

# Role of Nucleosides on Nickel Electroplating from a Formamide Bath

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**Abstract.** The outwardly growth mechanism during electrocrystallization results in appreciable thickness and reflectivity, whereas lateral growth leads to thin and inferior reflectivity. Outward growth deposits essentially depend upon the operating conditions. They also depend upon the release of cations in the catholyte from the metal-non-aqueous complex. The nucleoside additive has a large number of coordinating centres for complexation. In formamide medium, the availability of large number of such centres leads to better electrodeposition than those additives having a lesser number. Deoxyguanosine, having a maximum number of coordinating centres, and “N” and “O”, leads to electrodeposits having no peeling effect and better reflectivity. However, this peeling effect diminishes if a comparatively large concentration of nucleosides is used. The presence of nucleosides in a non-aqueous electroplating bath not only improves the quality of electrodeposits but improves the thickness too.

**Keywords:** nickel electrodeposits, nucleosides as additives, metal electrodeposition, electrocrystallization, formamide electrodeposition bath

## Introduction

When electrodeposition of metals is carried out in an aqueous bath, the deposit is found to have a high tensile stress due to adsorption and subsequent diffusion of hydrogen gas evolving at the cathode. This results in cracked topography. The evolution of hydrogen gas at the cathode can be reduced by using a non-aqueous bath. The rate of supply of metal ions in the catholyte depends upon the complexing tendency of the metal. This, in turn, depends upon the nature of the non-aqueous solvent, which may act as ligand having a perfect coordinating centre. Formamide (HCONH<sub>2</sub>) has a high dielectric constant and a perfect coordinating centre. It is cheap and easily available in pure form with the advantage that it has no toxic effects and no disposal problems. Formamide, thus, seems to be a better electrodepositing medium, since on disposal into the nature, it easily hydrolyses to produce ammonia, which has a positive effect on plant growth. The byproduct (formic acid) may undergo dilution and finally decompose into carbon monoxide and water, thus exhibiting no adverse effect on the growth of plants.

Many workers have chosen different non-aqueous solvents as electrodepositing media and have reported electrodeposits with improved qualities (Srivastava and Tikoo, 1987a; Biallozor *et al.*, 1984; Sultan and Tikoo, 1984; Samel and Gabe, 1983). Depositions with desirable mechanical properties, free from hydrogen codeposition, and with lower ductility have been attempted from non-aqueous baths (Srivastava and Tikoo, 1987b; Dini and Johnson, 1976) and in the presence of organic

additives (Sibley and Brook, 1974). The additive-free bath produces deposits with columnar grain structure, whereas a bath containing organic additives produces deposits having equiaxial grain (Reed, 2001).

Organic additives have been reported to produce electrodeposits with reduced tensile stress and hardness. Some inorganic additives have been reported to improve the surface morphology but they had no effect on cathode efficiency (Mohanty *et al.*, 2002). The effect of ammonium cations (Srivastava and Tikoo, 1987c) and various anions (Srivastava and Singh, 1995) on the electrodeposition of nickel from non-aqueous baths have also been studied. Mixed aqueous-non-aqueous-formamide/water (F/W), N-methylformamide/water (NMF/W), dimethylformamide/water (DMF/W), DMSO/W, THF/W baths have led to nickel electrodeposits with high cathode current efficiency and with non-cracked topography (Srivastava *et al.*, 2001). Corrosion protection efficiency of some of these electrodeposits has also been studied (Srivastava *et al.*, 2004).

This paper reports the effect of various nucleosides on the electrodeposition of nickel from a formamide bath, having an electrolytic combination of nickel acetate, nickel sulphate and nickel sulphamate.

## Materials and Methods

The solvent formamide was purified as given in literature (Dawson *et al.*, 1954). Copper strips, 15x10x1 mm were used as cathodes. These strips were first ground to produce a smooth

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surface, polished using various grades of emery papers (1/0 to 4/0), and finally disc polished. These strips were then cleaned, degreased in hot soap solution (idipol), electrolytically cleaned using sodium carbonate (pH 12.0), and finally solvent-degreased using acetone. The strips were pickled in 10% sulphuric acid and after degreasing adequately cleaned in hot and cold double distilled water. High purity nickel sheets were used as anodes. The copper strip cathode was placed in between two anodes and an interelectrode distance of 20 mm was maintained throughout the experiment. A copper coulometer was placed in series to measure the current. The thickness of the electrodeposited nickel was measured using an electropysik coating thickness gauge (Minitest, Germany, model 600B<sub>1</sub>). All the weighings were done on a digital electronic balance (Swiss). Bath composition and operating conditions are given in Table 1.

## Results and Discussion

**Operating conditions. Boric acid (buffer) fixation.** The actual role of boric acid during electrodeposition is not clearly understood. However, it has been established that buffers play an important role in the cathode deposition phenomena. It inhibits the hydrogen gas evolution at the cathode, thus hindering the inclusion and subsequent diffusion of hydrogen gas through the cathode surface. In the case of nickel electrodeposition, boric acid is mostly used as the buffering agent. The addition of boric acid to a formamide bath during the present study did not improve the brightness of the electrodeposited nickel. Instead, some peeling was observed. However, the addition of boric acid improved the cathode current efficiency. The effect of boric acid on the physical characteristics of nickel electrodeposition from the formamide bath is shown in Table 2.

**Current density fixation.** While studying the effect of current density on the electrodeposition of nickel from a formamide bath, it was observed that the reflectivity improved mildly on increasing the current density. The cathode current efficiency also showed a decreasing trend. However, the thickness improved only on raising the current density to 0.4 A/dm<sup>2</sup>, or above. Moderately high current density tended to enhance the rate of nucleation. After a limiting current density, at which the concentration of metal ions in the cathode film became optimum, the tendency to produce rough or treed deposit with peeling was enhanced. The effect of current density on electrodeposition of nickel from a formamide bath is shown in Table 3.

**Temperature fixation.** While studying the effect of temperature on the electrodeposition of nickel from a formamide bath, it was observed that at low temperatures the quality of the

electrodeposit was not good. It also exhibited heavy peeling effect. The quality was found to improve successively on raising the temperature. It was observed to have much better brightness at 25 °C to 35 °C, but was accompanied with a mild peeling effect. The peeling diminished along with the reflectivity at around 45 °C. No peeling effect was observed, thereafter, but the quality of nickel deposit deteriorated enormously. High efficiency and thick deposition was observed only at higher temperatures. The effect of temperature on electrodeposition of nickel from a formamide bath is shown in Table 4.

On the basis of observations presented in Tables 1-4, temperature of 45 °C, 0.5 A/dm<sup>2</sup> current density, and 0.4 M boric

**Table 1.** Electrodeposition bath composition and conditions of the experimental protocol for electrolysis

Constituents/ conditions	Protocol status
Nickel acetate*	0.2 M
Nickel sulphate**	0.2 M
Nickel sulphamate <sup>#</sup>	0.2 M
Boric acid	0.1-0.5 M
Ribocytidine	0.005-0.05 M
Deoxycytidine	0.005-0.05 M
Deoxyadenosine	0.005-0.05 M
Deoxyguanosine	0.005-0.05 M
Solvent	formamide
Temperature	15-65 °C
Current density	0.1-0.9 A/dm <sup>2</sup>
Duration of electrolysis	60 min
Agitation	nil

\*Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O; \*\*NiSO<sub>4</sub>·6H<sub>2</sub>O; <sup>#</sup>Ni(SO<sub>3</sub>NH)<sub>2</sub>·4H<sub>2</sub>O

**Table 2.** Effect of boric acid (BA) concentration, used as the buffering agent, on the electrodeposition of nickel

BA (M)	Nature of deposit	C (%)	Thickness (µm)	Hydrogen gas evolution**
0.0	greyish	50.65	3.40	significant
0.1	semi-bright	60.32	3.70	significant
0.2	hazy-bright*	85.92	4.08	significant
0.3	semi-bright*	63.50	3.37	reduced
0.4	semi-bright''	68.92	3.22	reduced
0.5	semi-bright''	65.32	3.0	mild

C = cathode current efficiency (%); \* = peeling; '' = mild peeling; \*\* = hydrogen gas evolution at cathode; bath composition: nickel acetate (0.2 M), nickel sulphate (0.2 M) and nickel sulphamate (0.2 M) in formamide; additive: boric acid (0.1 M-0.5 M); operating conditions: 0.5 A/dm<sup>2</sup> and 15 °C

acid concentration were chosen as the experimental operating conditions during further studies on the effect of nucleosides on the electrodeposition of nickel from a formamide bath.

**Effect of nucleosides.** Two sets of nucleosides were chosen. The first set consisted of ribocytidine and deoxycytidine, while the other set consisted of deoxyadenosine and deoxyguanosine (Fig. 1).

**Effect of ribocytidine.** The effect of ribocytidine as an additive in trace amounts on the electrodeposition of nickel from a formamide bath containing nickel acetate (0.2 M) nickel sulphate (0.2 M) and nickel sulphamate (0.2 M), along with boric acid (0.4 M) as the buffering agent was studied (Table 5). It was observed that addition of ribocytidine, even in trace amounts improved the quality of electrodeposits. On the addition of 0.005 M ribocytidine, peeling disappeared, while the brightness, smoothness and current efficiency also increased. The maximum cathode efficiency was observed at 0.007 M ribocytidine.

**Table 3.** Effect of current density (CD) on the electrodeposition of nickel

Cd (A/dm <sup>2</sup> )	Nature of deposit	C (%)	Thickness (μm)	Hydrogen gas evolution**
0.1	dark-grey	82.28	1.19	insignificant
0.2	semi-bright	55.99	1.04	insignificant
0.3	greyish-bright	40.86	1.04	a little
0.4	hazy-bright	97.2	3.03	a little
0.5	greyish-bright	50.65	3.40	significant
0.6	semi-bright	56.60	6.63	significant

C = cathode current efficiency (%); \*\* = hydrogen gas evolution at cathode; bath composition: nickel acetate (0.2 M), nickel sulphate (0.2 M) and nickel sulphamate (0.2 M) in formamide; operating conditions: 15 °C

**Table 4.** Effect of temperature on the electrodeposition of nickel

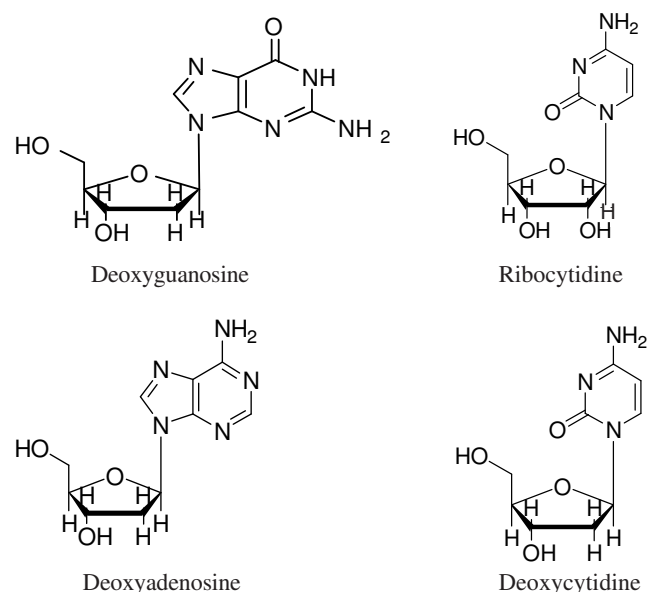
Temp (°C)	Nature of deposit	C (%)	Thickness (μm)	Hydrogen gas **evolution
15	semi-bright*	50.65	3.22	mild
25	bright**	63.94	3.37	mild
35	bright**	77.64	4.11	mild
45	greyish	52.61	2.84	increased
55	grey	78.12	4.04	increased
65	dark-grey	80.12	4.19	increased

C = cathode current efficiency (%); \* = peeling; = mild peeling; \*\* = hydrogen gas evolution at cathode; bath composition: nickel acetate (0.2 M), nickel sulphate (0.2 M), nickel sulphamate (0.2 M), boric acid (0.4 M) in formamide; operating condition: 0.5 A/dm<sup>2</sup> current density

**Effect of deoxycytidine.** On changing the additive from ribocytidine to deoxycytidine in the above system, peeling persisted, unless an optimum concentration of deoxycytidine was used (Table 6). Nevertheless, even a trace amount of deoxycytidine was able to improve the quality of electrodeposited nickel. It was observed that on increasing the concentration of deoxycytidine from 0.005 M to 0.05 M, the brightness diminished to some extent, but the smoothness and uniformness became more significant, and the thickness showed a rising trend up to 0.01 M deoxycytidine, whereafter it declined. The maximum cathode efficiency was exhibited at the 0.03 M concentration of deoxycytidine.

When temperature of the bath was raised from 25 to 45 °C, it was observed that the thickness, as well as the cathode efficiency, did not show any appreciable change. Moreover, the reflectivity declined mildly.

A comparative study of the electrodeposition of nickel in the presence of the two nucleoside additives, namely, ribocytidine and deoxycytidine showed that a peeling effect persisted unless 0.009 M deoxycytidine was added in the bath, whereas even a trace amount (0.005 M) of ribocytidine was sufficient to prevent the peeling effect. It seems that the number of -OH groups present in the furanose ring of a nucleoside affects the adhesion of electrodeposited materials. Ribocytidine having three -OH groups in the furanose ring exhibited better adhesion, as compared to deoxycytidine, which has only two -OH groups in its furanose ring. The nucleosides act as ligands in the formamide medium, which undergo complexation with Ni<sup>2+</sup>, facilitating the slow release of anions in the catholyte, leading



**Fig. 1.** The nucleosides used as the additives in a formamide bath for nickel electroplating.

to pronounced outward nucleation as compared to lateral nucleation. The higher the number of coordinating centres (-OH), the greater is the complexation. It seems that because of this factor, a better quality deposit was obtained with ribocytidine additive, as compared to deoxycytidine bath.

**Effect of deoxyadenosine.** As a second set, deoxyadenosine and deoxyguanosine were chosen for the experimental studies. Firstly, deoxyadenosine was added in instalments to the bath containing nickel acetate, nickel sulphate and nickel sulphamate, along with boric acid as the buffering agent,

**Table 5.** Effect of ribocytidine (RC) on the electrodeposition of nickel

RC (M)	Nature of deposit	C (%)	Thickness ( $\mu\text{m}$ )
0.000	semi-bright*	63.94	3.37
0.005	bright	74.28	5.28
0.007	bright	77.58	4.68
0.009	bright	62.46	4.0
0.01	bright, smooth	68.99	5.16
0.02	less bright	56.65	4.61
0.03	brightness reduced	62.36	4.60
0.04	greyish-bright	60.75	4.38
0.05	greyish-bright	70.55	4.86

C = cathode current efficiency(%); \* = peeling ; “ = mild peeling; \*\* = hydrogen evolution at cathode; bath composition: nickel acetate (0.2 M), nickel sulphate (0.2 M), nickel sulphamate (0.2 M), boric acid (0.4 M) in formamide; additive: ribocytidine (0.05 M); operating conditions: 0.5 A/dm<sup>2</sup> current density and 25 °C temperature

**Table 6.** Effect of deoxycytidine (DC) on the electrodeposition of nickel

DC (M)	Nature of deposit	C (%)	Thickness ( $\mu\text{m}$ )
0.000	semi-bright, mild-peeling	63.94	3.37
0.005	bright, mild-peeling	79.07	4.60
0.007	bright, mild-peeling	76.19	4.75
0.009	bright, no peeling	67.85	4.49
0.01	hazy-bright, smooth	78.39	5.35
0.02	bright	71.80	4.60
0.03	bright, smooth	80.24	4.00
0.04	bright	61.95	4.08
0.05	bright, smooth	60.27	4.49

C = cathode current efficiency (%); bath composition: nickel acetate (0.2 M), nickel sulphate (0.2 M), nickel sulphamate (0.2M), boric acid (0.4 M) in formamide; additive: deoxycytidine (0.005 M to 0.05 M); operating conditions: 0.5 A/dm<sup>2</sup> current density and 25 °C temperature

and its effect was studied on the electrodeposition of nickel. Table 7 shows the effect of the addition of this nucleoside on cathode efficiency, and the thickness and reflectivity of electrodeposits.

The cathode current efficiency showed a mild decreasing trend with the increasing concentration of deoxyadenosine. A similar trend was observed with the thickness of electrodeposited nickel. Mirror bright deposit was obtained only in the presence of little amount of deoxyadenosine. A higher amount of this nucleoside led to deterioration in the quality of the deposit.

**Effect of deoxyguanosine.** Deoxyguanosine was added in trace amounts to the formamide bath containing nickel acetate, nickel sulphate and nickel sulphamate, along with boric acid as the buffering agent, and deposition was monitored with successive additions of the nucleoside (Table 8).

It was observed that the greyish nickel deposit (in the absence of deoxyguanosine) turned hazy-bright in the presence of a trace amount (0.005 M) of this nucleoside. The reflectivity improved on successive increasing additions of deoxyguanosine and electroplates turned totally bright in the presence of 0.01 M of this nucleoside. The presence of (0.005 M) of the nucleoside resulted in improved thickness by two-folds, which remained almost unaffected on further addition of deoxyguanosine. The cathode efficiency also improved when the concentration of the nucleoside was 0.005 M. It exhibited a decreasing and fluctuating trend on further addition of deoxyguanosine.

**Table 7.** Effect of deoxyadenosine (DA) on the electrodeposition of nickel

DA (M)	Nature of deposit	C (%)	Thickness ( $\mu\text{m}$ )
0.000	greyish	2.61	2.84
0.005	mirror-bright	36.55	2.47
0.007	bright, thin black lines	50.45	2.39
0.009	bright, thin black lines	42.47	2.62
0.01	bright, thin black lines	48.60	2.02
0.02	bright, thin black lines	47.82	2.32
0.03	bright, thin black lines	38.95	1.64
0.04	black lines, darkness	30.92	2.20
0.05	black lines, darkness	32.32	1.76

C = cathode current efficiency (%); bath composition: nickel acetate (0.2 M), nickel sulphate (0.2 M), nickel sulphamate (0.2 M), boric acid (0.4 M) in formamide; additive: deoxyadenosine (0.005-0.05 M); operating conditions: 0.5A/dm<sup>2</sup> current density and 45 °C temperature

**Table 8.** Effect of deoxyguanosine (DG) on the electrodeposition of nickel

DG (M)	Nature of deposit	C (%)	Thickness ( $\mu\text{m}$ )
0.000	greyish	52.61	2.84
0.005	hazy-bright	83.92	4.56
0.007	semi-bright	64.15	4.49
0.009	semi-bright	59.99	3.39
0.01	bright	59.29	4.19
0.02	bright	65.71	4.30
0.03	bright	69.38	4.64
0.04	bright	64.02	4.30
0.05	bright	74.14	4.68

C = cathode current efficiency (%); bath composition: nickel acetate (0.2 M), nickel sulphate (0.2 M), nickel sulphamate (0.2M), boric acid (0.4M) in formamide; additive: deoxyguanosine (0.005-0.05 M); operating conditions: 0.5 A/dm<sup>2</sup> current density and 45 °C temperature

A comparative study of the effect of two nucleosides, namely, deoxyadenosine and deoxyguanosine, shows that the latter acted in a better way in improving the physical characteristics of the deposited nickel. The thickness data showed that the presence of deoxyguanosine resulted in thickness of around 4  $\mu\text{m}$ , while deoxyadenosine gave a thickness of approximately 2  $\mu\text{m}$ . The cathode current efficiency in the presence of similar concentrations of the two nucleosides always exhibited higher value with deoxyguanosine than deoxyadenosine.

The reflectivity also exhibited a better trend in the presence of deoxyguanosine, in the presence of which a bright plate was obtained. The better deposit with deoxyguanosine as the additive may be attributed to structural changes between the two nucleosides. Deoxyguanosine has one more coordinating centre for complexation as compared to deoxyadenosine. It facilitates slow release of cations in the catholyte leading to better outward lustre and the perfect growth results in thick deposition with appreciable cathode efficiency.

The purine ring in deoxyadenosine (Fig. 1) contains five coordinating (N-) centres, whereas in deoxyguanosine, the purine ring additionally contains one more coordinating centre (-OH). In both structures, the sugar ring is the same. This additional coordinating centre appears to affect the quality of the electrodeposit.

## Conclusion

It is concluded, from the observations presented, that the presence of nucleosides in trace amounts in the nickel acetate (0.2 M), nickel sulphate (0.2 M), nickel sulphamate (0.2 M) and

boric acid (0.4 M)/formamide bath leads to improved quality of nickel deposits. The addition of only 0.005 M ribocytidine completely prevented the peeling effect, which otherwise appeared at low temperature (15 °C). Mirror-bright electrodeposits were produced in the presence of 0.005 M deoxyadenosine. Thick deposits with good cathode efficiency appeared in the presence of deoxyguanosine, with completely bright deposits appearing when the concentration exceeded 0.01 M. Deoxycytidine when added at concentration of 0.01 M to nickel acetate (0.2 M), nickel sulphate (0.2 M), nickel sulphamate (0.2 M) and boric acid (0.4 M)/formamide bath, operated at 0.5A/dm<sup>2</sup> and 45 °C, resulted in thickest nickel electrodeposit (5.35  $\mu\text{m}$ ).

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