c. rectifier (6–30 amp; 0–25 volts). The cumulative ampere-hours (total coulombs) were recorded using an ampere–time meter.

2.2. *Electrolyte composition*

The electrolyte was prepared from reagent-grade zinc chloride. The cell solution contained 15 g dm^{-3} Zn^{2+} and 0.12 M HCl, and the feed solution

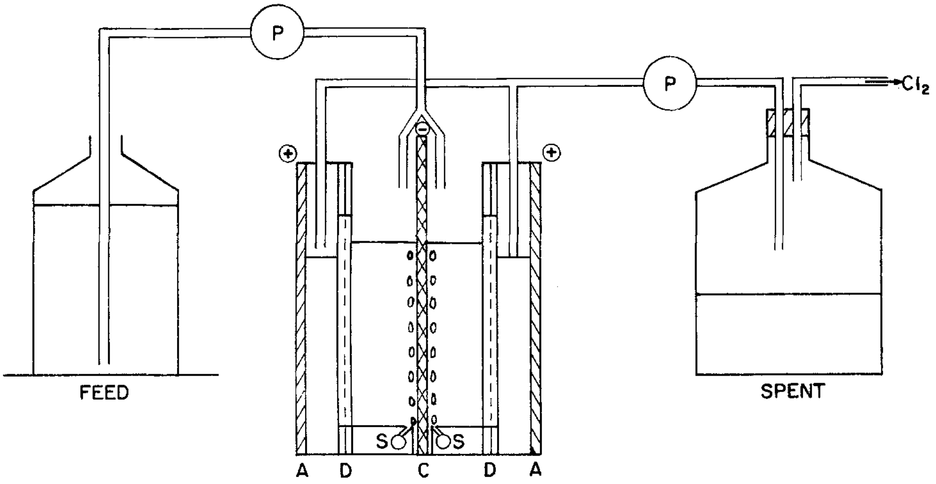


Fig. 1. Electrolysis cell and electrolyte circulation system. A, Anode; C, cathode; D, diaphragm; P, pump; S, sparger.

contained 30 g dm^{-3} Zn^{2+} and 0.12 M HCl. The desired concentration of organic additives in the electrolyte was obtained by adding the appropriate amount of their respective stock solutions.

The following organic additives were used:

(a) Pearl glue, obtained from Cominco Ltd; this is a standard animal glue supplied to Cominco by Croda Polymers Ltd, England. Molecular weight = 50 000.

(b) Separan NP10 (Dow Chemical); a high molecular weight (MW = 1000 000), synthetic polymer formed by the polymerization of acrylamide.

(c) Percol 140 (Allied Colloids); a high molecular weight cationic polyacrylamide.

(d) Tetraalkylammonium chlorides.

2.3. *Experimental procedure*

The electrolysis cell and electrolyte circulation system were set-up as shown schematically in Fig. 1. The cell electrolyte was maintained at 35° C using a thermistor controller and small immersion heater located in the cathode compartment of the cell. Feed solution was supplied to each side of the cathode at a rate of 2.2 cm^3 min^{-1} using a tubing pump. This feed rate was sufficient to maintain the Zn^{2+} concentration in the cell at 15 g dm^{-3} over the duration of the electrolysis. Both the cell and the feed electrolytes contained the appropriate level of addition agent.

A constant head of solution was maintained in the cathode compartment by withdrawing solution and Cl$_2$ from the anode compartments from below the catholyte level, as indicated in Fig. 1. Moist air was continuously sparged over the cathode faces at a rate of ~ 5 dm^3 min^{-1}, via the manifold at the base of the cathode.

Prior to use for the first time, the exposed faces of the aluminium cathode were hand polished, using 600-grit polishing paper. At the end of the electrolysis period, the cathode was pulled from the cell, and the zinc deposit was rinsed with water, stripped, dried and weighed. The surface of the stripped cathode was also rinsed and dried; no additional surface treatment was necessary before it was used in subsequent tests. Samples of anolyte and cathode were analysed for Zn, free acid and total Cl after each test.

2.4. *Electrolysis conditions*

Operating conditions of 323 A m^{-2} and 35° C were used for the experiments. Unless otherwise stated, all electrolysis tests were run for 24 hours.

2.5. *Deposit examination*

Sections of the deposits were examined by X-ray diffraction (XRD) to determine their preferred orientation relative to the ASTM standard for zinc powder and by scanning electron microscopy (SEM) to determine their surface morphology. Deposit cross-sections were examined by optical microscopy (OM) techniques.

2.6. *Current efficiency and energy requirement*

The current efficiency (CE) was calculated from the weight of the zinc deposited and the number of coulombs passed. The energy requirement (ER) was calculated in terms of kW h kg^{-1}, using the average cell voltage recorded during each test and the weight of the zinc deposits.

3. Results and discussion

3.1. *The effect of additives*

A series of 24-hour deposits obtained from zinc chloride electrolytes containing various additives is shown in Fig. 2. The deposit obtained from the addition-free electrolyte was rough and nodular over part of its surface and dendrite formation occurred along the edges (Fig. 2a). The additives, TBACl, Percol 140 and Separan NP10, were effective in producing a deposit with a smooth surface and dendrite-free edges (Figs. 2b, c and e). Pearl glue was less effective in producing a smooth zinc surface and in eliminating dendritic growth at the edges of the deposit (Fig. 2d).

The structural details of the zinc deposits electrowon from the addition-free electrolyte are shown in Fig. 3a. The SEM photomicrograph indicates that the deposit consists of large, poorly defined hexagonal zinc platelets. The deposit also contains pores and voids, as indicated by the OM photomicrograph. A photomicrograph of the cross-section of the zinc deposit electrowon from an electrolyte containing 15 mg dm^{-3} TBACl is

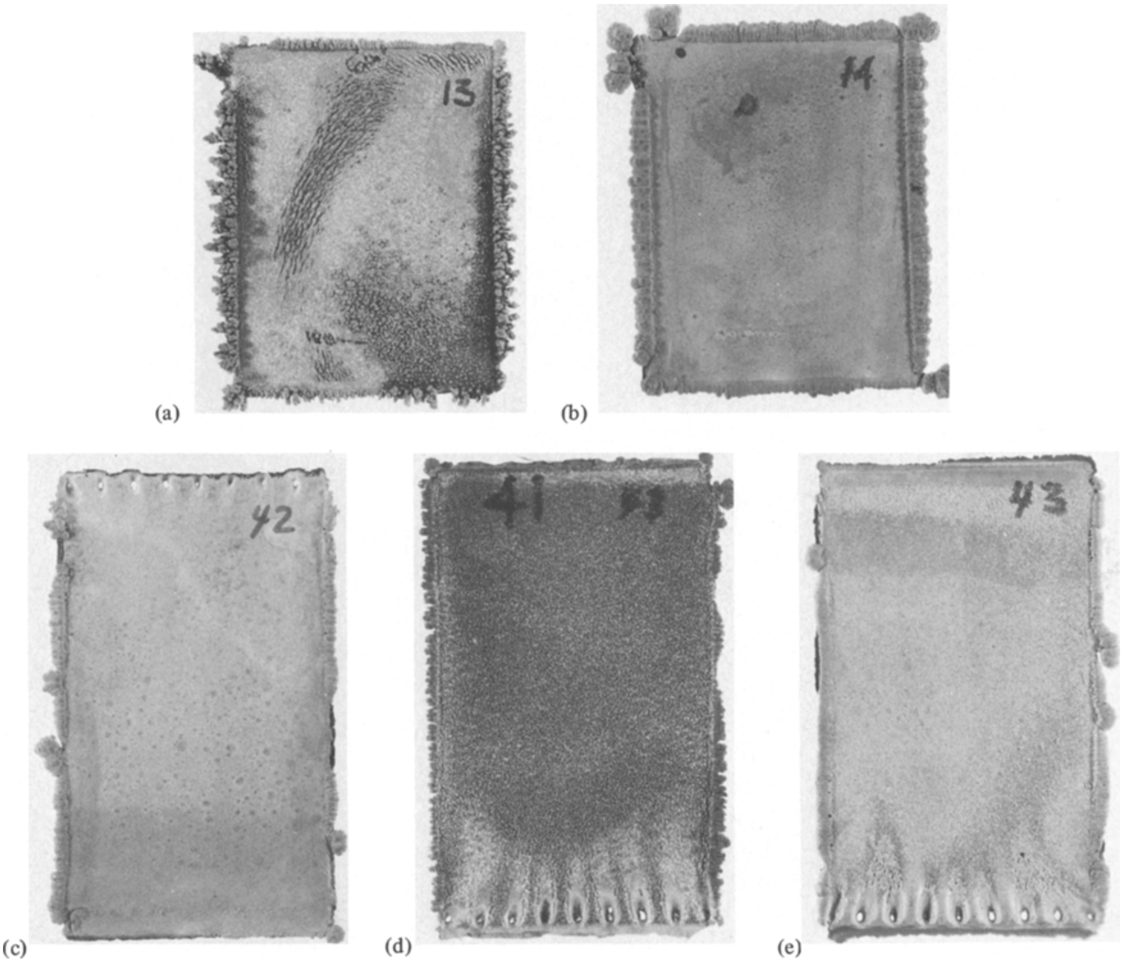


Fig. 2. The effect of various additives on zinc deposits electrowon from chloride electrolyte (magnification 0.2X). (a) No addition, (b) 15 mg dm^{-3} TBACl, (c) 6 mg dm^{-3} Percol, (d) 30 mg dm^{-3} glue, (e) 6 mg dm^{-3} Separan.

shown in Fig. 3b, which indicates the deposit to be compact and even. The deposit morphology obtained in the presence of 15 mg dm^{-3} TBACl is characterized by refined zinc platelets aligned at right angles to the aluminium cathode, resulting in a preferred [110] orientation.

The structural details of the zinc deposits obtained in the presence of the other additives are shown in the series of SEM and OM photomicrographs in Fig. 4. Percol 140 was effective in reducing the deposit grain size, and this resulted in a smooth, compact deposit (Fig. 4a). The deposit consists of fairly distinct hexagonal platelets, aligned at intermediate angles to the Al substrate. This deposit morphology bears a strong resemblance to the characteristic zinc deposit morphology obtained from acid sulphate electrolyte [11].

The presence of Separan NP10 in the zinc chloride electrolyte resulted in poorly defined zinc platelets which were vertically aligned to the Al substrate (Fig. 4b). Although the surface of the deposit appears smooth (Fig. 2e), the cross-section reveals it to be uneven and to contain large voids (Fig. 4b). The deposit electrowon from an electrolyte containing Pearl glue consisted of nodules having a fine grain structure which formed on the surface of the smooth initial deposit layer (Fig. 4c).

In general, TBACl was the most effective addition agent in terms of smoothing the deposit, refining the grain size and eliminating dendritic

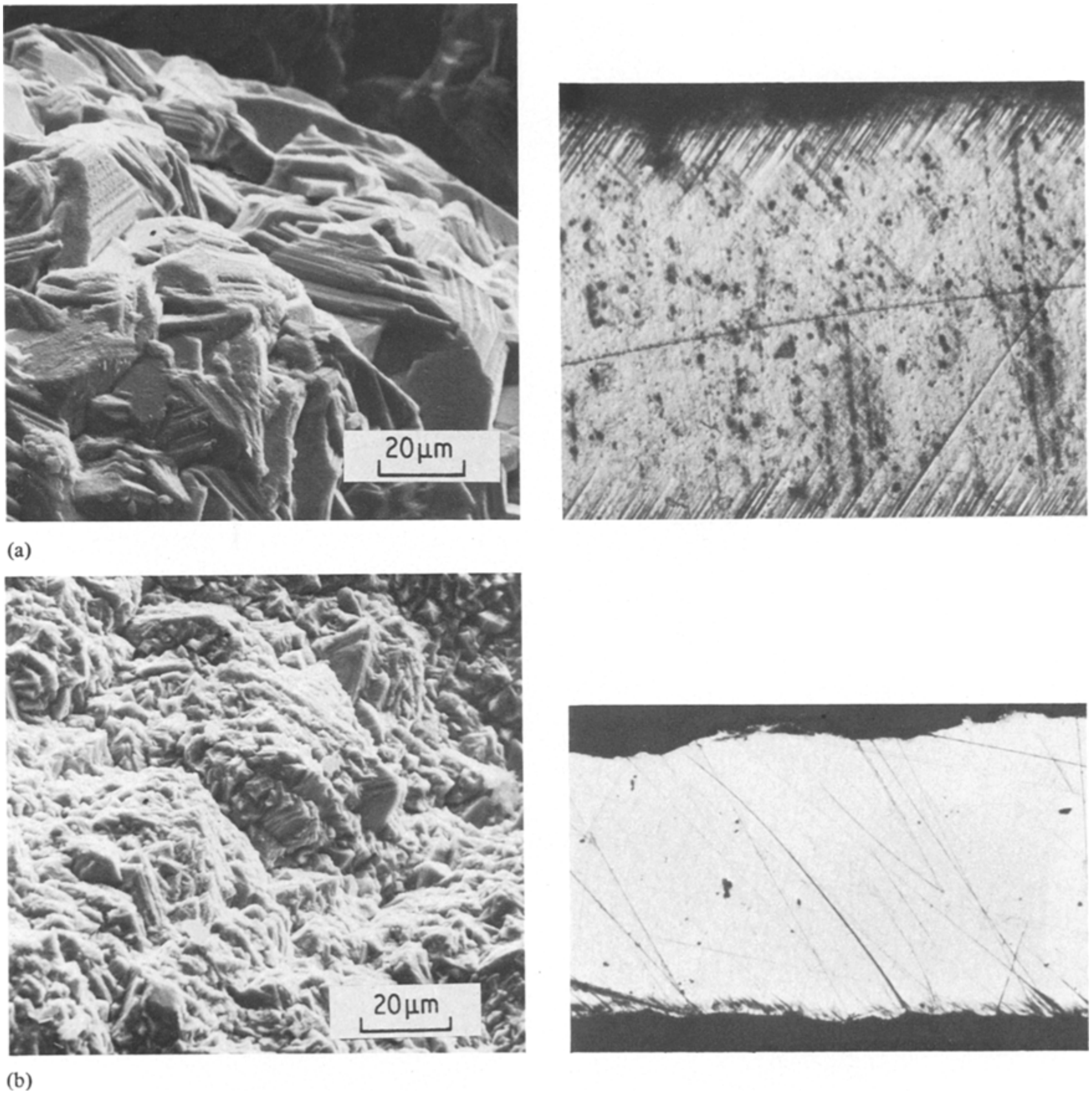


Fig. 3. Zinc deposit structures obtained from (a) addition-free and (b) TBACl-containing (15 mg dm^{-3}) electrolytes (magnification of cross-sections 68×).

edge growth (see Fig. 3b). It had the added advantage of being the least complex of the additives studied and as such would be least likely to form degradation products which might have harmful effects in other parts of a process circuit.

The current efficiency, energy requirement and orientation results obtained for zinc deposits electrowon from zinc chloride electrolytes containing various additives are summarized in Table 1. In all cases the CE was > 90% and the additives generally produced deposits with a predominantly [110] orientation; i.e., the zinc platelets are aligned vertically to the aluminium substrate.

3.2. *The effect of tetraalkylammonium chlorides*

In view of the fact that TBACl was effective in elimating dendritic growth and refining the deposit grain size, it was thought worthwhile to investigate the effect of some of its homologues, TEACl, TPrACl and TPACl, on the structure of the zinc deposits. A series of 24-hour zinc deposits was

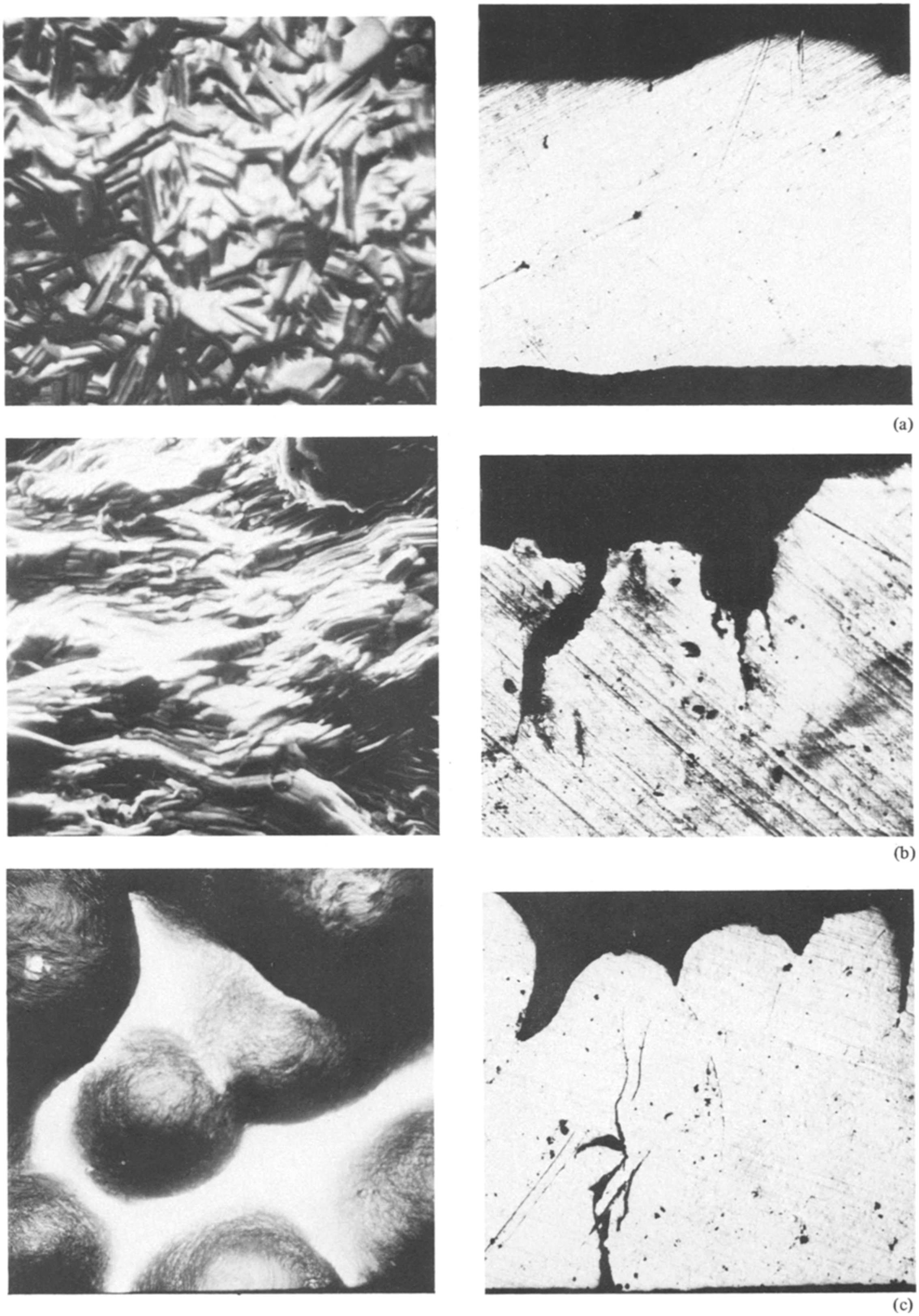


Fig. 4. The effect of various organic additives on the structure of zinc deposits electrowon from chloride electrolyte. (a) 6 mg dm^{-3} Percol 140, (b) 6 mg dm^{-3} Separan NP10, (c) 30 mg dm^{-3} glue. Magnifications: (a) 1300X, (b) 630X, (c) 66X; cross-sections 70X.

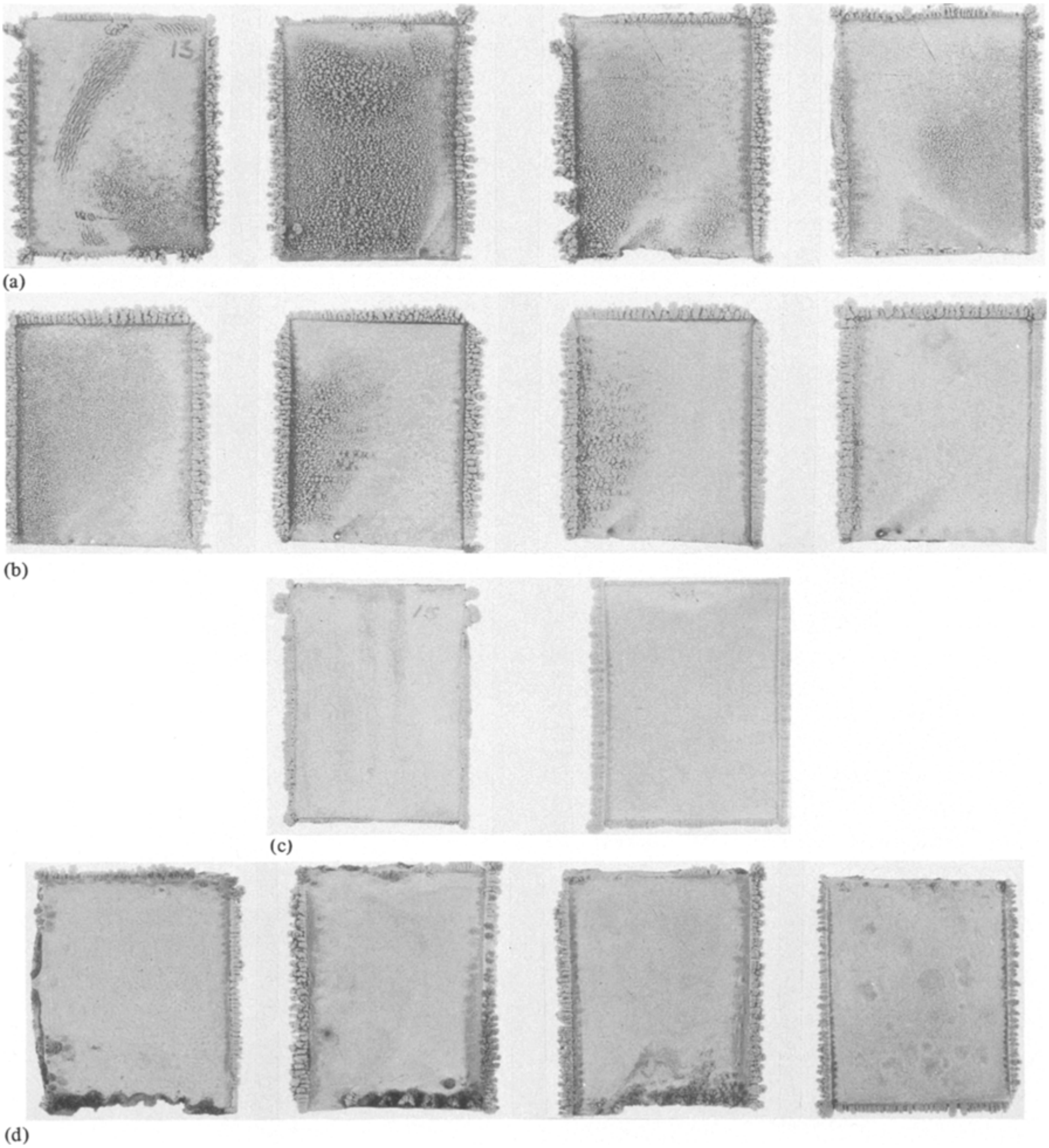


Fig. 5. The effect of various tetraalkylammonium chlorides on zinc deposits electrowon from chloride electrolyte. (a) TEACl; left to right 0, 15, 30 and 60 mg dm^{-3}. (b) TPrACl; 15, 20, 45 and 60 mg dm^{-3}. (c) TBACl; 7.5 and 15 mg dm^{-3}. (d) TPACl; 10, 15, 30 and 45 mg dm^{-3}. Magnification 0.5×.

electrowon from solutions containing various concentrations of these additives and these are shown in Fig. 5. The deposit electrowon from addition-free electrolyte is included with the TEACl series, Fig. 5a, for comparison.

The addition-free deposit exhibited significant edge growth with considerable dendrite formation along the vertical edges. The deposit was coarse and rough over large areas of its surface. The deposit obtained with the addition of 15 mg dm^{-3} TEACl to the electrolyte also featured dendritic edge growth and its surface was considerably rougher than that of the addition-free deposit. At 30 mg dm^{-3} TEACl, the deposit edge growth was still prominent but the surface was smoother in comparison to the deposit obtained for 15 mg dm^{-3} TEACl. At 60 mg dm^{-3} TEACl, both surface roughness and edge growth decreased but the deposit was not comparable to that obtained for lower concentrations of TBACl (Fig. 5c).

The series of deposits electrowon from solutions containing various concentrations of TPrACl is shown in Fig. 5b. The deposit obtained at 15 mg dm^{-3} TPrACl is similar to that obtained at 60 mg dm^{-3} TEACl (see Fig. 5a). The deposit surface is rough with significant edge growth. The edge growth and surface roughness decrease with increasing TPrACl such that the deposit obtained at 60 mg dm^{-3} TPrACl is quite similar to that at 15 mg dm^{-3} TBACl (Fig. 5c). The deposits electrowon from solutions containing TBACl are shown in Fig. 5c. These deposits were very smooth and compact with no significant edge growth. The TPACl series of deposits is shown in Fig. 5d. At 10 mg dm^{-3} TPACl, the deposit was smooth and compact with very little edge growth and was, in

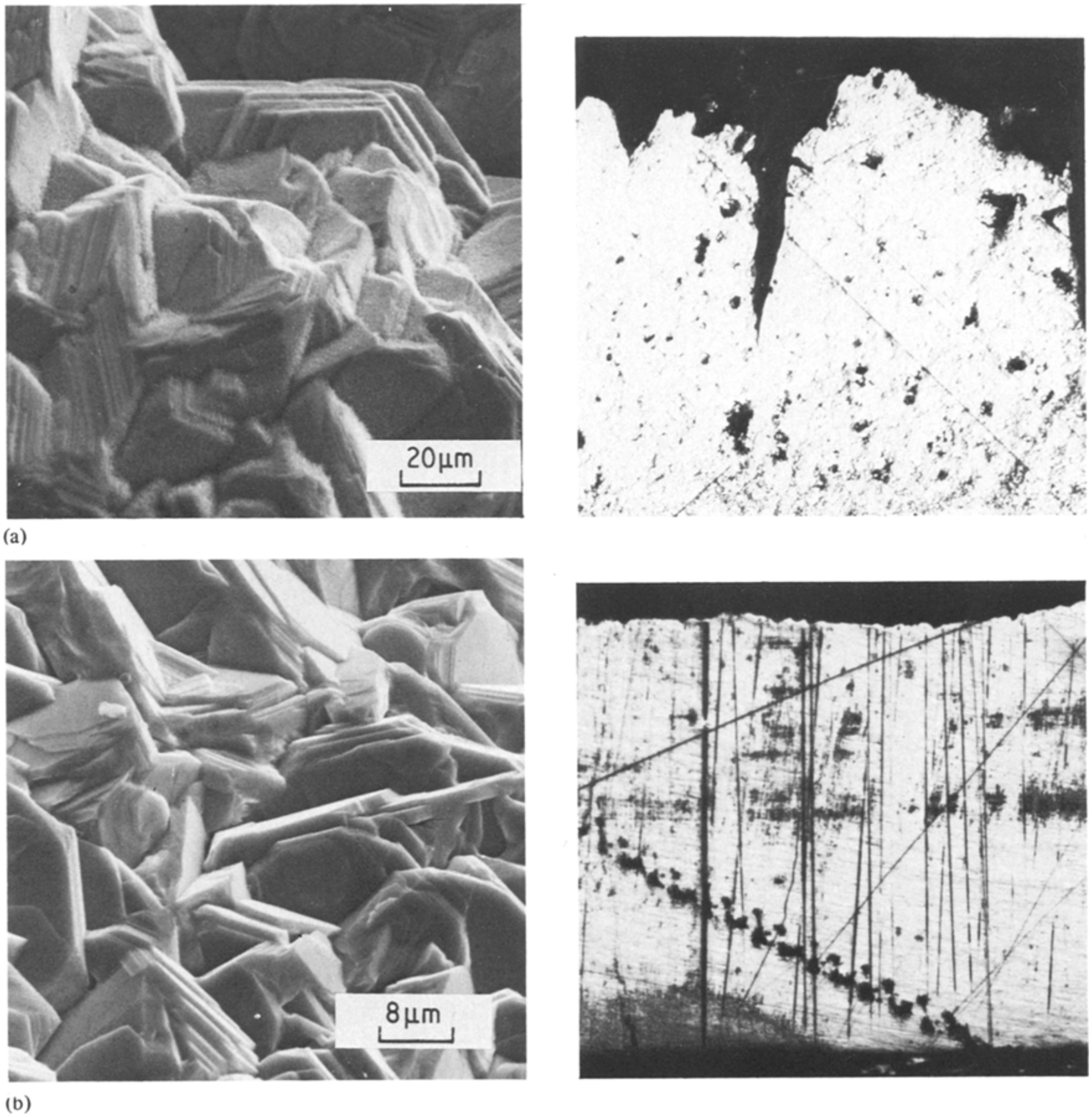
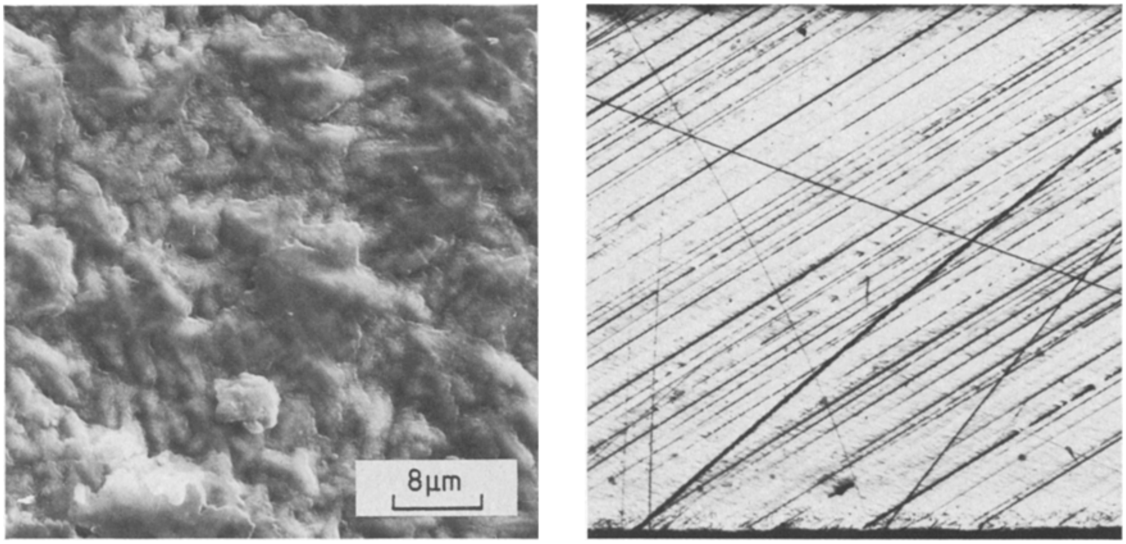


Fig. 6. The effect of TEACl, TPrACl and TPACl on the morphology and cross-section (70X) of zinc deposits. (a) 60 mg dm^{-3} TEACl, (b) 60 mg dm^{-3} TPrACl, (c) 10 mg dm^{-3} TPACl.



(c)

Fig. 6. *(Continued)*

fact, similar to the TBACl deposits. At higher concentrations of TPACl, the deposits remained smooth, but edge growth increased. At 45 mg dm^{-3} TPACl, the deposit surface 'bulged' out from the aluminium cathode creating a 'wet-back' condition.

The morphology and cross-section of zinc deposits electrowon from electrolytes containing TEACl, TPrACl and TPACl are shown in Fig. 6. The morphology of the deposits obtained from TEACl-containing electrolytes (Fig. 6a) was characterized by large hexagonal zinc platelets aligned at intermediate angles to the aluminium substrate, resulting in a preferred [112], [114], [103] orientation. At low magnification the surface appeared spheroidal, holed and irregular and the size of the spheres increased with increasing additive concentration. The cross-section (Fig. 6a) revealed that the deposit was uneven and contained voids.

Table 1. Current efficiency, energy requirement and orientation data for zinc deposits as a function of various additives

Additive (mg dm^{-3})	*CE* (%)	*ER* (kW h kg^{-1})	*Orientation*[†]
Addition-free	91.0	3.8	112, 114
TBACl (7.5)	91.0	3.9	110
TBACl (15)	99.4	3.7	101, 110
Pearl glue (30)	91.1	3.6	100, 110
Pearl glue (60)	96.9	3.1	110, 100
Percol 140 (6)	93.0	3.4	112, 110
Separan NP10 (6)	94.3	3.3	110

[†] Relative to ASTM standard for zinc powder.

The morphology of the deposit obtained from TPrACl-containing electrolytes (Fig. 6b) consisted of large hexagonal zinc platelets which decreased in size as the concentration of TPrACl was increased. At 15 mg dm^{-3} TPrACl, the deposit was coarse and contained numerous holes, as was the case for TEACl. At TPrACl concentrations > 15 mg dm^{-3}, the deposits were free from holes. The deposit cross-section (Fig. 6b) was even and compact. The deposit orientation at 15 and 30 mg dm^{-3} TPrACl was [110] but changed to [112], [114] at higher concentrations.

As noted earlier, the zinc deposits obtained from TBACl-containing electrolytes (Fig. 3b) consisted of zinc platelets with a refined grain size; the platelets were oriented vertically to the aluminium cathode resulting in a [110] preferred orientation. The deposit cross-sections were smooth and compact. The morphology of the deposits electrowon from TPACl-containing electrolytes (Fig. 6c) was similar to that for the TBACl-containing electrolytes. The cross-sections were even and compact. The preferred deposit orientation was [110]. Although TPrACl and

Table 2. Current efficiency, energy requirement and orientation data for zinc deposits as a function of various tetraalkylammonium chlorides

Additive (mg dm^{-3})	*CE* (%)	*ER* (kW h kg^{-1})	*Orientation*†
Addition-free	91.0	3.8	112, 114
TEACl (15)	91.2	4.0	114, 103
TEACl (30)	88.9	4.1	114, 103
TEACl (30)	92.4	4.0	112, 114
TEACl (60)	93.2	4.7	114, 112
TPrCl (15)	93.0	4.1	110
TPrCl (30)	95.1	4.2	110
TPrCl (45)	97.2	3.7	103
TPrCl (60)	97.9	4.0	114, 112
TBACl (7.5)	91.0	4.0	110
TBACl (15)	99.4	3.7	101
TBACl (15)	96.3	3.2	101, 110
TBACl (15)	94.6	4.0	–
TBACl (15)	96.7	3.7	110
TPACl (10)	92.7	4.2	110
TPACl (15)	94.8	3.9	110
TPACl (30)	95.3	3.8	110
TPACl (45)	95.8	4.3	110

† Relative to ASTM standard for zinc powder.

TPACl at certain concentration levels yield smooth, compact designs, TBACl remains the most effective additive in terms of smoothing the deposit, refining the grain size and eliminating dendritic growth.

The current efficiency, energy requirement and orientation results are summarized in Table 2. The TEACl series gave the lowest current efficiencies although they were generally $> 90\%$. However, for TPrACl concentrations $\geqslant 30$ mg dm^{-3} and for TBACl and TPACl concentrations $\geqslant 15$ mg dm^{-1}, the CE was generally $> 95\%$. The deposit orientation became more [110] preferred as the chain length of the alkyl group increased indicating an increase in the cathode polarization [12]. An increase in cathode polarization for metal deposition results in an increase in nucleation over growth and, hence, a more compact deposit with a finer grain size.

3.3. *Qualitative discussion of the results*

The zinc deposits electrowon from acid chloride electrolyte without additives were rough, nodular and had dendritic edges. The deposits consisted of poorly defined hexagonal platelets and contained pores and voids. Bressan and Wiart [13] attribute this condition to an autocatalytic step in the reaction mechanism that leads to multiple steady states [14] and to localized higher current densities which result in irregular growth of the deposits. It has been shown [8–10] that small amounts of certain additives which inhibit the irregular growth of zinc deposits also increase the cathodic overvoltage for zinc deposition. Additives which produce the largest increase in overvoltage generally result in zinc deposits with the finest grain size and a [110] preferred orientation [12]. It was shown previously [10] that in terms of increasing polarization some of the organic additives used in this work could be arranged in the order:

$$\text{TBACl} > \text{glue} > \text{TEACl}.$$

The strong polarizing effect of TBACl corresponded to the vertical or perpendicular [110] deposit orientation and a fine-grained compact zinc deposit. The weaker polarizing effect of TEACl corresponded to an intermediate orientation [112], [114] and the deposits consisted of large zinc platelets. The morphology and orientation of the deposits electrowon from electrolytes containing Separan NP10 and Percol 140 indicate that the degree of polarization produced by these additives lies somewhere between that of glue and TEACl. The same reasoning would further suggest that among the tetraalkylammonium chlorides, the order of polarization is:

$$\text{TPACl} > \text{TBACl} > \text{TPrACl} > \text{TEACl}.$$

That is, the longer the chain length of the alkyl group, the greater the polarization. Dingle and Damjanovic [9] found a similar behaviour in alkaline zincate solution in that the effectiveness of tetraalkylammonium bromides in eliminating dendrites increased from tetramethyl to tetrapentyl.

In addition to increasing the polarization, certain additives (such as lead acetate and tetrabutylammonium bromide) were shown by Bressan and Wiart [8] to eliminate multiple steady states in acid chloride electrolyte. In terms of electrode kinetics this results in a weaker autocatalytic step and an accelerated nucleation rate ensuring a faster renewal of active growth sites.

4. Conclusions

The presence of an organic additive in the electrolyte was essential for the electrowinning of smooth, compact, dendrite-free zinc deposits from chloride media. Tetrabutylammonium chloride (TBACl) was more effective than glue, Separan NP10 or Percol 140 in smoothing the deposit, refining the grain size and eliminating dendritic growth. Various tetraalkylammonium chlorides were tested and a relative order of effectiveness in smoothing the deposit was determined:

$$\mathrm{TBACl} > \mathrm{TPACl} > \mathrm{TPrACl} > \mathrm{TEACl}.$$

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