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EVALUATION OF THE EFFECT OF
IMPURITIES IN NICKEL PLATE
DEPOSITED FROM A WATTS-TYPE BATH

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MASTER

May 1978

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OAK RIDGE, TENNESSEE

*prepared for the U.S. DEPARTMENT OF ENERGY under
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IN NICKEL PLATE DEPOSITED FROM A WATTS-TYPE BATH

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Special Services Department
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Oak Ridge Gaseous Diffusion Plant
Union Carbide Corporation
Oak Ridge, Tennessee

Prepared for the U.S. Department of Energy under U.S. Government
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ABSTRACT

This report covers a study made to evaluate the effect of ≤ 5 ppm of an octyl ortho-phthalate ester and varied amounts of iron contamination on the hardness of nickel plate deposited from a Watts-type nickel plating bath. The effect of iron contamination on the plate hardness was evaluated at 200, 400, 800, and 1,200 ppm in the bath. The amount of iron codeposited with the nickel at the various levels of iron contamination in the bath was also evaluated.

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EVALUATION OF THE EFFECT OF IMPURITIES
IN NICKEL PLATE DEPOSITED FROM A WATTS-TYPE BATH

INTRODUCTION

During 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.*

The hardness specifications for plated items to be used in this program are presented in Union Carbide's Job Specification JS-1396, Revision 4, entitled *Electroplated Nickel Coating on Steel Parts*. The maximum hardness specifications are 200 Vickers hardness HV₁₀₀ for Watts nickel and 250 HV₁₀₀ 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.

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. A number of controllable variables influence the plate hardness. Those which were evaluated during an earlier study include the following: bath composition, pH, current density, anode-cathode area ratio, and bath temperature.**

This report covers a study of the effects of trace amounts of an octyl ortho-phthalate ester (≤ 5 ppm) and varied amounts of iron contamination on plate hardness.

Octyl ortho-phthalates are plasticizers in the polyvinyl chloride (PVC) lining used on many plating tanks, and iron is a contaminant easily picked up from drillings, grindings, and other operations performed near the plating area or from carryover from the acid pickling tank into the plating solution.

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

**Petit, G. S., Wright, R. R., and Neff, W. A., *Evaluation of Variables Which Affect the Hardness of Nickel Plate Deposited from Watts-Type Baths*, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee, January 21, 1976 (K-1869). UNCLASSIFIED.

SUMMARY

Trace amounts of the octyl-ortho-phthalate ester (≤ 5 ppm) increase the nickel plate hardness and causes stress cracks in the deposit. Iron contamination at levels of 200, 400, 800, and 1,200 ppm in the bath was evaluated. The plate hardness increases with the amount of iron in the bath. The amount of iron codeposited with the nickel at the various levels of iron in the bath was also evaluated.

EXPERIMENTAL

BATH COMPOSITION

The bath was prepared similar to Bath No. 2 reported in K-1869.* The exact composition is presented as follows:

<u>Reagent Chemical</u>	<u>oz/gal</u>	<u>g/liter</u>
NiSO ₄ ·6H ₂ O	44.2	332
NiCl ₂ ·6H ₂ O	7.3	55
Ni ⁺⁺ Total	11.7	88
H ₃ BO ₃	7.0	53
Sodium Lauryl Sulfate	0.2	1

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 160 liters (42 gal) with distilled water. The surface tension was adjusted and maintained at 32 to 33 dynes/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).

*K-1869, *loc. cit.*

BATH ANALYSIS FOR METALLIC IMPURITIES

A sample of the bath after purification was analyzed by spectrochemical analysis for metallic impurities. The results are presented in Table 1.

Table 1

METALLIC IMPURITIES FOUND IN NICKEL PLATING BATH

<u>Element</u>	<u>ppm</u>	<u>Element</u>	<u>ppm</u>
Aluminum	<2	Lead	<2
Calcium	85	Magnesium	150
Chromium	0.5	Potassium	5
Cobalt	100	Sodium	600
Copper	<1	Zinc	.7
Iron	<0.5		

SAMPLES PLATED FROM 160-LITER TANK

The 160-liter (42 gal) tank was used in the earlier study,* and the initial coupons were plated from this tank to serve as reference coupons before using a smaller container (26 liters) for the contamination study. A schematic of the smaller setup is presented in Figure 1. This will provide data on any changes of hardness caused by the smaller volume, change in agitation, and anode arrangement in the smaller container used for the contamination study.

The pH of the solution was adjusted to 3.4 and different sets of three coupons (0.40 ft² total area) were plated at current densities of 10, 20, 30, and 40 ASF. The hardness of these coupons ranged from 50 to 70 HV₁₀₀ units higher than the coupons plated earlier under the same conditions.* Several of these coupons showed stress cracks, Figure 2.

The plating tank had been relined with PVC after the initial study, but had been treated with 10% sulfuric acid followed with water. Both the acid and water were heated to 60°C to leach the plasticizer from the lining. The plating solution was analyzed by infrared spectroscopy for octyl ortho-phthalate, the plasticizer used in PVC. It was determined that the solution was contaminated with 5 ppm of the octyl ortho-phthalate ester.

*K-1869, *loc. cit.*

DWG. NO. G-77-796
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Figure 1

PLATING BATH SET-UP FOR IMPURITIES STUDY

NEGATIVE NO. A-4800

IX

NEGATIVE NO. A-4799

IX

Figure 2
NICKEL-PLATED COUPONS FROM BATH CONTAMINATED WITH
5ppm OCTYL ORTHO-PHTHALATE
(Note Cracks in Deposits)

EVALUATION OF CHANGE IN HARDNESS BY OCTYL ORTHO-PHTHALATE

The 26-liter container was used to evaluate the change in hardness versus concentration of octyl ortho-phthalate. Coupons were plated at 10, 20, and 30 ASF at a contaminant level of 5 ppm. Half of the solution (13 liters) was then treated with activated carbon to remove the contaminant, returned to the 26-liter container, and blended with the untreated portion to obtain a level of 2.5 ppm octyl ortho-phthalate. Coupons were then plated at 10, 20, 30, and 40 ASF.

The entire solution was then treated with activated carbon to remove the contaminant. The container was rinsed to remove any trace of contaminant and the filters in the pumps were replaced. The purified solution was returned to the tank, and coupons were plated at 10, 20, 30, and 40 ASF. The results are presented graphically in Figure 3. Many of the coupons plated at the 5-ppm level of octyl ortho-phthalate had stress cracks, as shown in Figure 2.

The pH of a bath containing 2.5 ppm of octyl ortho-phthalate was lowered to 2.5 with sulfuric acid and coupons were plated at 10, 20, 30, and 40 ASF. The coupons plated at pH 2.5 were lower in hardness by 20 to 30 hardness units (HV₁₀₀) than were the coupons plated at pH 3.4, Figure 4.

This demonstrates very emphatically the effect of trace organic impurities on the quality of the deposited nickel. Other organics, such as plasticizers used for other types of tank linings, could cause the same effect.

Attempts to plate nickel foils onto a titanium substrate were unsuccessful because of the high stress in the deposited nickel.

EVALUATION OF THE EFFECT OF IRON ON PLATE HARDNESS

The purified 26-liter bath was adjusted to pH 2.5 for a study of the effects of iron in the nickel plating bath. The bath was contaminated with iron at levels of 200, 400, 800, and 1,200 ppm iron. Coupons were plated at 10, 20, 30, and 40 ASF at each level of iron contamination. The changes in hardness at these different levels of iron contamination are presented in Figure 5.

IRON IN NICKEL DEPOSIT VERSUS IRON CONTENT OF BATH

Nickel foils were plated onto titanium so that they could be easily stripped from the substrate and analyzed for iron concentration codeposited with the nickel at the various concentrations of iron in the bath. All foils for this test were plated at 20 ASF, and an additional point at 1,000 ppm iron in the bath was also obtained. The results are presented in Figure 6.

Figure 3

HARDNESS OF NICKEL PLATE VERSUS CONCENTRATION OF ORGANIC IMPURITY

Figure 4
HARDNESS OF NICKEL PLATE VERUS pH OF BATH

Figure 5

HARDNESS OF NICKEL PLATE VERSUS IRON CONCENTRATION IN BATH

Figure 6

IRON IN NICKEL PLATE VERSUS CONCENTRATION OF IRON IN BATH

IRON IN NICKEL DEPOSIT VERSUS CURRENT DENSITY

Nickel foils were plated onto titanium at 10, 20, 30, and 40 ASF from a bath containing 1,200 ppm iron. The foils were analyzed for iron concentration in the nickel plate. The results are presented in Figure 7.

DISCUSSION

The effect of trace amounts of organic contamination in a nickel plating bath on the quality of the deposited nickel has been demonstrated by octyl ortho-phthalate. Trace amounts of other organics can also cause the same effect. The separation and identification of many different organics as impurities require considerable effort, but the plater can remove the contaminant and maintain a good quality plate by routine carbon filtration of the bath.

The amount of iron used in the study far exceeds that found in any of the plating baths analyzed at the Oak Ridge Gaseous Diffusion Plant. Routine plating of scrap metal at low current densities will remove iron and many other impurities. If analysis of metallic impurities in the bath by spectrochemistry shows a high impurity level, a high pH, precipitation and filtration should be performed.

ACKNOWLEDGMENTS

The authors wish to acknowledge the valuable assistance of R. R. Wright, Special Services Department, in setting up the test apparatus and R. G. Vornehm, Special Services Department, for supervising the hardness measurements.

Figure 7
IRON IN NICKEL PLATE VERSUS CURRENT DENSITY

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