Pit-Free Nickel Electroplating

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The wide use of nickel coatings is due to their valuable properties.[1–2] Nickel coatings are used primarily for decorative and industrial purposes. The uses of nickel in the decorative field are numerous including automobile parts, furniture, general hardware and fasteners, bicycles, as undercoats in low-cost jewelry, sporting equipment, toys, cutlery, lamps and plumbing fixtures. Most of the decorative applications involve products that are used almost daily by the average consumer—the highly decorative, smooth, bright, pit-free and corrosion-resistant nickel-chromium deposits.

Less familiar is the industrial use of electrodeposited nickel for electroforming and other engineering applications where it is expected to provide resistance to corrosion, oxidation and wear.

Decorative nickel coatings are obtained by plating from solutions containing organic additives. Nickel coatings for engineering purposes are, on the other hand, produced from solutions that deposit pure nickel. In general, deposit properties such as corrosion resistance, strength and ductility are influenced by composition of the solution.

In decorative nickel plating, the most common defects are darkening of recessed areas, surface roughness and pitting.[3] Among these defects, pitting is very common, resulting in heavy rejections. Pitting in nickel deposits may be due to substrate surface defects, firm attachment of air or gas bubbles on the surface, presence of organic or inorganic contaminants in solution or the presence of oily globules formed over the solution due to incomplete dissolution of additives. Pitting is normally reduced either by motion of the cathode during plating, by cathode-rod or by solution-agitation. Pitting can also be brought down by reducing the surface tension of the solution with a suitable wetting agent. The use of compressed air for agitating the electrolyte may introduce finely divided oil droplets.

In this paper, the authors report on the usefulness of potassium chloride versus nickel chloride as a bath constituent for substantial minimization of pitting of deposits. The effects of sodium chloride or ammonium chloride instead of nickel chloride in the nickel bath is also reported.[4–6] Other deposit characteristics studied are the effects of operating parameters on bath characteristics such as surface tension and throwing power, and deposit properties such as stress, microhardness and structure.

MATERIALS AND METHODS

Experiments were carried out by nickel plating from solutions of different compositions on cold-rolled steel specimens (7.5 × 5.0 × 0.5 cm). After a visual inspection of the deposits, their microhardness and surface structure were examined. The electrolytes were tested for surface tension, throwing power, current efficiency and rate of build-up as well as their suitability for producing bright deposits in the as-plated condition.

PRETREATMENTS

The steel specimens were degreased and subsequently electrocleaned in an alkaline solution consisting of 35 g/L sodium hydroxide and 25 g/L sodium carbonate cathodically for 2 minutes, and anodically for 1 minute at 70°C and at a current density of 14 A/dm^2. The specimens were then washed under running tap water. After a 15-second dip in a 5% by volume sulfuric acid solution, each specimen was again washed under tap water. Following a rinse in distilled water, the specimens were subjected to the plating operation.

PREPARATION OF THE PLATING BATHS

Laboratory grade chemicals were used for preparation of baths. The Watts nickel bath was prepared by dissolving the required quantity of boric acid in hot distilled water followed by the addition of nickel chloride and nickel sulfate. Finally, the solution was made up to the required volume (2 liters).

The baths consisting of potassium chloride, sodium chloride and ammonium chloride were prepared in the same manner. Although a solubility of more than 40 g/L of potassium chloride was difficult to achieve at room temperature, complete dissolution was easily obtained at 50°C, the temperature at which plating was carried out. Dissolution to an extent of more than 80 g/L of potassium chloride was not possible even when temperatures were elevated further.

CURRENT EFFICIENCY AND RATE OF BUILD-UP

Cold-rolled steel specimens were plated with nickel using an electrolytically pure nickel anode on either side of each specimen. A regulated power supply (15 V, 25 A) was used as the source of direct current and a digital ammeter (0–10 A) was employed for current measurement. All the specimens were cleaned in the same manner, then plated at different current densities (1, 2, and 3 A/dm^2) at 30, 40 and 50°C to adequate thickness for microhardness measurements. The cathode and anode current efficiencies and the rate of build-up or dissolution in each case was respectively calculated on the basis of the actual mass of nickel deposited or dissolved by using Faraday's laws. Duplicate experiments were carried out for each set of conditions under study.

NATURE OF DEPOSIT

Each deposit was examined visually. SEM photomicrographs of certain deposits were also taken at a magnification of 5000×. Pitting was determined by visual inspection.

ADHESION OF DEPOSITS

Adhesion was tested by bending the specimen until fracture of the basis metal occurred.

Table I. Effects of Temperature on Metal Deposition Characteristics of Watts Nickel Bath[a]

Temperature (°C)	*Current Density (A/dm²)*	*Current Efficiency (%)*	*Rate of Build-up (µm/h)*	*Vickers Hardness (kg/mm²)*	*Nature of Deposit*
30	1	—	—	242	dull, white, numerous pits
	2	87.7	21.7	242	dull, white, numerous pits
	3	92.8	33.5	231	dull, white, numerous pits
40	1	97.9	12.5	230	slightly bright, numerous pits
	2	96.4	23.7	237	slightly bright, numerous pits
	3	96.2	34.8	239	slightly bright, fewer pits
50	1	98.3	12.1	237	slightly bright, a few pits in the middle portion
	2	96.9	23.9	231	slightly bright, a few pits
	3	92.2	33.3	247	semibright, no pits

[a] Bath composition: 240 g/L nickel sulfate, 40 g/L nickel chloride, 30 g/L boric acid.

MICROHARDNESS

The microhardness measurements were determined using a load of 25 g. The load was allowed to act on the inverted pyramidal diamond indentor for a duration of 5 seconds.

THROWING POWER

The throwing power is a measure of the ability of a plating bath to produce a coating of even thickness on a cathode shape. The Haring-Blum method is commonly used for determining throwing power. This method uses a cell consisting of a rectangular PVC container (15 × 5 × 7.5 cm) with two 9 × 5 × 0.1-cm sheet-metal cathodes at both ends filling the entire cross section, and a perforated anode of the same size. The anode was placed between the cathodes so that its distance from one of the cathodes was one-fifth the distance from the other. Field's formula, a modified form of the Blum and Haring formula, was used for calculation of the percentage of throwing power.

SURFACE TENSION OF ELECTROLYTE

The surface tension determination was carried out by employing the capillary rise method at 50°C.

BRIGHT PLATING OF NICKEL

Bright deposits were obtained in the as-plated conditions from the different nickel plating baths used by the addition of 1,4-butyne diol (0.6 g/L), saccharin (1.5 g/L) and sodium lauryl sulfate (0.15 g/L). A visual inspection was made of them, and photographs were taken.

RESULTS AND DISCUSSION

The results of different experiments are presented in Tables I–IX.

CURRENT EFFICIENCY

Table I pertains to the effect of temperature on the current efficiency of the Watts nickel bath, its rate of build-up, deposit microhardness and nature of deposits at different current densities (i.e., 1, 2 and 3 A/dm²). In general, with an increase in temperature, the current efficiency increases to some extent and reaches a maximum of 50°C. At 40 and 50°C the current efficiency slightly decreases with an increase in current density. It can thus be concluded that the Watts bath may be operated at 50°C for best results. Further experiments at very high temperatures were not carried out because of the possibility of evaporation. Table II shows the effects of changing the nickel chloride concentration from 10–80 g/L in a solution consisting of

Table II. Effects of Change of Nickel Chloride Concentration in Watts-Type Electrolyte on its Metal Deposition Characteristics at 50°C

Concentration of Nickel Chloride (g/L)[a]	*Current Density (A/dm²)*	*Current Efficiency (%)*	*Rate of Build-up (µm/h)*	*Vickers Hardness (kg/mm²)*	*Nature of Deposit*
10	1	—	—	168	dull, white, full of pits
	2	90.6	22.3	168	white with uniformly distributed pits
	3	94.6	34.2	204	dull, white with fewer number of pits
20	1	94.6	11.6	204	dull, white, full of pits
	2	89.5	22.0	168	dull, white, full of pits
	3	94.2	34.0	196	dull, white, full of pits
60	1	94.6	11.6	291	dull, white, full of pits
	2	94.1	23.2	247	smooth, white, full of pits
	3	92.0	33.2	231	smooth, white with uniformly distributed pits
80	1	99.1	12.2	226	dull, white, full of pits
	2	93.5	23.3	247	smooth, white with a few pits
	3	92.6	33.4	213	dull, white with very few pits

[a] Concentration of other bath constituents: 240 g/L nickel sulfate, 30 g/L boric acid.

Table III. Effects of Substitution of Nickel Chloride in Watts-Type Bath with Potassium Chloride on Metal Deposition Characteristics at 50°C

Concentration of Potassium Chloride (g/L)[a]	*Current Density (A/dm²)*	*Current Efficiency (%)*	*Rate of Build-up (µm/h)*	*Vickers Hardness (kg/mm²)*	*Nature of Deposit*
10	1	99.0	12.2	213	dull, white with a few uniformly distributed pits
	2	94.7	23.3	196	smooth, white with a few pits at the top
	3	—	—	188	dull, white with very few pits at the top
20	1	98.5	12.1	213	smooth, white with a few pits
	2	95.7	23.6	204	smooth, white with no pits
	3	99.6	36.0	196	smooth, uniform, dull, white with no pits
40	1	97.9	12.1	242	smooth, uniform, semibright with no pits
	2	98.8	24.3	231	smooth, uniform, semibright with no pits
	3	99.1	33.8	231	smooth, uniform, semibright with no pits
60	1	97.2	12.0	253	smooth, uniform, dull with no pits
	2	93.2	22.9	265	smooth, uniform, white with no pits
	3	90.5	33.7	253	smooth, dull, white with no pits

[a] Concentration of other bath constituents: 240 g/L nickel sulfate, 30 g/L boric acid.

Table IV. Effects of Sodium Chloride or Ammonium Chloride in Nickel Bath on Deposition Characteristics at 50°C[a]

Salt and Concentration Used	*Current Density (A/dm²)*	*Current Efficiency (%)*	*Rate of Build-up (µm/h)*	*Vickers Hardness (kg/mm²)*	*Nature of Deposit*
40 g/L Sodium chloride	1	98.1	12.1	265	smooth, uniform, dull, white with no pits
	2	93.0	22.9	253	uniform, smooth, white with no pits
	3	91.3	33.0	213	uniform, smooth, semibright with no pits
40 g/L Ammonium chloride	1	94.71	11.7	168	white, full of pits
	2	94.90	23.3	222	dull, white, full of pits
	3	94.30	34.0	188	semibright, full of pits

[a] Concentration of other bath constituents: 240 g/L nickel sulfate, 30 g/L boric acid.

nickel sulfate (240 g/L) and boric acid (30 g/L) at 50°C. The current efficiency increases with an increase in nickel chloride concentration up to 40 g/L, then decreases. A concentration of 40 g/L is the most suitable for the best current efficiency. The bath containing low nickel chloride concentration behaves inconsistently. Table III illustrates the effect of potassium chloride instead of nickel chloride in the Watts-type solution. The current efficiency is more or less steady at all concentrations of potassium chloride and at all current densities employed. In general, there is a marginal increase in current efficiency when potassium chloride is used instead of nickel chloride.

The effects of adding 40 g/L of sodium chloride and 40 g/L of ammonium chloride instead of nickel chlo-

Table V. Effects of Additives in Nickel Electrolyte on Deposition Characteristics at 50°C

Bath Composition			*Current Density (A/dm²)*	*Current Efficiency (%)*	*Rate of Build-up (µm/h)*	*Nature of Deposit*
Bath 1:	240 g/L	Nickel sulfate	1	98.0	10.8	matte white with uniformly distributed pits
	40 g/L	Nickel chloride	2	97.2	22.3	white with pits at the edges
	30 g/L	Boric acid	3	98.5	34.0	white with very few pits at the edges
Bath 2:	240 g/L	Nickel sulfate	1	98.9	10.5	uniformly mirror bright with a few pits
	40 g/L	Nickel chloride	2	97.0	22.7	uniformly mirror bright with pits
	30 g/L	Boric acid	3	96.8	34.9	uniformly mirror bright with pits at the edges
	0.15 g/L	Sodium lauryl sulfate				
	1.5 g/L	Saccharin				
	0.6 g/L	1,4-Butyne diol				
Bath 3:	240 g/L	Nickel Sulfate	1	97.5	11.2	uniformly mirror bright
	40 g/L	Potassium chloride	2	98.7	24.0	uniformly mirror bright
	30 g/L	Boric acid	3	99.6	34.8	mirror bright at the middle and matte white at the edges
	0.15 g/L	Sodium lauryl sulfate				
	1.5 g/L	Saccharin				
	0.6 g/L	1,4-Butyne diol				

Table VI. Effects of Agitation of the Addition of Nickel Chloride and Potassium Chloride in Watts-Type Electrolyte on Metal Deposition Characteristics at 50°C[a]

Agitation	*Current Density (A/dm²)*	*Current Efficiency (%)*	*Nature of Deposit*
No	1	99.2	slightly bright with a few pits at the bottom
	2	98.6	dull, white with a few pits at the edges
	3	98.0	dull, white with more pits
Yes	2	99.9	dull, white with no pits

[a] Bath composition: 240 g/L nickel sulfate, 20 g/L nickel chloride, 20 g/L potassium chloride, 30 g/L boric acid.

ride to the Watts-type composition are indicated in Table IV. The introduction of sodium chloride causes a small loss of current efficiency compared with potassium chloride. In this case, the increase in current density also decreases the current efficiency to some extent at 50°C. With the addition of ammonium chloride, however, an increase in current density has no significant effect on the current efficiency.

The effects of brightener additives in the nickel-plating baths studied are shown in Table V. There is not much appreciable change in the current efficiency with the introduction of brightener additives.

How the addition of both potassium and nickel chlorides (each 20 g/L) to a Watts-type bath affects its performance is indicated in Table VI. The current efficiency of the nickel plating electrolyte is not much affected by a combination of the chlorides used in place of nickel chloride.

RATE OF BUILD-UP

Rates of build-up are presented in Tables I–VI. The rate of build-up continues to increase with an increase in current density and temperature in the case of all the electrolytes studied.

ANODE EFFICIENCY

The purpose of a nickel-chloride additive is mainly to avoid passivation of the anode and to avoid its corrosion; therefore, the effect of potassium chloride on anode corrosion was studied (Table VII). It is observed from the results that the anode corrosion is more or less equal with both systems regardless of whether brightener was added.

MICROHARDNESS

The results on microhardness of nickel deposits obtained from various electrolytes are presented in Tables I–IV. In the case of Watts nickel deposits, the microhardness remains almost the same at all temperatures (Table I); however, when the nickel chloride concentration is increased to 60 g/L (Table II), there is an increase in microhardness. Subsequent increases in nickel chloride concentration cause a decrease in hardness.

It appears that a change of current density does not have any effect on the deposit microhardness. Table III indicates the results of similar studies, with potassium chloride in place of nickel chloride as a bath constituent. In these studies, the microhardness of the deposits increases with an increase in nickel chloride concentration up to 60 g/L. It is of interest that the microhardness corresponding to a 40-g/L-concentration of either potassium chloride or nickel chloride is more or less the same.

Table IV gives the results of experiments with ammonium chloride or sodium chloride instead of nickel chloride as a bath constituent. Ammonium chloride reduces the microhardness of the deposit at all current densities to a considerable extent, whereas sodium chloride acts the same as other electrolytes in this regard.

NATURE OF DEPOSIT

Table I shows the effect of change of temperature on the Watts nickel bath. It is observed that an increase in temperature strikingly improves the brightness of the deposit while bringing down the tendency for pit formation. Tables I and II indicate that pitting is reduced with an increase in current density and that pitting occurs with an unagitated Watts solution at all temperatures and at all current densities; however, as shown in Table III, the use of potassium chloride instead of nickel chloride is associated with considerably less pitting of deposits. Since less pitting occurs as the concentration of potassium chloride is increased, even pit-free nickel deposits could be obtained when a bath containing not less than 20 g/L potassium chloride was operated at any current density in an unagitated condition. On the other hand, when ammonium chloride is used instead of potassium chloride, deposits full of pits could only be produced at 50°C, the temperature at

Table VII. Results of Experiments on Anodic Efficiency at 50°C

Bath Composition			*Current Density (A/dm²)*	*Anodic efficiency (%)*
Bath 1:	240 g/L	Nickel sulfate	1	100.00
	40 g/L	Nickel chloride	2	99.90
	30 g/L	Boric acid	3	99.80
Bath 2:	240 g/L	Nickel sulfate	1	99.20
	40 g/L	Potassium chloride	2	100.00
	30 g/L	Boric acid	3	99.60
Bath 3:	240 g/L	Nickel sulfate	1	98.60
	40 g/L	Nickel chloride	2	99.20
	30 g/L	Boric acid	3	99.60
	0.15 g/L	Sodium lauryl sulfate		
	1.5 g/L	Saccharin		
	0.6 g/L	1,4-Butyne diol		
Bath 4:	240 g/L	Nickel sulfate		
	40 g/L	Potassium chloride	1	99.70
	30 g/L	Boric acid	2	100.00
	0.15 g/L	Sodium lauryl sulfate	3	—
	1.5 g/L	Saccharin		
	0.6 g/L	1,4-Butyne diol		

Table VIII. Throwing Power Values for Various Baths at 50°C

Bath Composition			Throwing power (%)
Bath 1:	240 g/L	Nickel sulfate	7.1
	40 g/L	Nickel chloride	
	30 g/L	Boric acid	
Bath 2:	240 g/L	Nickel sulfate	7.7
	20 g/L	Nickel chloride	
	20 g/L	Potassium chloride	
	30 g/L	Boric acid	
Bath 3:	240 g/L	Nickel sulfate	7.8
	40 g/L	Potassium chloride	
	30 g/L	Boric acid	

Table IX. Surface Tension Values for Various Baths at 50°C

Bath Composition			Surface Tension (dynes/cm)
Bath 1:	240 g/L	Nickel sulfate	69.1
	40 g/L	Nickel chloride	
	30 g/L	Boric acid	
Bath 2:	240 g/L	Nickel sulfate	66.2
	20 g/L	Potassium chloride	
	20 g/L	Nickel chloride	
	30 g/L	Boric acid	
Bath 3:	240 g/L	Nickel sulfate	62.1
	40 g/L	Potassium chloride	
	30 g/L	Boric acid	

which the experiments were carried out, and at all current densities employed. Even though sodium chloride as an alternative constituent was found to yield pit-free nickel deposits under the conditions used, the deposits were inferior to those obtained with either sodium chloride or nickel chloride electrolytes.

Results as given in Table V show that with an increase in either of the brightener additives (unagitated nickel chloride or potassium-chloride-based electrolytes) mirror-bright deposits can be produced, although with pitting in the former case.

THROWING POWER

Table VIII gives the percentage of throwing power values obtained for different nickel-plating electrolytes. One can infer from the results that the use of potassium chloride instead of nickel chloride marginally increases the throwing power. The throwing power value of the mixed chloride bath lies in between throwing power values for baths with one of the chlorides. It is clear that the potassium chloride bath produces a more uniformly distributed deposit, even on irregularly shaped articles.

SURFACE TENSION

Table IX presents the results of the surface tension measurements carried out at 50°C for three different nickel plating electrolytes. The value for the Watts-type electrolyte containing nickel chloride is higher than the one for potassium chloride solution. Since the surface tension value of the potassium-chloride-containing electrolyte is lower, hydrogen bubbles formed during plating escape quicker and easier from the bath than from the other electrolytes studied. This is probably why little or no pitting occurred in the deposits obtained from the potassium chloride electrolyte. Introducing a wetting agent such as sodium lauryl sulfate when the bath is operated at 50°C, brings the surface tension still further down, resulting in the quick escape of hydrogen bubbles and in the formation of uniform nickel deposits with no pitting, even from a unagitated bath.

CONCLUSIONS

From this study it may be concluded that the following bath composition is suitable for the production of uniform deposits free from surface defects such as pitting, even without bath agitation or moving the work:

Nickel sulfate	240 g/L
Potassium chloride	40 g/L
Boric acid	30 g/L
pH	4.5–5.5
Temperature	50°C
Current density	1.0–3.0 A/dm^2

If necessary, a brightener system may also be introduced into the solution to produce defect-free bright deposits. **MF**

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