Bright Zinc - Nickel Alloy Plating from Sulphate-Chloride Bath

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Thiamine hydrochloride is an effective brightener for zinc-nickel alloy plating in acid sulphate-chloride bath. Effect of various parameters on Hull cell cathode, optimum plating conditions, deposit properties and metallurgical properties are discussed. Current efficiency of the bath is 95%. Polarization data indicates that the addition agents increase the cathode potential to a more negative value.

In recent years efforts have been made to enhance the corrosion resistance of the galvanized coating [1]. One such development is the electrodeposition of zinc with other alloying metals like Co, Ni, Cr, Cd, Fe etc. A major work has been done in developing Zn-Ni alloy deposition [2]. The Zn-Ni alloy deposit is reported to be a few times more corrosion resistant than pure Zn coatings [3]. These alloys can be used in cases where improved physico-mechanical properties - such as wear resistance, low temperature characteristics, solderability etc. - are required. These can also be used in the case of continuous electrodeposition of Zn on strips, wires, etc. The Zn-Ni deposits are resistant to marine conditions and claimed to be viable substitute for Cd in marine exposure [4]. This article reports the results pertaining to the deposition of Zn-Ni alloy from sulphate-chloride bath.

EXPERIMENTAL

Standard experimental procedures were adopted for the Hull cell, polarization, throwing power and current efficiency measurements. The bath composition shown in Table 1 was used as a standard; the solution was prepared from commercial grade chemicals. The bath solution was used after purification by following the procedure given elsewhere [5]. Experimental conditions for Hull cell tests are also given in Table 1. Boric acid (one of the ingradients in the bath) acts as a buffer while sodium chloride and sodium sulphate enhance the conductivity of the bath solution. The pH of the bath solution was adjusted using dilute sulphuric acid or sodium hydroxide to the required value.

Table 1

Standard Bath Composition and Operating Conditions

Constituent	g/l	Operating Conditions
$ZnSO_4.7H_2O$	200	Anode Zn Sheet (99.99%)
Na_2SO_4	30	Cathode Mild Steel
NaCl	15	Total Current 1 - 3 Amps
H_3BO_3	30	Plating Time 10 mts
$NiSO_4.H_2O$	40	Temperature 25 - 30°C
		pH 4.5

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The deposits obtained under each set of plating conditions were observed under a high resolution microscope. The deposits produced under optimum plating conditions were used to measure the physical properties as well as for outdoor exposure testing by salt spray method.

RESULTS AND DISCUSSION

Optimisation of Parameters

To judge the quality of the electrodeposited Zn-Ni alloy under different current densities, Hull cell experiments were carried out at ambient temperature (30°C) with a cell of 267 ml capacity, using the standard bath solution at pH 2.5 and at different cell currents (1 to 3A) with and without air agitation. White, dull deposits were obtained in the current density range of 20 to 80 A/ft², patchy deposits at low current density and burnt deposits at high current density range. No improvement was observed in the appearance of deposit with air agitation.

In order to optimise bath constituents, Hull cell experiments were conducted in baths varying one constituent at a time. The cell currents in all cases was maintained at 2 A. Nature of the deposit at different current density area are examined.

Addition Agents

To improve the uniformity of the coating with smaller grain size, Hull cell experiments were carried out at 2A cell current using the bath solution containing different amounts of Triton X-100 (0.1 to 1 ml/l), sodium lauryl sulphate (0.25 to 2 g/l), polyvinyl alcohol (0.2 to 2 g/l) and dextrin (0.5 to 8 g/l).

Triton-x-100 gave black deposit at all cell currents. Sodium lauryl sulphate and polyvinyl alcohol gave only white dull deposits in the current density range of 10 to 50 A/ft² with and without air agitation. Dextrin in the concentration range of 3 to 4 g/l was found to give uniform, dull white deposits with smaller grain size in the current density range of 10 to 120 A/ft².

Brightener

Specified amounts of different organic compounds containing S, O and N were used in Hull cell experiments as brightners in the bath. Among the various compounds used, only thiamine hydrochloride (Th) was found to give satisfactory mirror-bright Zn-Ni deposits over wide current density range. The effect of thiamine hydrochloride on the deposit was examined on the Hull cell panel and the results are given below.

Table 2

Effect of Thiamine hydrochloride and Current density on the Nature of Deposit

Thiamin	Nature of Deposit	over CD Range
0.05 g/l	Semibright	20 - 40 A/ft²
	Dull	40 - 80 A/ft²
	Burnt	> 80 A/ft²
	Cloudy dull	< 20 A/ft²
0.1 g/l	Semi bright area increases	
0.2 g/l	Bright	15 - 45 A/ft²
0.3 g/l	Very bright	10-90 A/ft²
>0.3 g/l	C.D. for bright deposit increases	

Thiamine hydrochloride concentration was fixed at 0.3g/l as optimum.
The Hull cell patterns are given in fig. 1(b).

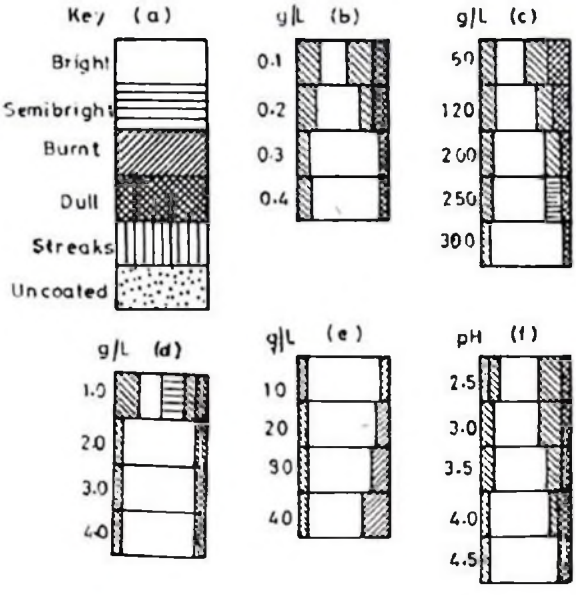


Fig.1. Results of Hull Cell experiments showing the effect of
thiamine hydrochloride (b);
$ZnSO_4 7H_2O$ (c); dextrin (d);
Ni content (e) and pH (f).

Table 3

Effect of Zn Content and CD on the Deposit

Zinc	Nature of deposit over CD Range
60 g/l	Semibright 10 - 20 A/ft² Undesirable deposit at all other C.d
120 g/l	Bright 10 - 50 A/ft² Burnt deposit on higher Cd area
200 g/l & 250 g/l	shining & defect-free 10 - 60 A/ft² Dull deposit Low high Cd area
300 g/l	Mirror shining 8 - 85 A/ft² Unsatisfactory below & above this range
>300 g/l	No improvement on the deposit

300 g/l of zinc sulphate was fixed as the optimum concentration. Hull Cell patterns are shown in Fig. 1(c).

Zinc Content

The bath solution as given in Table 1 was taken and the optimised concentration of dextrin (3g/l) and Th (0.3 g/l) were added. The Hull cell experiments were carried out and in each experiment the presence of nickel content in the deposit was tested. The concentration of zinc sulphate in the bath was varied from 60 to 400 g/l. The results are shown in Table 3.

Effect of Dextrin

Dextrin concentration was varied from 1 g/l onwards in order to know its effect on the nature of deposit. All other constitutents were taken as given in Table 1, whereas zinc sulphate (300 g.l) and Th (0.3 g/l) were taken in their optimised concentration.

Table 4

Effect of Dextrin and CD on the Nature of the Deposit

Dextrin	Nature of Deposit over CD Range
Low conc.	Unsatisfactory at all C.d
2 g/l	Defect free 10 - 50 A/ft² Undesirable deposite at higher & lower CD range
3 g/l	Bright, defect-free 6 - 85 A/ft² Burnt deposit at higher CD range of panel Dull deposit at lower range
> 3g/l	No improvement in nature of deposit

The Hull Cell patterns are shown in fig.1(d). Optimum conc of Dextrin was fixed at 3 g/l.

Nickel Content

Different concentration of Nickel sulphate were used in the bath solution. After each Hull cell experiment (at different current density value), the panel was given bright dip and Ni content in the deposit was determined.

Effect of pH

The Hull cell experiments were conducted with optimised concentration of all the constitutent to see the effect of pH of the bath solution on deposit.

Table 5

Effect of Nickel content and CD on the nature of deposit

Nickel	Nature of deposit over CD Range
<10 g/l	Bright, but Ni content in the deposit low at lower CD
10 g/l	Bright & defect-free over 10 - 80 A/ft^2 Burnt at higher CD Dull at lower CD Ni is present in the deposit at all CD
20 g/l	As above; Bright over 8 - 80 A/ft^2
40 g/l	Bright over 10 - 40 A/ft^2 bright deposit obtained turned to black or VIBGYOR colour after bright dip. Course dull deposit at lower CD Smooth deposit at higher CD
> 40 g/l	bright deposit obtained turned black after bright dip.

Effect of Nickel content on Hull cell pattern is given in fig.1(e).
10 g/l nickel sulphate was fixed as optimum concentration.

Effect of Conductivity Salts

Sodium chloride and sodium sulphate present in the solution were responsible for conductivity of the solution. Sodium chloride increased the anodic dissolution. In order to see the effect of these salts on deposits, Hull cell experiments were conducted at different concentrations of sodium chloride and sodium sulphate.

Table 6

Effect of pH of the Bath on the Deposit

pH	Effect on Deposit over CD Range
2.5	Deposit only in region 30 - 70 A/ft^2 But occational pitting Burnt deposit at high CD Dull deposit at low CD
3.0	Range of Bright deposit same as above; But density of pitting reduced Burnt deposit at high CD Dull deposit at low CD
3.5	Bright over 20 - 80 A/ft^2 No pittings observed
4.0	Bright, defect-free over 10 - 75 A/ft^2 Dull deposit over 75 - 90 A/ft^2 Burnt at high CD range
4.5	Shining, defect-free over 10 - 80 A/ft^2 Burnt deposit at high CD Dull deposit at low CD
> 4.5	No improvement

The pH 4.5 was fixed as optimum value.
Hull cell patterns are given in Fig. 1(f).

Effect of Boric Acid

Further Hull Cell experiments were carried out in order to see the effect of different concentration of boric acid on the electrodeposit.

Effect of Bath Parameters on Current Efficiency

The effect of pH and bath constitutents at different current densities are shown in Fig. 2. The current efficiency was maximum in the pH range of 3 to 5. At pH values less than 2.5, the current efficiency was minimum. At pH values greater than 5.5, the current efficiency values were not

Table 7

Effect of Conducting Salts and CD on Nature of Deposit

Salt	Effect on Deposit over CD Range
Effect of NaCl	
10 g/l	Bright over 40 - 80 A/ft² Semi bright over 15 - 40 A/ft² Unsatisfactory deposit above & below this CD range
20 g/l	Bright over 15 - 80 A/ft² Semi bright over 5 - 15 A/ft² Unsatisfactory deposit above & below this CD range
30 - 200 g/l	Bright over narrow range of CD

The optimum concentration of sodium chloride was fixed at 20 g/l.

Effect of Na_2SO_4	
10 g/l	Bright over 35 - 80 A/ft² Unsatisfactory deposit over other CD area
20 g/l	Shining bright over 10 - 80 A/ft² Unsatisfactory deposit over other CD area
>20 g/l	Bright over narrow range of CD

The optimum concentration of sodium sulphate was fixed at 20 g/l.

Table 8

Effect of Boric acid on the Deposit

Conc.	Effect on Deposit over CD Range
20 g/l	Bright deposit over 55- 70 A/ft² Semi bright between 30 - 55 A/ft² Unsatisfactory deposit over other CDs
40 g/l	Bright over 25- 75 A/ft² Patchy, cloudy deposit at < 25 A/ft²
60 g/l	Bright shining over 25- 70 A/ft²
80 g/l	Bright deposit over narrow range of CD

The optimum concentration of boric acid was fixed at 60 g/l.

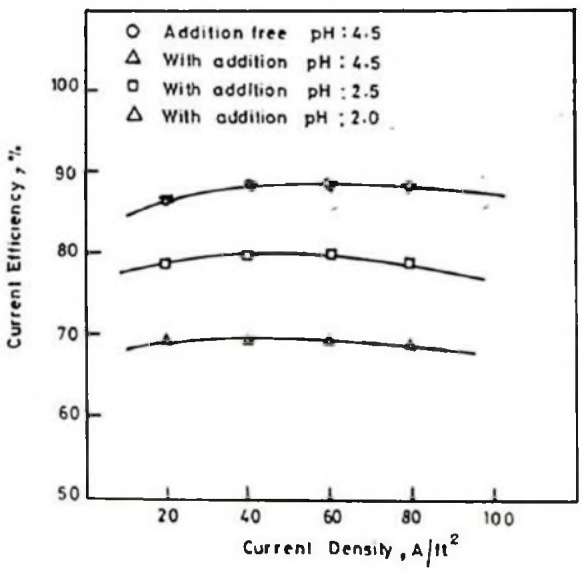


Fig.2. Effect of pH and addition agents on current efficiency.

Table 9

Bath Constituent Concentration and Current Efficiency

Constituent	conc. range g/l	Current Eff.
$ZnSO_4.7H_2O$	50 - 400	88 - 96
Ni_2SO_4	10 - 60	95 - 96
NaCl	15 - 90	95 - 96
Na_2SO_4	15 - 120	95 - 96
H_3BO_3	10 - 80	94 - 96
Dextrin	1 - 5	92 - 95
ThiamineHCl	0.05 - 0.4	91 - 96

measured because of unsatisfactory deposits. In most cases the current efficiency values were more than 90% with a bath solution of pH 4.5. The current efficiency remained almost constant between 20 - 70 A/ft² current density. At higher current densities, the efficiency decreased slightly due to hydrogen evolution. The metal (both Zn and Ni), conductivity salts, primary and secondary addition agents do not have much influence on current efficiency. The values of current efficiency are given in Table 9.

Polarization Studies

The cathodic potentials were recorded under galvanostatic condition at different current densities with and without the addition of brighteners. The results are given in Table 10. It is seen that the potential values shifted to more cathodic direction in the presence of addition agents.

Throwing Power

A Haring and Blum cell was used to measure the throwing power of the bath solution under optimum condition of the solution. Experiments were conducted

Table 10

Effect of Addition Reagent on Cathode Potential

Addition Agent	Cathode Potential
No addition	-500 mV
Dextrin (4g/l)	-510 mV
Thiamine HCl (0.3g/l)	-536 mV
All Additives	-550 mV

varying bath constitutents, pH, and current densities in order to see the effect of these on throwing power. The values of throwing power under different conditions are given in Table 11. It was found that the presence of Dextrin and Thiamine hydrochloride enhanced the throwing power of the bath solution. The optimum value of throwing power was found to be 16 at 60 A/ft².

Table 11

Effect of Bath Constituents on Throwing Power

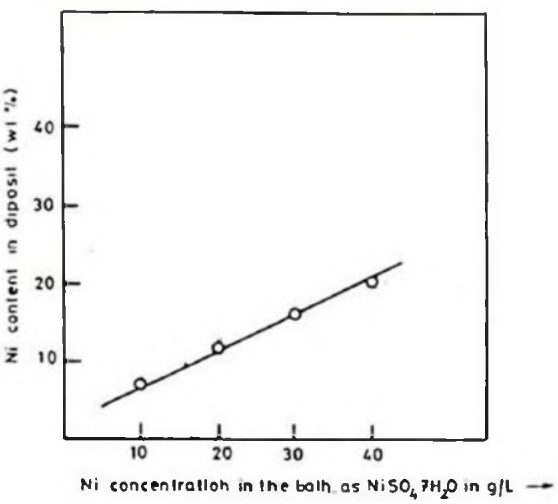
Constituent	Conc.range g/l	Throwing power
$ZnSO_4.7H_2O$	50 - 400	7 - 10
$Ni_2SO_4.7H_2O$	10 - 60	9 - 10
Dextrin	1 - 5	11 - 13
ThiamineHCl	0.05 - 0.4	12 - 16
All Additives	optimum	16
pH	2 - 5	13 - 16
C Density	10 - 100	13 - 16

The Deposit

It was observed that the Ni content included in the deposit was increasing with nickel content in the bath and it increased linearly with current density for a given concentration of Nickel in the bath. The optimum bath composition and operating conditions for obtaining bright deposits are given in Table 12.

Corrosion resistance test of deposits was carried out by adopting conventional

method as well as accelerated corrosion test (salt spray). The specimens for the test were plated to different thickness and chromated. The alloy deposit of 4 µm thick was immersed in 3.5 M sodium chloride solution. No deterioration in the appearance of the deposit was observed even after 200 hours of immersion. In salt spray test, the white rust spots were observed only after 260 hours.



Pig. 3.

Table 12

Optimum Bath Composition and Operating Conditions

Constituent	g/l	Operating Conditions
$ZnSO_4.7H_2O$	300	Anode Zn Sheet (99.99%)
$NiSO_4.7H_2O$	30	Cathode Mild Steel
NaCl	20	Total Current 2 Amps (for Hull cell)
H_3BO_3	60	Plating Time 10 mts
$Na_2SO_4.H_2O$	20	Temperature 30°C
Dextrin	4	pH 4.5
ThiamineHCl	0.3	

Pores are the active centers for corrosion to occur, so a good deposit should be pore free. To test the porosity of the deposit, the mild steel samples were plated to different thickness at 40 A/ft². A filter paper soaked in 2% potassium ferricyanide solution was placed over the deposit and the number of blue spots developed on the filter paper were taken as a measure of porosity. It was found that the deposit from the solution containing brightners was pore free.

The adhesion of the coating to the base metal is one of the important properties of plating. The Zn-Ni alloy coating has a very good adhesion as indicated by the standard bend test. The deposit was found to be highly ductile as it does not produce any crack in the deposit even after 180 bending. The measured values of the hardness and strees of Zn-Ni deposit were well within the industrial requirements.

CONCLUSION

The bright, highly ductile and corrosion resistant deposit could be obtained from the optimised bath. The deposit could be used successfully in place of nickel plating.

ACKNOWLEDGEMENT

The author wishes to express gratitude to Prof. G.H. Kulkarni, Head of the Department of Chemistry for providing laboratory facilities and Prof. P.S Shetty, Princial, K.R.E. College, Surathkal, for financial support.

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