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Evaluation of Organic Additives For Use in Zinc Electrowinning

R. C. KERBY, H. E. JACKSON, T. J. O'KEEFE, AND YAR-MING WANG

Organic additives are used extensively in zinc electrowinning to assist in controlling the process. A cyclic voltammetry technique has been developed to provide a rapid, quantitative evaluation of the effectiveness of selected organic additives in minimizing the deleterious effects that impurities, such as antimony, have on zinc deposition. Results have indicated that animal glues are more effective than the other organic additives tested, which included several gums, enzymes, and amino acids, in relation to the current efficiency of zinc production. Of the various animal glues compared in this research, the most effective appeared to have average molecular weights in the 25,000 to 30,000 range. The effects of certain process variables on the test results have also been evaluated; these included the acid concentration of the zinc sulfate solution and the cathode preparation.

THE addition of animal glue to the zinc electrolyte used in zinc electrowinning plants¹⁻⁴ serves several purposes. The glue additions control cathode growth¹ to give smooth cathode zinc deposits, inhibit the deleterious effects that impurities such as antimony have on the current efficiency of zinc electrodeposition,¹ and decrease acid mist evolution by forming stable foam layers on the electrolytic cell tops in conjunction with additives such as m-p-cresol.⁵

A large number of solid and liquid animal glues are available commercially, with variations in physical and chemical properties due to different raw material sources and methods of preparation. These animal glues are often evaluated for use in zinc electrowinning by testing in small pilot electrolysis cells prior to their use in the zinc tankrooms. This technique has the disadvantage of being both tedious and not particularly sensitive to variations in additive properties among the various glues.

A cyclic voltammetry technique has been developed⁷ in which the effects of various parameters on the overpotentials associated with zinc electrowinning can be readily observed and measured. Antimony, an electrolyte impurity which is harmful to the current efficiency of zinc electrowinning, was shown to decrease the overpotentials associated with zinc electrodeposition. Animal glue, an organic additive which modifies the growth of the zinc deposits and inhibits impurity effects, increased the overpotential when added to the zinc electrolyte and thereby counteracted the effect that antimony as an impurity had on the overpotential. These opposing effects that impurities and organic additives have on the zinc overpotential were used to develop a cyclic voltammetric method for rapidly evaluating the effectiveness of various organic additives in counteracting impurity effects in zinc electrowinning.

EXPERIMENTAL

The cyclic voltammetry tests for the evaluation of organic additives and of the effects of electrolytic acid concentrations, which were done at Cominco's Technical Research Centre at Trail, were made on 500 ml acid zinc solutions (55 g/l Zn, 150 g/l H₂SO₄, 0.02 mg/l Sb) held at 25°C. The additives were added to the electrolyte as concentrated aqueous solutions 5 min prior to the start of the tests. High purity (6'9) aluminum mounted in Teflon was used as the cathode substrate. The aluminum cathode was polished with 600 grit paper and washed with acetone and distilled water prior to every test. Platinum foil was used for the anode and a calomel electrode (SCE) for the reference electrode. The cathodic potential was cycled between -700 and -1400 mV *vs* (SCE) at a potential sweep rate of 100 mV/min. The cyclic voltammograms were recorded as *i vs V* plots on an X-Y recorder. A typical cyclic voltammogram is shown in Fig. 1. The recorded voltage sweep was started at point A and the curve AB is the initial decreasing voltage portion of the curve in which the applied potential is greater than the zinc reversible potential, therefore no zinc electrodeposition occurs. The point B is the potential at which the curve DE crosses the zero current line and approximates the zinc reversible potential for the solution being tested. The line BC corresponds to the activation overpotential associated with zinc deposition onto the Al cathode substrate. The point C corresponds to the initial zinc deposition onto the aluminum cathode. The curve CD is the polarization overpotential associated with zinc deposition onto the aluminum substrate. At point D the decreasing potential applied to the cell by the potentiostat is changed to an increasing potential. The curve DB corresponds to the polarization overpotential associated with zinc deposition onto freshly deposited zinc, which is normally less than the polarization overpotential for zinc deposition onto aluminum (CD). The curve CDB in fact represents a nonsteady-state condition in which the Al substrate is increasingly covered by zinc, hence the shape of the curve will vary depending on the voltage scanning speed. The curve BE represents the anodic dissolution of the previously electrodeposited zinc.

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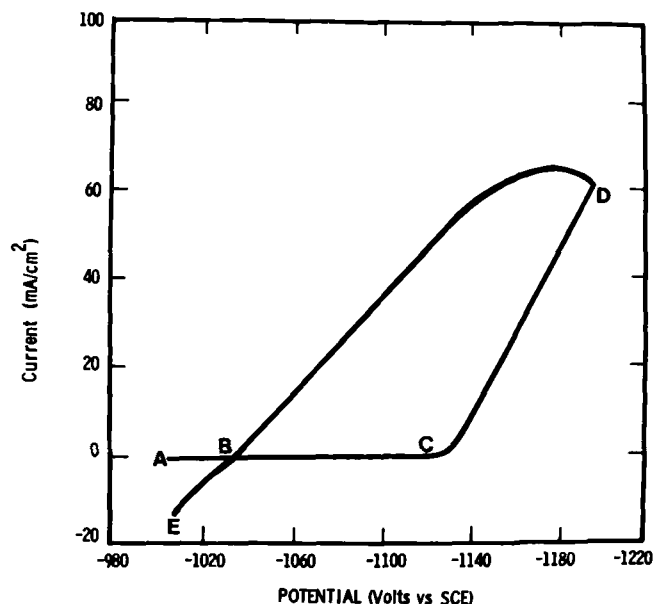


Fig. 1—Cyclic voltammogram for acidified zinc sulfate electrolyte. (a) start of recorded signal, (b) crossover potential, (c) potential at which zinc deposition is first observed, (d) reversing potential, (e) end of recorded signal.

The activation overpotential for zinc deposition onto aluminum, *i.e.* the voltage difference between points B and C, was the measurement used to determine the presence of impurities and organic additives in zinc electrolyte. Point B was taken where line DE crosses the zero current line, while point C was taken at 0.4 mA/cm² current density. Activation overpotential measurements were reproducible to within 2 mV. The cyclic voltammetry tests for the effect of cathode substrate preparation on the activation overpotential, which were done at the metallurgical laboratories at the University of Missouri-Rolla, were generally similar to the organic additive evaluation tests. A potential sweep rate of 60 mV/min was used in these tests. The cyclic voltammograms were recorded as log *i* vs V plots on an X-Y recorder. The log *i* vs V plots allowed cathodic overpotential effects at small currents to be examined in greater detail. To obtain zinc deposits for scanning electron microscope (SEM) studies, the potential was started at -700 mV vs SCE, swept in a cathodic direction until a current density of 50 mA/cm² was obtained, then the potential sweep was reversed until the current density reached 35 mA/cm², held for two min at this current, then the cathode was removed from solution.

The 24 h zinc deposits in the current efficiency tests for organic additive evaluation were obtained from small pilot electrowinning cells at Cominco's Technical Research Centre at Trail. Each cell held 7.5 l of solution, 1 aluminum cathode, 2 0.75 wt pct Ag-Pb anodes and a stirrer. A temperature of 40°C was maintained using hot water baths. Neutral solution (150 g/l Zn) containing the additives was fed to the cells during the course of the runs. Cell electrolyte (55 g/l Zn, 150 g/l H₂SO₄, 0.02 mg/l Sb) was prepared from neutral degypsumized zinc sulfate solution obtained from the Cominco zinc plants at Trail, B.C. (analysis: Zn 155 g/l, Mn 1.5 g/l, Fe 0.01 g/l, Cd 0.3 mg/l, Sb 0.02 mg/l, Co 0.3 mg/l, Ge 0.01 mg/l, Ni

< 0.05 mg/l, Cl 70 mg/l, F 5 mg/l, no electrochemically active organics). All tests were run at a current density of 43 mA/cm². The deposits were examined by optical and scanning electron (SEM) microscopy.

The pearl glue used in the tests was a standard sample of the animal glue supplied by Croda Polymers Ltd., England, for use in the Cominco zinc tankrooms at Trail, B.C. The gums which were tested were obtained from Stein Hall and Company Ltd, while the gelatins, amino acids and enzymes were obtained from chemical suppliers. The Swift glue samples were supplied by the Swift Chemical Company, along with their average molecular weights. Most of the Swift glue samples had been prepared by proteolytic enzyme degradation of high molecular weight protein derived from collagen. Six of the Swift TPCIV glues had been treated with 6N NaOH at 71°C for various periods of time and then neutralized with HCl. These glues tended to have low average molecular weights. The concentrations reported for the liquid glues were based on the dry weight of the glues, taken after heating samples of the glues for seven h at 105°C.

RESULTS AND DISCUSSION

Effect of Substrate and Acid Concentration on Overpotential and Morphology

The polarization behavior of a system is directly influenced by the chemical, physical and electrochemical parameters used for the process. The nature of the cathode substrate and the ionic nature of the electrolyte are two such variables whose effects on activation overpotential have to be determined in order to standardize the cyclic voltammetry technique.

The influence of aluminum cathode surface preparation (*i.e.* by 600 grit polishing or wheel polishing with alumina powder) on the activation overpotential for zinc deposition onto the aluminum substrate is listed in Table I. The observed decreases in overpotential with increasing antimony additions to the electrolyte were greater for the wheel polished cathodes than for the grit polished cathodes, as were the observed increases in overpotential with increasing glue additions. The zinc deposits obtained on the wheel polished aluminum cathodes were less adherent, had a larger crystallite size (Fig. 2) and their crystallite structure was more influenced by antimony and glue additions than the zinc deposits obtained on the 600 grit polished aluminum cathodes.

Increases in zinc electrolyte concentrations between 40 and 70 g/l and acid electrolyte concentrations be-

Table I. Effects of Cathode Surface Preparation on Overpotential of Zinc Deposition as Measured by Cyclic Voltammetry (55 g/l Zn, 150 g/l H₂SO₄, Cathode Sweep 60 mV/min)

Sb Content, mg/l	Glue Additive, 15 mg/l	Overpotential (mV)	
		600 Grit	Wheel Polished
0.0035	—	85	92
0.0035	Swift EZ3	117	145
0.0200	—	80	77
0.0200	Swift TPC IV (treated 16 hours)	95	122
0.0200	Swift EZ3	111	135

Table II. Effect of Antimony and Glue Additions on the Activation Overpotential for Zinc Deposition from Neutral and Acid Zinc Electrolyte (Cathode Sweep 100 mV/min, Al polished to 600 grit)

Zn, g/l	H ₂ SO ₄ , g/l	Sb, mg/l	Pearl Glue, mg/l	Overpotential, mV
55	0	0.01	0	91
55	0	0.03	0	84
55	0	0.01	15	106
55	50	0.01	0	112
55	50	0.03	0	70
55	50	0.01	15	172
55	100	0.01	0	105
55	100	0.03	0	69
55	100	0.01	15	168
40	150	0.01	0	121
40	150	0.03	0	72
40	150	0.01	15	181
55	150	0.01	0	104
55	150	0.03	0	70
55	150	0.01	15	151
70	150	0.01	0	104
70	150	0.03	0	78
70	150	0.01	15	152
55	200	0.01	0	92
55	200	0.03	0	71
55	200	0.01	15	123

tween 50 and 200 g/l decreased the activation overpotentials for zinc electrolytes with or without antimony and glue additions (Fig. 3). Neutral (pH 5.2) zinc electrolyte gave decreased polarization effects from antimony and glue additions as compared to acid zinc electrolyte (Table II). Zinc crystallite size was significantly larger for neutral zinc electrolyte than for acid zinc electrolyte (compare Fig. 2(b) to Fig. 4), which would indicate a decreased crystallite nucleation rate in neutral electrolyte.

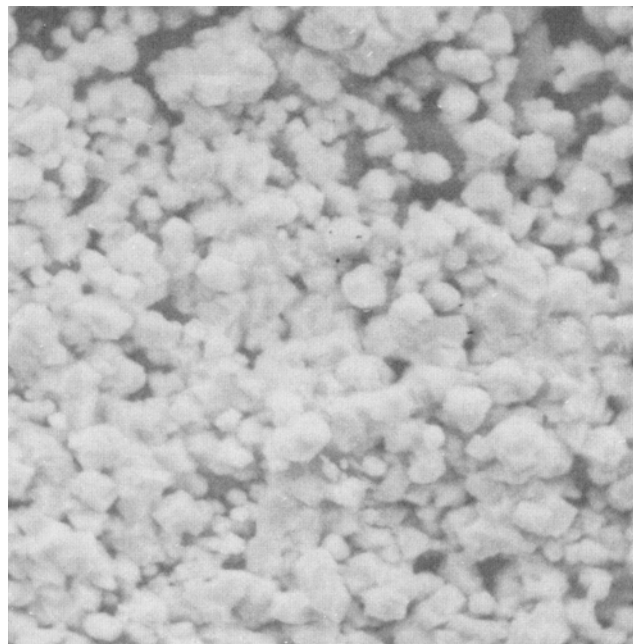
Evaluation of Organic Additives for Zinc Electrowinning

The increased activation overpotentials for zinc deposition onto aluminum cathodes (600 grit polished) arising from various additions of animal glues, gums, amino acids and enzymes to acid zinc electrolyte were measured by cyclic voltammetry and are listed in Table III. The relative glue additive strengths in Table III were computed by assigning glue sample Swift EZ3 (Sample 2) a value of 100 and then comparing the average activation overpotential changes caused by this glue at 5, 10 and 15 mg/l concentration in zinc electrolyte with those caused by the other additives, based on a scale of 100. Marked differences were observed among the various organic additives in their ability to increase the activation overpotential.

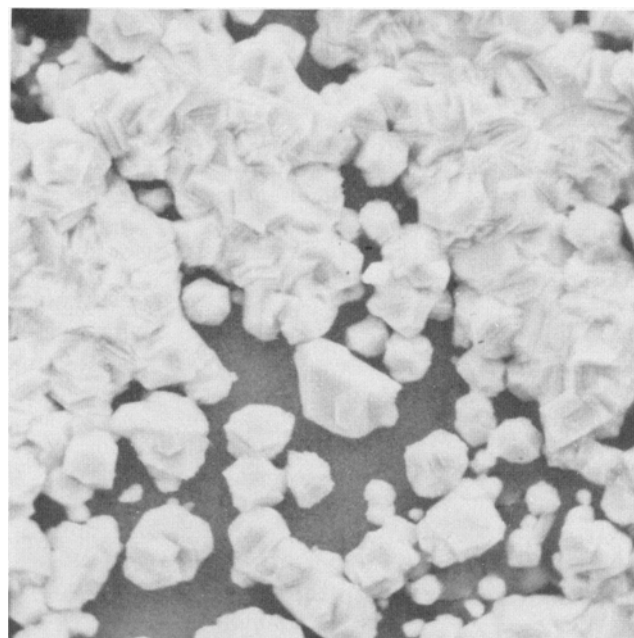
Animal glues were the most active in increasing the activation overpotential of zinc deposition, with the most active glues falling in the average molecular weight range of 25,000 to 30,000 (Fig. 5). However, even among the most active glues, significant differences were noted in their effects on activation overpotential. For example, Swift EZ3 (Sample 1) and Swift EZ3 (Sample 2) gave different changes in overpotential at the same addition level (Table III). This would suggest that the normal criteria such as gel point and viscosity which are specified during the manufacture of "standardized" glue products are not

completely successful in providing reproducible glue products for use in zinc electrowinning.

The current efficiency of zinc electrodeposition (Table IV) from acid zinc electrolytes, each containing 15 mg/l of a glue and 0.02 mg/l total Sb, was generally found to be greater when glues with high relative glue additive strengths were used than when glues with low additive strengths were used, indicating



(a)



(b)

Fig. 2—(a) Scanning electron micrograph of deposit obtained from acidified zinc sulfate electrolyte (55 g/l Zn, 150 g/l H₂SO₄, 4 μg/l Sb) using a 600 grit polish aluminum cathode. Magnification 950 times. (b) Scanning electron micrograph of deposit obtained from acidified zinc sulfate electrolyte (55 g/l Zn, 150 g/l H₂SO₄, 5 μg/l Sb) using a wheel polished aluminum cathode. Magnification 950 times.

Table III. Effects of Various Organic Additives on Increasing the Overpotential of Zinc Deposition, as Measured by Cyclic Voltammetry (55 g/l Zn, 150 g/l H₂SO₄, Cathode Sweep 100 mV/min, 600 Grit Polished Al)

Organic Additive + 0.02 mg/l Total Sb	Change in Overpotential, mV			Relative Glue Additive Strength*	Average Molecular Weight
	5 mg/l Additive	10 mg/l Additive	15 mg/l Additive		
A. Glues					
Swift TPC IV (untreated)	25	34	42	64	47,000
Swift TPC IV (treated 10 min)	31	40	47	75	18,000
Swift TPC IV (treated 2 h)	22	31	35	56	1,200
Swift TPC IV (treated 4 h)	19	25	27	45	1,050
Swift TPC IV (treated 8 h)	17	22	32	45	910
Swift TPC IV (treated 16 h)	9	9	16	22	760
Swift TPC IV (treated 24 h)	7	20	18	28	850
Swift EZ2 (sample 1)	33	47	56	86	27,000
Swift EZ3 (sample 2)	44	52	62	100	≈29,000
Swift TPC 5V (CPE no. 5)	36	37	51	78	45,000
Swift TPC 5V (sample 2)	32	41	49	77	≈50,000
Swift TPC 2185	29	38	41	68	≈10,000
Swift TPC 2226	32	38	47	74	≈80,000
Swift TPC 2268	28	32	34	59	≈10,000
Swift TPC 69C	29	41	55	80	≈30,000
Gelatin (sample 1)	30	44	47	77	≈80,000
Gelatin (sample 2)	19	28	42	56	≈80,000
Pearl Glue	30	39	55	78	≈50,000
B. Gums					
Gum Shiraz	9	14	25	30	≈240,000
Gum Arabic	26	23	25	47	
Guar Gum	14	7	16	12	
C. Amino Acids					
Glycine	—	0	—	0	75
Proline	—	7	—	15	115
Lysine	—	10	—	22	146
D. Enzymes					
Trypsin	16	18	15	31	24,000
Pepsin	17	22	29	43	34,500
Catalase	8	6	5	12	240,000
*Relative glue additive strength calculated on basis of average overvoltage for 5, 10 and 15 mg/l additions, after assigning Swift EZ3 (sample 2) a value of 100.					

*Relative glue additive strength calculated on basis of average overvoltage for 5, 10 and 15 mg/l additions, after assigning Swift EZ3 (sample 2) a value of 100.

that glues with high relative glue additive strengths were the most effective in controlling the deleterious effects that impurities such as antimony have on zinc electrowinning (Fig. 6).

Amino acids, which are formed during the hydrolysis of animal glues and hence have low molecular weights, were relatively inactive as addition agents in zinc electrodeposition (Tables III and IV). Three enzymes, sometimes found in animal glues, were also tested for additive activity (Table III). Trypsin and catalase were relatively inactive as addition agents, even though they had molecular weights similar to glues. Pepsin showed some activity as an addition agent in zinc electrodeposition. Of the gums which were tested, guar gum and gum shiraz were inactive, whereas gum arabic showed some activity as an organic additive. Gum arabic is used as an additive in some electrolytic zinc plants.¹⁰

There is no clear consensus on the mechanisms by which organic additives, in particular animal glues, alter zinc crystal growth and inhibit impurity effects during electrowinning. The molecular forms that organic additives such as glues assume in acid zinc electrolyte apparently play an important role. Animal glues are proteinaceous material derived from collagen, a fibrous protein found in skins and fibrous tissues.⁶

The collagen molecule, shown schematically in Fig. 7, consists of long chains of amino acids, principally glycine and proline, jointed by peptide linkages (*i.e.* the amide grouping—CONH—). The molecular weight

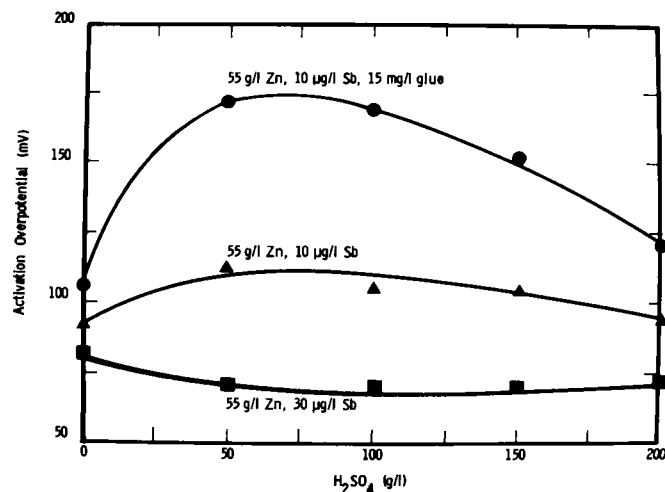


Fig. 3—Effect of acid concentration on the activation overpotential associated with zinc deposition from sulfate electrolyte.

Table IV. Effect of Organic Additions on the Current Efficiency of Zinc Electrowinning
(24 h Deposits, 43 mA/cm², 40°C)

Glue + 0.02 mg/l Total Sb	Current Efficiency, Pct				Average CE, Pct	Average Molecular Weight of Glues
	7.5 mg/l Glue	15 mg/l Glue	25 mg/l Glue	40 mg/l Glue		
No organic additives					83.0	
Swift TPC IV (untreated)	89.9	91.9	90.5	88.9	90.3	47,000
Swift TPC IV (treated 10 min)	89.7	91.8	91.2	90.7	90.9	18,000
Swift TPC IV (treated 2 h)	83.9	87.8	87.1	90.3	87.3	1,200
Swift TPC IV (treated 4 h)	87.6	89.2	87.0	88.5	88.1	1,050
Swift TPC IV (treated 8 h)	89.0	90.6	87.1	88.7	88.9	910
Swift TPC IV (treated 16 h)	—	—	86.1	88.2	87.2	760
Swift TPC IV (treated 24 h)	80.6	88.3	85.8	87.0	85.4	850
Swift EZ2 (sample 1)	—	93.0	90.1	90.0	91.0	27,000
Swift EZ3 (sample 2)	90.6	—	89.9	—	90.3	≈29,000
Swift TPC 5V (CPS no. 5)	90.8	93.7	90.9	90.2	91.4	45,000
Swift TPC 5V (sample 2)	90.3	—	90.9	—	90.6	≈50,000
Swift TPC 2185	90.1	—	90.6	—	90.4	≈10,000
Swift TPC 2226	90.3	—	90.8	—	90.6	≈80,000
Swift TPC 2268	88.5	—	89.8	—	89.2	≈10,000
Swift TPX 69C	93.8	—	91.0	—	92.4	≈30,000
Lysine	86.0	—	—	—	86.0	146
Cominco pearl glue	91.2	91.0	91.0	89.4	90.7	≈50,000
Glycine	85.0	—	—	—	85.0	75

(MW) of the collagen molecule is at least 300,000. Native collagen is insoluble in water, but is converted into warm water soluble gelatin during the processes of curing and extraction. This gelatin may be degraded into smaller molecules by the application of heat, steam, acids, alkalis or enzyme action to give rise to derived proteins (MW 50,000–250,000), proteose fractions (MW 5000–50,000), peptone fractions (MW 200–5000) and finally amino acids. The production of gelatin is controlled so as to produce a product containing primarily derived proteins. Less care is normally taken in the production of animal glues,

hence they normally contain larger proportions of proteose fractions and insoluble products. Enzymes are also proteineous materials, with each having a different sequence of amino acids in the protein chain. Animal glues, gelatins and enzymes all tend to hydrolyze in acid solution to form lower weight molecular fractions.

The additive activities of the glues were shown to be related to their average molecular weight (Fig. 5), with glues of an average molecular weight of 25,000 to 30,000 (measured prior to solution in acid zinc electrolyte) having the most activity. This would suggest that it is the proteose content of the animal glues which is the most active in controlling the effects of the impurities on zinc deposit growth. An analysis (for method, see Ref. 8) of four of the glues showed increasing relative proteose contents with increasing relative glue additive strengths (Table V). The proteose fractions of animal glues tend to exhibit mildly complexing properties in the presence of many metal cations,^{6,8} and would therefore affect the distribution of impuri-

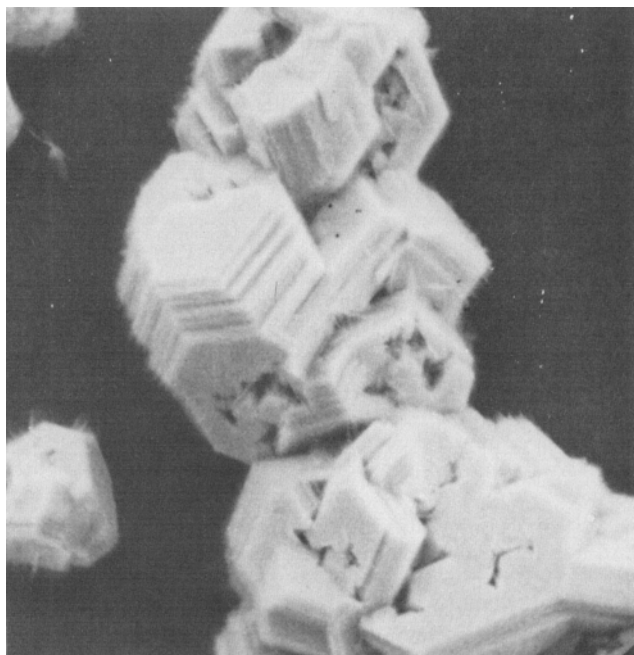


Fig. 4—Scanning electron micrograph of deposit obtained from neutral zinc sulfate electrolyte (55 g/l Zn, 4 μg/l Sb) using a wheel polished aluminum cathode. Magnification 950 times.

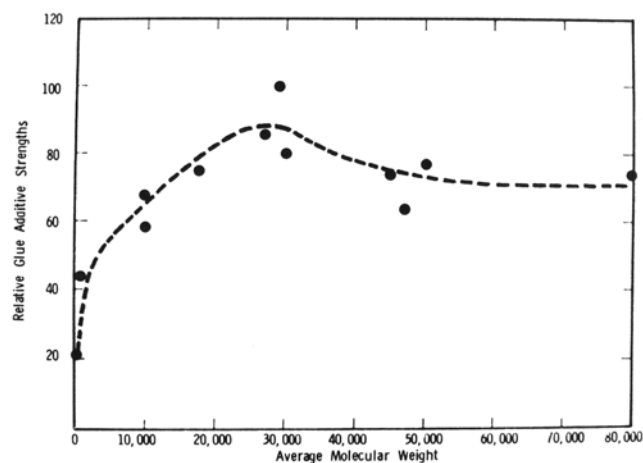


Fig. 5—Relationship between relative glue additive strengths, as determined from overpotential data, and the average molecular weights of the glues.

ties in the deposits. For example, increasing the glue concentration in zinc electrolyte containing antimony resulted in increased antimony concentrations in the zinc deposits (Fig. 8), yet current efficiencies were also higher. This would indicate that the antimony in the deposits produced from these solutions, even though higher in concentration, was distributed in such a manner so as to minimize zinc resolution. This would result if the impurities were distributed in a more even manner throughout the deposit rather than concentrating in localized spots on the deposit. Inhibition of zinc resolution by impurities could also result if the proteinaceous material incorporated into the deposit with the impurities prevented the impurities from participating in a resolution process.

All glues with average molecular weights above 10,000 showed good levelling properties, (as determined by visual examination of zinc deposits recovered from tests listed in Table IV) indicating that zinc crystal growth during electrowinning is affected by both the proteose and protein fractions of the glues. The colloidal properties of the proteose fractions of the glues are thought to play an important role in altering the crystal growth of the zinc deposit.⁹ The colloids block active growth sites through incorporation into the zinc deposit and thereby facilitate increased nucleation of zinc crystallites, resulting in a fine-grained crystal growth.

Effect of Hydrolysis on Glue Additive Strengths

The proteins present in animal glues hydrolyze (*i.e.* break apart) to form smaller molecular weight fractions when they are allowed to stand under acid conditions such as occur in acid zinc electrolyte.

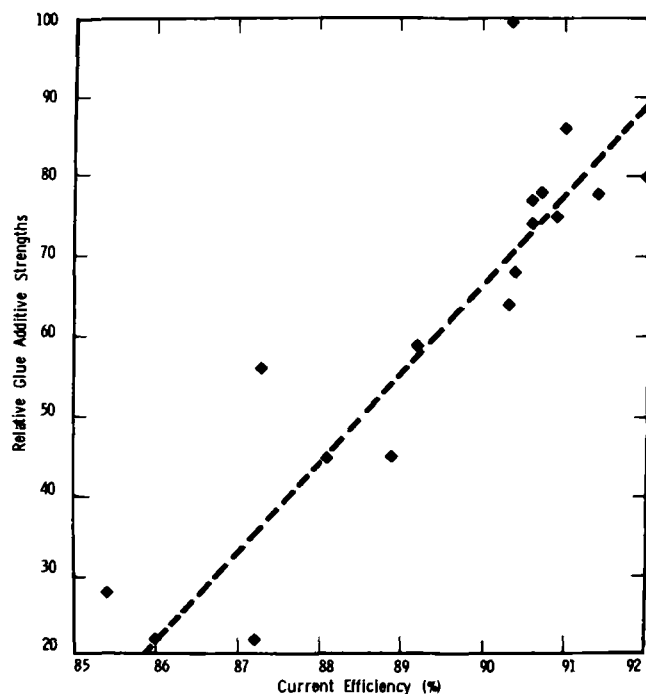
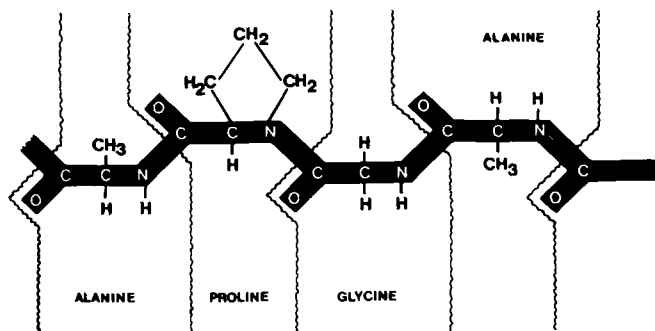


Fig. 6—Relationship between relative glue additive strengths as determined from overpotential data, and the average current efficiency of zinc deposition from acid zinc electrolytes (55 g/l Zn, 150 g/l H_2SO_4 , 20 $\mu g/l$ Sb) containing 7.5 mg/l, 15 mg/l, 25 mg/l, or 40 mg/l glue.



PORTION OF PROTEIN MOLECULE

Fig. 7—Schematic representation of a portion of the proteinaceous material present in animal glues, which is composed of a number of amino acids joined by α -peptide linkages.

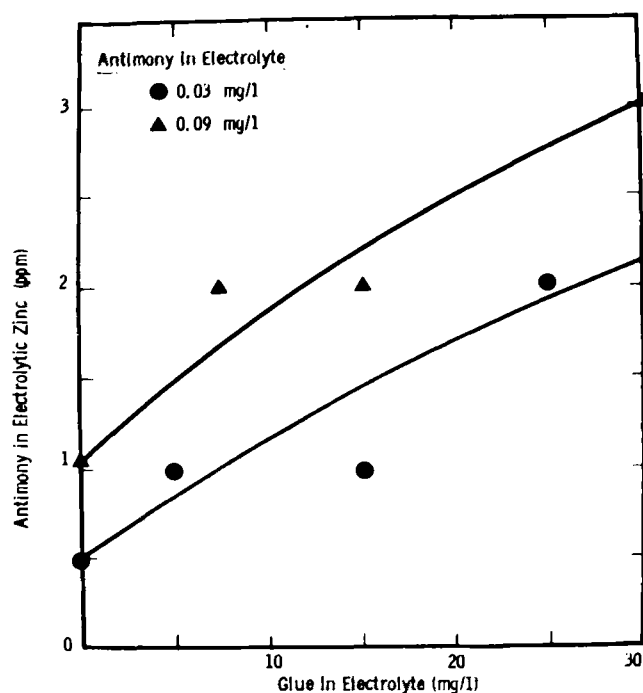


Fig. 8—Effect of antimony and glue concentrations in acid zinc electrolyte on antimony reporting in electrolytic zinc.

Amino acids, previously shown to be relatively inactive as addition agents in zinc electrowinning, are formed during the process. Several tests were made to determine how quickly animal glues would become ineffective as addition agents when allowed to stand for several days in acid zinc electrolyte.

Synthetic return acid solutions (55 g/l Zn, 150 g/l H_2SO_4 , 0.02 mg/l Sb) containing 15 mg/l glue or other additives were maintained at 40°C for specified periods of time. At the end of these times, the samples were tested by cyclic voltammetry to determine if there had been any changes in overpotential effects as compared to freshly prepared electrolyte solutions containing similar glue concentrations (Table VI). Many of the glues showed apparent slight increase in additive strength after standing for 4 h in acid zinc electrolyte, as indicated by slightly increased overpotential. (Fig. 9) After standing for 24 h in acid zinc electrolyte, the low molecular weight Swift TPC IV (NaOH) glues

Table V. Glue Analysis*

Glue	Protein, Wt Pct	Protease, Wt Pct	Peptone, Wt Pct	Amino Acid, Wt Pct
Pearl	26.7	37.3	4.6	31.3
Gelatin	87.8	11.3	0.7	0.2
Swift 2226	0.0	31.9	27.8	40.3
Swift EZ-3	5.5	41.7	17.4	30.4

*The weight percentages of protein, protease, peptone and amino acid are based on their respective nitrogen contents relative to the nitrogen content of the original glue after removal of water and insoluble fractions.

Table VI. Changes in Glue Additive Strengths, as Indicated by Overpotential Measurements, After Standing in Acid Zinc Electrolyte for Varying Periods of Time (55 g/l Zn, 150 g/l H₂SO₄, Cathode Sweep 100 mV/min, 600 Grit Polished Al)

15 mg/l Glue + 0.02 mg/l Total Sb	Overpotential (mV), After Standing at 40°C			
	0 h	4 h	24 h	7 Days
Swift TPC IV (untreated)	117	125	119	—
Swift TPC IV (treated 2 h)	110	—	97	—
Swift TPC IV (treated 8 h)	107	—	93	—
Swift EZ3 (sample 1)	131	135	129	—
Swift EZ3 (sample 2)	137	139	133	—
Swift TPC 5V (CPE no. 5)	126	140	127	—
Swift TPC 5V (sample 2)	126	138	127	118
Swift TPC 2185	120	122	132	—
Swift TPC 2226	128	147	128	—
Swift TPC 2268	120	128	130	—
Swift TPC 69C	123	132	124	—
Gelatin (sample 1)	122	144	140	116
Pearl glue	125	131	122	114

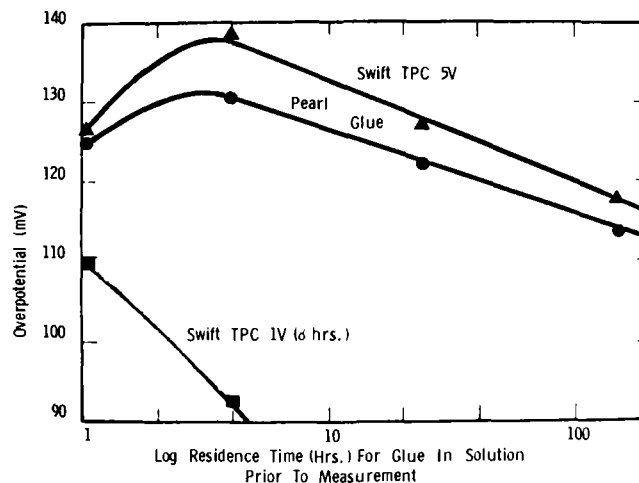
Table VII. Effect of Glue Hydrolysis on the Current Efficiency of Zinc Electrowinning (24 h Deposits, 43 mA/cm², 40°C)

15 mg/l Glue + 0.05 mg/l Total Sb	Current Efficiency, Pct
Pearl glue	90.4
Glue allowed to stand in acid zinc solution for 3 days prior to electrolysis	86.0
Glue allowed to stand in acid zinc solution for 5 days prior to electrolysis	82.2
Glue boiled in 150 g/l H ₂ SO ₄ for 2 h prior to adding to electrolyte	37.8

showed a significant decrease in additive strengths, whereas the other glues still showed good additive strengths. However, after standing for seven days all the glues tested showed a decrease in additive strength.

The initial activation may be due to the exposure of additional active sites (*i.e.* complexing groups) on the proteins comprising the animal glues. The slow decrease in the activity of the glues would suggest a relatively slow hydrolysis rate in acid zinc electrolyte at 40°C.

To check the above results, zinc electrowinning tests

Fig. 9—Effect of glue hydrolysis on the activation overpotential associated with zinc deposition from acid sulfate electrolyte (55 g/l Zn, 150 g/l H₂SO₄, 20 μg/l Sb) containing 15 mg/l glue.

were made with pearl glue samples that had been allowed to hydrolyze. As shown in Table VII, the current efficiency for zinc deposition dropped when the glues were allowed to hydrolyze prior to the electrowinning tests. A particularly sharp drop in current efficiency was found for the glue sample that had been boiled in sulfuric acid, indicating that the glue had been almost completely hydrolyzed and was no longer affecting zinc deposition. These results are similar to those reported for glue hydrolysis in heated acid copper electrolytes.¹¹

SUMMARY

Organic additives, in particular animal glues, are used in zinc electrowinning to control cathode deposit growth so as to provide smooth deposits, control the adverse effects that impurities such as antimony and cobalt have on the current efficiency of zinc deposition, and assist in acid mist control over the cells. A cyclic voltammetry technique has been developed to provide a rapid, quantitative evaluation of the effectiveness of organic additives in controlling impurities in zinc electrowinning. The technique involved measuring the relative increases in activation overpotential for zinc deposition onto an aluminum cathode as caused by specified addition of various organic additives to similar zinc electrolytes. Additives which showed the greatest overpotential effect for similar amounts added to the electrolyte (*i.e.* had the greatest relative glue additive strength) were also the most effective in controlling impurity effects in zinc electrowinning.

Animal glues were the most effective of the additives tested, which included several gums, enzymes and amino acids. The most effective animal glues had average molecular weights of 25,000 to 30,000. The effectiveness of the glues in controlling impurity effects appeared to be related to the protease content of the glues, whereas the requirements for good leveling properties was for the glues to have a molecular weight of at least 10,000.

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