

EFFECT OF ORGANIC ACIDS IN NICKEL PLATING

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Electrodeposition of nickel is largely carried out as an undercoat in decorative nickel-chromium plating. During the process of nickel plating, the solution pH tends to rise because of depletion of hydrogen ions due to hydrogen evolution from the layer of solution surrounding the cathode. It thus becomes necessary to maintain the pH of the plating solution within the appropriate range for ensuring production of deposits with desirable properties. In this paper the authors report the effects of certain buffering ingredients, namely acetate, citrate, succinate and tartrate salts in nickel plating solutions. The experimental results point to the suitability of acetate as a superior buffering agent for a nickel plating bath.

Keywords: Nickel plating, acetate and Hull cell

INTRODUCTION

Nickel coatings are applied to substrates of steel, brass, zinc, metallized platinum etc., in order to obtain surfaces resistant to corrosion, erosion and abrasive wear [1,2]. Most of the nickel is used as 5-40 μm decorative coatings with top coats of approximately 0.3 μm thick chromium on parts like automobile bumpers, bicycle parts and door handles. Heavy nickel plating is also of importance in chemical processing industry as plated nickel provides a chemically resistant surface.

The electrodeposition of nickel is carried out in a solution of nickel salts in water with addition of conducting salts and buffers etc. In practice, a small percentage of the cathodic current as a side reaction causes discharge of hydrogen ions and thus hydrogen evolution, leading to a decrease in hydrogen ion concentration in the solution and an increase in its pH. In order to restrict the change of pH of the solution, a weak acid or its salt is normally added to it to provide a buffering action. Boric acid is a well known buffer additive [3].

This paper reports the results of studies on certain organic acid salts added separately as a buffering agent to nickel plating baths, and also on their deposition characteristics.

EXPERIMENTAL

Hull cell experiments were conducted in a standard 257 ml cell using a polished mild steel cathode and a pure nickel anode, in order to observe the nature of the deposited nickel over a range of current densities (Fig. 1) and choose a bath composition and related operating conditions.

Cathode current efficiency determination were done by carrying out plating experiments with steel cathode (5 x 4 0.1 cm) using nickel anode of equal surface area. The efficiency was, as usual, calculated as the effective percentage utilization of the cell current used.

The buffering ability of each of the different organic acids salts tested was assessed by noting the change in pH of the solution after carrying out plating for a duration of 6 hours. Measurements of solution pH were done with an Elico make digital pH meter.

Deposit microhardness values in vickers were determined using a PMT - 3 Microscope Hardness Metel with a load of 25 g.

RESULTS AND DISCUSSION

The bath used, was a low concentration nickel plating solution optimised earlier and composed of nickel sulfate (120 g/l) and potassium chloride (20 g/l) along with boric

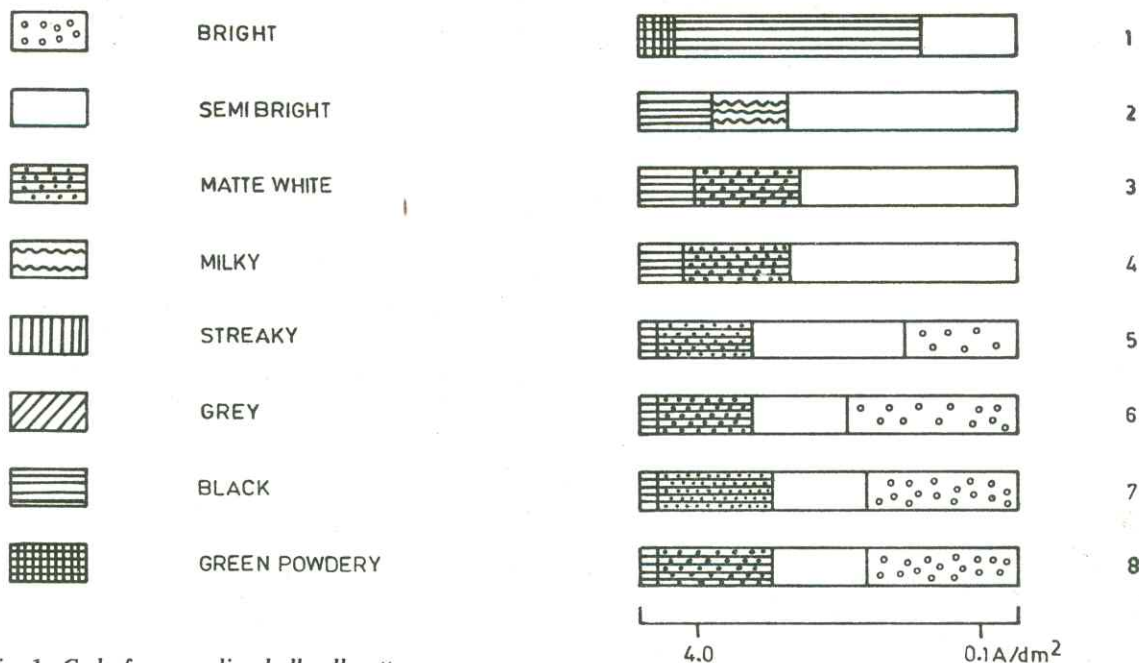


Fig. 1: Code for recording hull cell patterns

acid, as a buffer. The buffers investigated as alternative to boric acid were sodium acetate, trisodium citrate, sodium potassium tartrate and sodium succinate.

Fig. 2 and Table I show the effect of adding varying concentrations of sodium acetate to the basic nickel salt solution on the Hull Cell behaviour. In the absence of sodium acetate, a green powdery deposit was obtained over the high current density area and a black film at low current densities, a result indicating the precipitation of nickel hydroxide due to substantial alteration of pH, especially in the cathode diffusion layer. With the introduction of sodium acetate the quality of the deposit was found to improve, matte white, semibright and bright layer being obtained at the high, middle and low current density areas. With increase in the concentrations of sodium acetate the nature of the deposit also improved and for 30 g/l concentration of the same, a bright layer was obtained over a wide current density. The nature of the deposit did not change much with further increase in sodium acetate concentrations upto 50 g/l.

Fig. 3 presents the Hull cell patterns from solutions containing varying concentration of trisodium citrate. Even for a small concentration of trisodium citrate in the solution, the pattern exhibited a significant change and semibright and bright deposits were obtained over high and low current density areas respectively (Table II). When the concentration of trisodium citrate reached 50 g/l a fully bright pattern was obtained over the entire range. Further increase in concentration of trisodium citrate to 75 g/l and 100 g/l did not

Fig. 2: Effect of variation of sodium acetate concentration in solution containing nickel sulphate 120 g/l, potassium chloride 20 g/l, sodium acetate 1) 0, 2) 5, 3) 10, 4) 15, 5) 20, 6) 30, 7) 40 and 8) 50 g/l

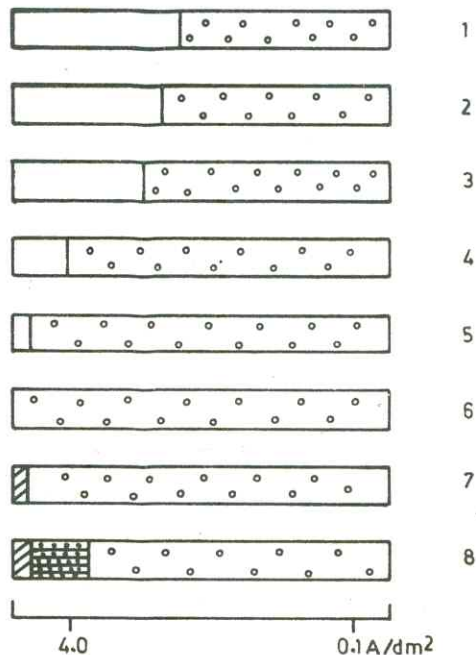


Fig. 3: Effect of variation of trisodium citrate concentration in solution containing nickel sulphate 120 g/l, potassium chloride 20 g/l, trisodium citrate 1) 5, 2) 10, 3) 20, 4) 30, 5) 40, 6) 50, 7) 75 and 8) 100 g/l

TABLE I: Results of hull cell experiments with different buffering additives

Details of composition and operation of nickel bath:
 Nickel sulphate 120 g/l, Potassium chloride 20 g/l,
 pH 5, Temperature = 323 K

Buffering additive	Concentration (g/l)	Range corresponding to Bright/ Semibright/ Dull white nickel	
		Distance (cm)	Maximum current density (based on equation)
1. Sodium acetate	0	7.5-10	0.5
	5	4-10	2.0
	10	1.5-10	4.2
	20	0.5-10	6.1
	30	0.5-10	6.1
	40	0.5-10	6.1
2. Trisodium citrate	5	0-10	6.1
	10	0-10	6.1
	20	0-10	6.1
	30	0-10	6.1
	40	0-10	6.1
	50	0-10	6.1
	75	0.4-10	6.1
	100	2-10	3.5
3. Sodium potassium tartrate	5	0-10	6.1
	10	0-10	6.1
	20	0-10	6.1
	30	0-10	6.1
	40	5-10	1.4
4. Sodium acetate	5	0.5-10	6.1
	10	1.2-10	4.7
	15	1.5-10	4.2

prove to be of any advantage, as only layer, a little duller, especially at the high current density end were formed.

TABLE II: Deposition characteristics of baths with different buffering additives

Buffering additive	Current		Nature of deposit
	density A/dm ²	efficiency (%)	
1. Sodium acetate 30 g/l	1	98	Smooth, uniform, dull white
	2	95	" "
	3	96	" "
2. Trisodium citrate 50 g/l	4	98	Smooth, uniform, dull white
	2	99	" "
	3	95	" "

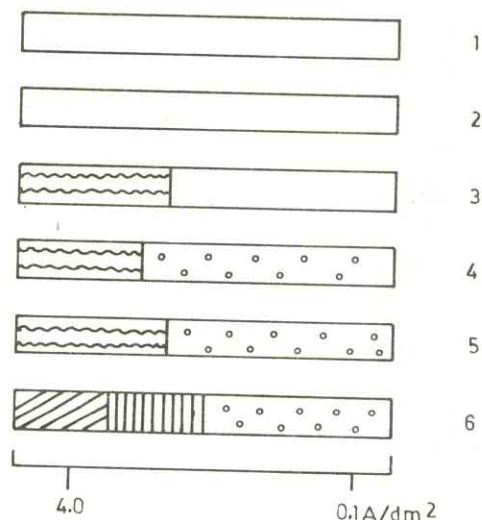


Fig. 4: Effect of variation sodium potassium tartrate concentration in solution containing nickel sulphate 120 g/l, potassium chloride 20 g/l, sodium potassium tartrate 1) 5, 2) 10, 3) 15, 4) 20, 5) 30 and 6) 40 g/l

The improvement in Hull cell pattern brought about by addition of sodium potassium (5-30 g/l) tartrate is shown in Fig. 4 and Table I. At 40 g/l, the nickel layer started becoming streaky and grey especially at higher current densities. Higher concentrations could not be tried because of limited solubility of the salt in the bath.

The beneficial effect of sodium succinate in producing bright/semibright deposits is clearly noticeable at 5-15 g/l concentration (Table I). But an increase in succinate concentration to 10 and 15 g/l tends to render the nickel layer gray coloured, especially at the high current density end and the current density range associated with semibright/bright layers gets reduced (Fig. 5).

On the basis of Hull cell studies, it can be concluded that addition of sodium acetate or trisodium citrate is favourable

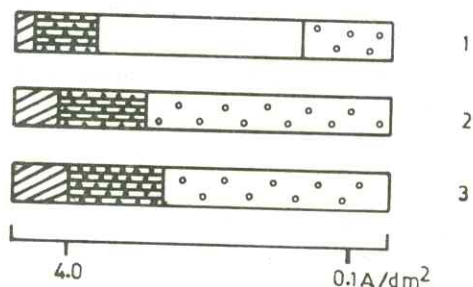


Fig. 5: Effect of variation of sodium succinate concentration in solution containing nickel sulphate 120 g/l, potassium chloride 20 g/l, sodium succinate 1) 5, 2) 10, 3) 15 g/l

TABLE III: Change of solution pH with different buffering additives

Buffering additive (g/l)	Initial pH	Final pH	Micro-hardness kg/mm ²
1. Sodium acetate (30)	5	5.02	377
2. Trisodium citrate (50)	5	5.32	291
3. Sodium potassium tartrate (30)	5	4.91	339
4. Sodium succinate (10)	5	5.12	265
5. Boric acid (30)	5	5.08	291

for producing acceptable deposits of nickel. Current efficiencies for solutions containing either of these (Table II) are all higher than 95% and comparable to those for boric acid buffered baths. In all the cases, the deposit was smooth, uniform and matte white.

Data included in Table III shown the relative buffering characteristics of the various additives investigated as ingredients of nickel plating solutions. Sodium acetate however, appears to be the most efficient, it is even better than boric acid whereas trisodium citrate has the least buffering effect.

A comparison of deposit microhardness values (Table III) shows that the acetate buffered bath produces deposits with higher hardness.

CONCLUSIONS

Uniform, smooth, dull white deposits of nickel of higher microhardness can be deposited with a higher current efficiency from a nickel bath of composition and operating parameters as below

Nickel sulphate	120 g/l
Potassium chloride	20 g/l
Sodium acetate	30 g/l
pH	5
Temperature	323 K
Current density	1.0-3.0 A/dm ²

The solution is better buffered than the one with the usually added boric acid as buffering additive.

REFERENCES

1. R Brugger, *Nickel Plating*, Robert Draper Ltd, Teddington (1970)
2. J K Dennis and T E Such, *Nickel and Chromium Plating*, 2nd Edition, Butterworths Co Ltd, London (1986)
3. J P Hoare, *J Electrochem Soc*, 134 (1987) 3102