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EVALUATION OF VARIABLES WHICH AFFECT THE
HARDNESS OF NICKEL PLATE DEPOSITED
FROM WATTS-TYPE BATHS

G. S. Petit, R. R. Wright and W. A. Neff

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Oak Ridge Gaseous Diffusion Plant
Union Carbide Corporation
Oak Ridge, Tennessee

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ABSTRACT

In the course of the Cascade Improvement Program many component equipment parts will be electroplated with nickel for corrosion protection. The maximum hardness which will be acceptable in the electroplated deposit is specified in Union Carbide's Job Specification JS-1396, Revision 3, entitled *Electroplated Nickel Coatings on Steel Parts*. The hardness specification is intended primarily as a control over both organic and inorganic impurities in the deposit.

This report covers a study evaluating several of the numerous controllable variables which influence the hardness of the nickel plate deposited from a Watts-type bath. The variables tested were: 1) bath composition, 2) pH, 3) current density, 4) anode-cathode area ratio, and 5) bath temperature. Within the tested ranges of the variables studied, the pH and current density had the most influence on the plate hardness. The softest deposit was obtained with a bath pH of 1.5, a current density of 30 to 40 amperes/square foot, and with the anode-cathode area ratio in the range of 3:1 to 1:1.

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EVALUATION OF VARIABLES WHICH AFFECT THE
HARDNESS OF NICKEL PLATE DEPOSITED
FROM WATTS-TYPE BATHS

In the course of the Cascade Improvement Program (CIP) many component equipment parts will be electroplated with nickel for corrosion protection. For the Process Equipment Modification (PEM) phase of this program, the three gaseous diffusion plants will receive parts plated from both Watts- and sulfamate-type electro nickel plating baths.⁽¹⁾

The hardness specifications for plated items to be used in this program are presented in Union Carbide's Job Specification JS-1396, Revision 3, entitled *Electroplated Nickel Coating on Steel Parts*. The hardness specifications (max.) are: 200 diamond pyramid hardness (DPH) for Watts nickel and 250 DPH for sulfamate nickel. The hardness specification is intended as a control over both organic and inorganic impurities in the plate, since they may contribute to poor weldability. Excessive hardness implies either moderately high organic impurities or high inorganic impurities.

There is very limited information available in the literature on the plating variables which affect the hardness of nickel plated from a purified Watts-type bath. As a consequence, the Plating Development Group of the Chemical Analysis Department, Laboratory Division, was requested by the Engineering Division and the Gaseous Diffusion Development Division to evaluate the variables which affect the plate hardness of nickel deposited from such a plating bath.

A number of controllable variables influence the plate hardness. Those which were evaluated during this portion of the study are: 1) bath composition, 2) pH, 3) current density, 4) anode-cathode area ratio, and 5) bath temperature.

Most of the testing was done with coupons of 0.14 sq ft area, and an anode area of 3 sq ft, providing an anode-cathode area ratio of 21:1. The bath volume was 160 liters (approx. 42 gal). It was realized at the outset that these conditions were not optimum to achieve the lowest hardness. They were used, nevertheless, during the initial phases of coupon testing to minimize the effects from variance in the bath composition, pH adjustment, cathode area, etc., while evaluating the effects of the more specific variable being studied. After the optimum bath conditions were established for plating coupons, a more realistic (production practice) anode-cathode area ratio range (3:1 to 1:1) was used to study the specific effect of this area ratio.

SUMMARY

Several variables in the electroplating of nickel from a Watts-type bath have been evaluated to determine their influence on plate hardness, a specification parameter used to limit organic and inorganic impurities

in the plate. Such impurities result in poor weldability. The variables tested were: 1) bath composition, 2) pH, 3) current density, 4) anode-cathode area ratio, and 5) bath temperature. Within the tested ranges of the variables studied, the pH and current density had the most effect on the plate hardness. The softest deposit was obtained with a bath pH of 1.5, a current density of 30 to 40 amperes/square foot (ASF), and an anode-cathode area ratio in the range of 3:1 to 1:1.

EXPERIMENTAL

BATH COMPOSITION

Two different Watts-type bath compositions were evaluated during the course of the study. The baths were 42-gal, composed as follows:

Reagent Chemical	Bath No. 1		Bath No. 2	
	oz/gal	g/l	oz/gal	g/l
NiSO ₄ ·6H ₂ O	57.2	428	44	330
NiCl ₂ ·6H ₂ O	9.4	70	6.9	52
Ni ⁺⁺ (total)	15.1	113	11.6	87
H ₃ BO ₃	6.8	51	6.4	50
Sodium Lauryl Sulfate	0.1	1	0.1	1

Various Watts-type bath formulations all contain the same nickel salts and boric acid but the nickel concentrations can vary by greater than 40%. To evaluate the effect of bath composition, two baths were evaluated which were in the high and medium range of nickel content; as seen in the table above, Bath No. 1 contained about 25% more nickel than Bath No. 2.

BATH PREPARATION

Concentrated solutions of nickel sulfate and nickel chloride were mixed in proper proportions to give the desired final amount of nickel after pH adjustment to 5.7 with nickel carbonate. Adjustment to pH 5.7 causes the precipitation of many inorganic metallic impurities. The solution was filtered to remove any precipitated impurities, and refiltered through activated carbon to remove organic contaminants. The boric acid was dissolved in water, filtered, and refiltered through activated carbon before adding to the bath. The bath volume was adjusted to 42 gal with distilled water. The surface tension was adjusted and maintained at 30 to 32 dyne/cm with sodium lauryl sulfate.

pH ADJUSTMENT

After dilution to 160 liters (42 gal), the resultant pH was approximately 4.7. Subsequent adjustments to lower the pH were made with dilute (10% vol/vol) sulfuric acid (H₂SO₄).

The plate hardness was evaluated for Bath No. 1 at pH levels of 4.2, 3.8, 3.3, 2.8, 2.4, 2.0, 1.5, and 1.3. Bath No. 2 was evaluated at pH levels of 4.7, 4.2, 3.6, 3.2, 2.6, 2.0, 1.75, 1.5, and 1.3.

CURRENT DENSITY

The current density range of 10 to 60 ASF was investigated at each pH for each bath.

ANODE-CATHODE AREA RATIO

Most testing was done using two 2.5-in.-dia disks (0.14 sq ft total area) as the cathode for each set of conditions studied. The cathodes were placed between two banks of anodes and approximately 7 in. from each bank. The total anode area at the outset was approximately 3 sq ft; this gradually decreased with usage over the period during which these tests were conducted. The solution volume was maintained at 160 liters. Keeping the cathode area small, as provided by the two coupons, was instrumental in minimizing changes in pH and anode area during the plating operations, and permitted operation in an optimum (lower) voltage range at the higher current densities. Larger cathode areas, varying from 1 to 3.6 sq ft, were also plated at intervals to obtain the desired anode-cathode area ratios.

BATH TEMPERATURE

Most of the plating was performed at 55°C; however, at pH 1.5, bath temperatures of 47 and 62°C were also investigated over the current density range of 10 to 60 ASF.

RESULTS

The test results are presented with graphical and tabular data, accompanied by general interpretations. First presented is the large amount of data obtained using a cathode area of 0.14 sq ft, provided by two coupons. These results are followed by a limited amount of data obtained under comparable conditions of pH, current density, and temperature, using a larger cathode area. These latter data show the influence of anode-cathode area ratio on the hardness of nickel deposited under otherwise similar conditions.

COUPON STUDIES

The effects of pH and current density while plating two coupons in Bath No. 1, the more concentrated bath, are presented graphically in figures 1 and 2. Comparable results for coupons plated in Bath No. 2 are presented in figures 3 and 4. The data were presented in two ways to emphasize the effects of current density and pH; both presentations from each bath are useful in understanding the relationships of these variables.

These graphs, figures 1 through 4, are plotted as the best curves, in the authors' judgment, from the actual data obtained on measurement of hardness and the controlled variables. Because of the numerous curves on each figure, the points have been omitted from these plots. The values obtained for each current density and pH which establish these curves are presented in tables 1 and 2 in order to enable the reader to better evaluate the data.

Figure 1

EFFECTS OF pH AND CURRENT DENSITY ON HARDNESS OF ELECTRO NICKEL PLATE
BATH NO. 1 AT 55°C (COMMON - pH CURVES)
ANODE AREA 3 SQ FT (APPROX.)
CATHODE AREA 0.14 SQ FT

Figure 2
EFFECTS OF pH AND CURRENT DENSITY ON HARDNESS OF ELECTRO NICKEL PLATE
BATH NO. 1 AT 55°C (COMMON - ASF CURVES)
ANODE AREA 3 SQ FT (APPROX.)
CATHODE AREA 0.14 SQ FT

Figure 3
EFFECTS OF pH AND CURRENT DENSITY ON HARDNESS OF ELECTRO NICKEL PLATE
BATH NO. 2 AT 55°C (COMMON - pH CURVES)
ANODE AREA 3 SQ FT (APPROX.)
CATHODE AREA 0.14 SQ FT

Figure 4

EFFECTS OF pH AND CURRENT DENSITY ON HARDNESS OF ELECTRO NICKEL PLATE
BATH NO. 2 AT 55°C (COMMON - ASF CURVES)
ANODE AREA 3 SQ FT (APPROX.)
CATHODE AREA 0.14 SQ FT

Table 1
PLATED COUPON HARDNESS
BATH NO. 1 AT 55°C

Bath pH	Hardness, DPH at Current Density, ASF				
	10	20	30	40	60
4.2	299	294	262	264	242
3.8	312	295	285	272	247
3.3	312	289	274	256	240
2.8	322	294	266	254	238
2.4	309	292	276	270	254
2.0	342	289	238	247	249
1.5	279	209	209	207	230
1.3	299	209	216	218	213

Table 2
PLATED COUPON HARDNESS
BATH NO. 2 AT 55°C

Bath pH	Hardness, DPH at Current Density, ASF					
	10	15	20	30	40	60
4.7	336	-	317	292	287	283
4.2	274	-	251	242	243	256
3.6	322	304	256	235	245	258
3.2	347	310	286	263	262	267
2.6	336	318	288	233	216	256
2.0	270	221	247	232	231	230
1.75	314	242	218	210	213	230
1.5	299	249	238	188	197	198
1.3	299	258	216	209	199	215

General Interpretations

Examination of the coupon data leads to the following general interpretations:

1. The hardness decreases most sharply as the pH is lowered from 2.5 to 1.5.

2. A sharp decrease in hardness occurs as the current density is increased from 10 to 20 ASF.
3. The optimum current density range for producing a soft plate (under the other test conditions) is approximately from 30 to 40 ASF.
4. Except at a current density of 10 ASF, a slightly softer plate is obtained from Bath No. 2 (lower nickel concentration).

LARGER CATHODE STUDIES

The effect of cathode area on plate hardness was investigated at several pH conditions for Bath No. 2 at current densities of 10 and 20 ASF. Table 3 compares the nickel hardness obtained on coupons (0.14 sq ft area) to that obtained on large cathodes (2 sq ft area) under similar conditions of pH and current density. Similar comparisons with a greater variety of cathode sizes in Bath No. 1, and limited to pH 1.5 conditions, are presented in table 4.

Table 3

CHANGE IN HARDNESS VERSUS CHANGE IN CATHODE AREA

Bath No. 2

Anode Area Approx. 3 sq ft

pH	Current Density, ASF	Coupon Cathode		Large Cathode		Δ DPH (coupon- large cathode)
		Area, sq ft	Hardness, DPH	Area, sq ft	Hardness, DPH	
3.2	10	0.14	327	2	260	67
2.6	10	0.14	336	2	232	104
2.0	10	0.14	270	2	238	32
1.75	10	0.14	314	2	249	65
3.2	20	0.14	270	2	260	10
2.6	20	0.14	247	2	225	22
1.75	20	0.14	218	2	206	12

Table 4

CHANGE IN HARDNESS VERSUS CHANGE IN CATHODE AREA

Bath No. 1 at pH 1.5

Anode Area Approx. 3 sq ft

Current Density, ASF	Coupon Cathode		Large Cathode		Δ DPH (coupon- large cathode)
	Area, sq ft	Hardness, DPH	Area, sq ft	Hardness, DPH	
10	0.14	279	1	209	70
10	0.14	279	1.5	215	64
10	0.14	279	3.6	199	80
20	0.14	209	1	186	24
20	0.14	209	1.5	171	38
20	0.14	209	2.0	199	10
20	0.14	209	3.6	183	26

To characterize more fully the effect of cathode area on plate hardness at pH 1.5 in Bath No. 2, a series of tests was performed using two sizes of cathode and plating over the current density range of 10 to 60 ASF. The results are presented graphically in figure 5. In the current density range of 20 to 60 ASF, the plate specimens with the larger cathode area were an average of at least 25 DPH units softer than the smaller specimens. At 10 ASF, the larger plate specimens were in excess of 60 DPH units softer than the smaller ones.

General Interpretations

Examination of these data and graphs related to the studies with larger cathodes leads to the following general interpretations:

1. The hardness is consistently lower at a current density of 20 ASF than at 10 ASF.
2. In the current density range of 20 to 60 ASF, the plate specimens with the larger cathode area are softer than with the coupons.
3. The effect of pH change is not linear.
4. An anode-cathode area ratio in the range of 3:1 to 1:1 yields the softest deposit.

Figure 5
EFFECT OF CATHODE AREA ON HARDNESS
BATH NO. 2 AT 55°C
ANODE AREA 3 SQ FT (APPROX.) pH 1.5

TEMPERATURE STUDIES

The effect of bath temperature on plate hardness was investigated for both bath compositions at pH 1.5. Coupons were plated at 47, 55, and 62°C with current densities varying from 10 to 60 ASF. The results for baths 1 and 2 are presented in figures 6 and 7, respectively.

General Interpretations

Examination of these results leads to the following general interpretations:

1. At 47°C, the hardness at 20 ASF is appreciably lower than in the region of 40 to 60 ASF, for both bath compositions.
2. In the current density range of 30 to 60 ASF, the choice of temperature in the region of 55 to 62°C, would have little effect on the plate hardness, using either bath.

DISCUSSION AND CONCLUSIONS

A large number of variables are involved in any electro-nickel plating operation. Although a few of these (bath composition, pH, current density, anode-cathode area ratio, and temperature) have been evaluated in this study, extrapolation of the findings to a production facility cannot be made directly. The hardness values of the nickel plate obtained by a production vendor using operating conditions intended to be similar to those employed in this study will probably vary from those presented in this report. Variations in size and design of plating tanks, different anode-cathode area ratios, unique configuration of parts being plated, and method of bath agitation are only a few parameters which might affect the hardness of plate obtained in practical commercial experience.

The effects of pH and current density on the hardness of electro-nickel plate obtained by a vendor should follow the trends shown in this study. The lower anode-cathode area ratios employed in production plating should result in a softer plate.

The tests performed in this study indicate that operation of an electro-nickel plating bath at a pH of 1.5, a current density between 20 and 40 ASF, and with an anode-cathode area ratio in the range of 3:1 to 1:1, will produce a soft plate. In that region of ASF, a solution temperature of 55°C would be optimum.

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1. Dibari, George A., "Nickel Plating", *Metal Finishing Guidebook and Directory*, 42nd Ed., Metals and Plastics Publications, Inc., Hackensack, New Jersey, 1974, pp. 340-373.

Figure 6
EFFECT OF TEMPERATURE ON HARDNESS
BATH NO. 1 - pH 1.5
ANODE AREA 3 SQ FT (APPROX.)
CATHODE AREA 0.14 SQ FT

Figure 7
EFFECT OF TEMPERATURE ON HARDNESS
BATH NO. 2 - pH 1.5
ANODE AREA 3 SQ FT (APPROX.)
CATHODE AREA 0.14 SQ FT

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