Appendix I – Capsule Report: Coventya Low Nickel EN Bath Chemistry

Introduction

This capsule report was prepared under EPA Grant Number 00E02050, funded through the EPA Source Reduction Assistance Grant Program. This program funds Pollution Prevention (P2) assistance projects that provide technical assistance and/or training to businesses/facilities to help them adopt source reduction approaches.

Various tasks have been performed under this EPA grant. The purpose of this particular project was to demonstrate certain pollution prevention (P2) aspects of a new electroless nickel (EN) bath chemistry. The new EN solution contains approximately 50% less nickel than a conventional EN bath. The P2 project focused on the potential reduction of water use, reduction of nickel discharges to the treatment system, reduction of sludge generation, reduction of off-site disposal, and reduction of air emissions.

The project was performed at a metal finishing facility in Michigan that operates an automated EN barrel line for plating small automotive parts. During the P2 demonstration a conventional mid-phosphorus 6 g/l nickel bath was replaced with a mid-phosphorous 3 g/l nickel concentration bath (RI8712) formulated by Coventya Chemicals Company.

Background Information

EN plating is an autocatalytic process used to deposit nickel-phosphorus or nickel-boron alloy onto metal or plastic substrates to impart corrosion and/or wear resistance. Performed without the use of an electric current, this process gained commercial popularity in the 1950s and has grown into an immensely popular surface coating technology.

The majority of EN plating is done using nickel phosphorus chemistry with resulting deposits that provide a low coefficient of friction, are anti-galling and have superior as-plated hardness that can be further hardened by post-plating heat treatment processes. These deposits also have excellent corrosion performance in many types of environments. Nickel boron alloys are widely used in electronics and aerospace applications. The deposits provide high electrical conductivity, low contact resistance, excellent as-plated hardness, a high melting range, outstanding wear resistance, and are easily soldered or brazed. For some applications nickel boron is used as a replacement for hard chrome plating.[1]

EN is often referred to as a self-limiting process, because chemical reactions taking place during its use cause the formation of by-products that eventually force replacement of the bath. The main constituents of a nickel phosphorus EN bath are nickel ions (added as nickel sulfate other nickel salt), sodium hypophosphite, buffers and complexors. During use, while nickel is being deposited, sodium hypophosphate reacts with water to form sodium orthophosphate and hydrogen gas. Chemical additions of nickel solution and hypophosphate will allow the EN bath to continue working, but eventually the buildup of sodium orthophosphate and other constituents reduces the deposition rate and affects the quality of the deposit (e.g., reduction in smoothness and brightness) as well as physical properties such as magnetics and solderability. At some point, the EN bath is partially (bleed and feed) or entirely replaced with fresh chemistry. Used EN solution is treated on-site or sent off-site for recovery or disposal.[2]

The conventional EN phosphorus chemistry is formulated with 6 g/l nickel and 25 g/l or higher sodium hypophosphate. EN bath use is measured in metal turnovers (MTO). One MTO occurs for each 6 g/l of nickel added back to the system. In a sodium hypophosphite bath using nickel sulfate, the by-products include sulfate, sodium and orthophosphite. About 45-60 g/l of reaction by-products are formed every MTO. Because of the buildup of bath impurities and ensuing deposition problems, the practical number of MTOs before disposal is necessary is 4 to 10 MTOs. Therefore, over the course of the bath's life, a total of approximately 24 to 60 g/l nickel is deposited as a useful surface coating.[1]

Evaluation

An evaluation of potential P2 benefits and associated cost savings was conducted using existing facility data, established emission factors, information provided by the chemical supplier, and testing. This work is discussed in this section.

The project was performed at a metal finishing facility in Michigan that operates an automated EN barrel line for plating small automotive parts. On the average, this facility operates their EN line two days per week and processes approximately 40 barrels per day.

Dragout and Rinsing Test. Dragout volumes were measured during the study for both the high nickel and low nickel bath chemistries using the methodology presented in the *Rinsing Manual*.

The rinse system (Figure I-1) consists of a stagnant dragout rinse, followed by a two stage counterflow flowing rinse (1.9 gpm). The dragout tank is drained to the wastewater treatment (WWT) system after each day of processing. The counterflow rinse is operated continuously during production and shut off during idle periods.

Prior to the start of each test, the dragout and rinse tanks were emptied and refilled with fresh water. Then, barrels were processed through the plating line. After removal from each process and rinse tank, the barrels were rotated above the tanks to improve drainage. The time between barrels being processed was approximately the same in each case, about 15 minutes. Samples were collected from the dragout tank and first counterflow rinse tank after each barrel was processed.

This procedure was performed for both the high and low nickel concentration baths. A total of 12 barrels were processed for the high nickel bath and 11 barrels for the low nickel bath. The data for the dragout rinse and flowing rinse are presented respectively in Tables I-1 and I-2.

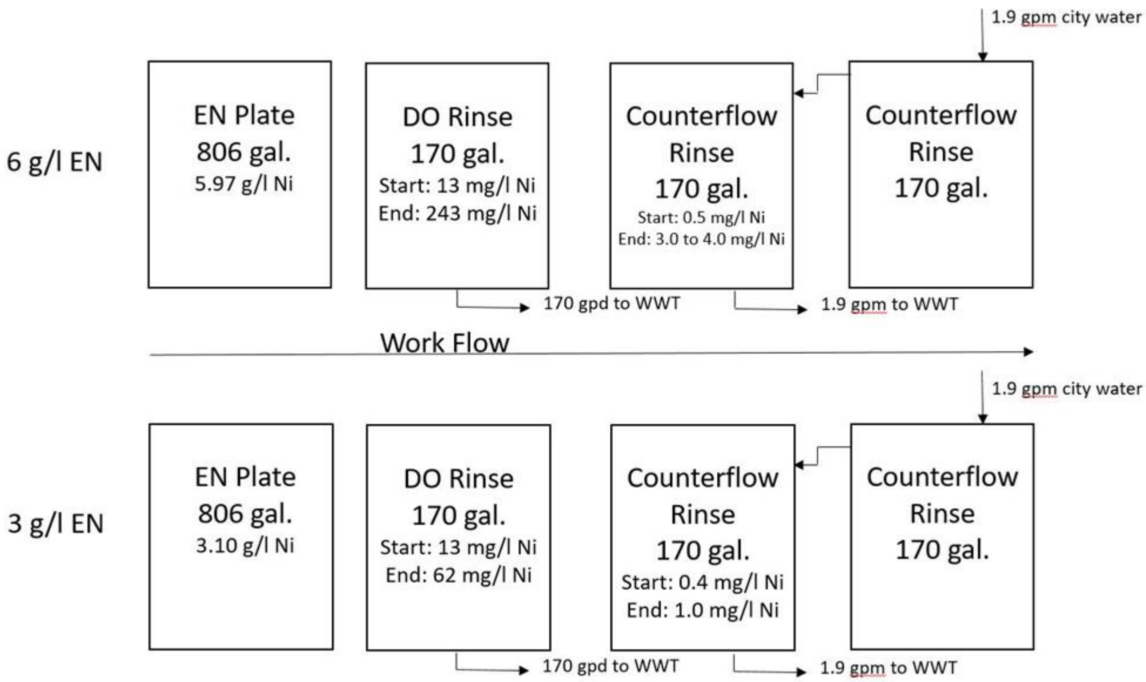

Figure I-1. EN Barrel Plating and Rinse System

Table I-1. Dragout Rinse Tank Measurements

	Nickel, mg/l	
Barrels Rinsed	**6 g/l Electroless Nickel Bath**	**3 g/l Electroless Nickel Bath**
0	13	13
1	22	18
2	92	20
3	125	23
4	131	24
5	151	30
6	165	35
7	170	42
8	190	44
9	202	50
10	219	56
11	232	62
12	243	-

Table I-2. Flowing Rinse Tank Measurements

	Nickel, mg/l		
Barrels Rinsed	**Following the 6 g/l Electroless Nickel DO Tank**	**Following the 3 g/l Electroless Nickel DO Tank**	**Ratio of Nickel Concentration 6 g/l:3 g/l**
0	0.5	0.4	1.3
1	0.8	0.5	1.6
2	1.0	0.6	1.7
3	2.0	0.6	3.3
4	1.0	0.6	1.7
5	2.0	0.8	2.5
6	1.0	0.9	1.1
7	3	0.9	3.3
8	3	1	3.0
9	4	1	4.0
10	4	1	4.0
11	4	1	4.0
12	3	-	-
Average Ratio			2.6

The volume of dragout for the test was calculated using the equation:

$$D_{total} = (C_{end} - C_{start}) * V / C_{bath}$$

And the average dragout volume per barrel was calculated as follows:

$$D_{avg} = D_{total} / N$$

where:

- D_{total} = Total dragout volume during test (gal.)
- D_{avg} = Average dragout volume per barrel (gal.)
- C_{start} = Concentration of nickel in the dragout rinse tank at start of test (mg/l)
- C_{end} = Concentration of nickel in the rinse tank at end of test (mg/l)
- N = Number of barrels processed through the dragout rinse tank during the test
- V = Volume of rinse tank (gal.)
- C_{bath} = Concentration of nickel in the process bath (mg/l)

The results of the dragout test show that the average dragout per barrel (D_{avg}) for the two baths were:

- D_{avg} for 6 g/l bath = 0.55 gal/barrel
- D_{avg} for 3 g/l bath = 0.24 gal/barrel

The dragout volume for the 6 g/l nickel bath is 2.3 times greater than for the 3 g/l bath. This difference is due to the higher total dissolved solids and resultant higher viscosity of the 6 g/l nickel bath. Liquids with high viscosity drain slowly and therefore more dragout is retained by the plated parts and barrel.

Data for the flowing rinse (Table I-2) show that the concentration of nickel in the first counterflow rinse reaches equilibrium after approximately 6 to 8 barrels being processed. The concentration of nickel at equilibrium is 3 to 4 mg/l for the high nickel bath and 1 mg/l for the low nickel bath. The ratio of nickel concentration for the two baths (nickel concentration of 6 g/l divided by 3 g/l) in the flowing rinse is shown in the last column. The average ratio was 2.6, which is similar to the dragout volume ratio discussed above.

Air Emissions. Nickel air emissions were evaluated during the project using emission factors generated by the Metal Finishing Association of Southern California (MFASC), with collaboration of the South Coast Air Quality Management District (SCAQMD) and the California Air Resources Board (Table I-3). As shown, air emissions from EN plating are approximately an order of magnitude lower than nickel electroplating with air agitation, which is presented here for comparison.

Emissions are proportional to the concentration of the "pollutant" of concern in the process tank.[3] Therefore, assuming that the SCAQMD emission factors were based on a conventional 6 g/l nickel bath, the approximate emissions from a 3 g/l nickel bath is 3.8×10^{-7}.

Table I-3. SCAQMD Emission Factor Summary From Test Reports

Process	Pollutant	Emission Factor
Electroless Nickel (6 g/l bath)	nickel	7.5×10^{-7} lb./hr-ft^2 tank
Nickel Plating w/ air agitation*	nickel	6.5×10^{-6} lb/hr-ft^2 tank

The EN tank surface area at Finishing Services is 46 ft^2. Typical operation of the EN bath is 16 hrs/week, 50 wks/yr. Therefore, for the two EN baths, estimates of annual nickel emissions are:

- 6 g/l EN Bath: 0.0276 lb Ni/yr.
- 3 g/l EN Bath: 0.0138 lb Ni/yr.

Bath Disposal. As discussed previously, EN baths can be replenished with nickel and reused up to a point and then must be discarded due to a buildup of by-products. At the demonstration facility, the average life of the 6 g/l bath is 8 MTOs. Theoretically, the 3 g/l bath will be able to be operate 9 to 9.5 MTOs if the operating contamination level is the same as the 6 g/l bath. This is due to the lower dissolved solids present in a new 3 g/l bath, which results in a chemical system that is able to hold more reaction by-products than a 6 g/l solution.[1], [4]

Historically, the volume of spent 6 g/l bath shipped off-site for disposal is approximately 21,000 gal/yr. The cost is $1.53/gal, including freight and disposal. Assuming an increase from 8 MTOs to 9 MTOs for the 3 g/l bath, the disposal rate for the lower nickel solution will be approximately 18,700 gal/yr. The annual disposal projections for the two baths are:

- 6 g/l EN Bath: $32,130/year
- 3 g/l EN Bath: $28,611/year

When discarded, the baths contain approximately 100% of their operational nickel concentration or 6.0 g/l and 3.0 g/l respectively for the 6 g/l and 3 g/l baths.[6] The volume of the EN bath is 806 gal., therefore, the mass of nickel annually discarded is:

- 6 g/l EN Bath: 1,050 lb Ni/yr.
- 3 g/l EN Bath: 468 lb Ni/yr.

Wastewater Treatment

Wastewater from the EN plating line includes daily discharges the dragout tank and the continuous discharge from the counterflow rinse. The annual volume of wastewater generated by the 6 g/l bath is 108.2 Kgal. The projected annual volume for the 3 g/l bath is 52.1 Kgal.

Dragout tank discharges are pretreated using a high pH process to precipitate the complex nickel and then processed through the general WWT system. The discharge of the counterflow rinse goes directly to the general WWT system (pH adjustment, precipitation/clarification and sludge dewatering).

P2 Benefits and Cost Savings

Projected pollution prevention benefits and cost savings attributed to the 3 g/l bath are shown in Table I-4.

Table I-4. Pollution Prevention Benefits and Cost Savings

EN Bath	Water/Sewer		WWT (dragout and rinse)		WWT Sludge Disposal		Bath Replenishment		Bath Disposal	
	Kgpy	$/yr	Kgpy	$/yr	Lbs./yr	$/yr	gpy	$/yr	gpy	$/yr
6 g/l	108.2	$866	108.2	$1,499	448	$892	21,000	$84,000	21,000	$32,130
3 g/l	52.1	$417	52.1	$722	216	$430	18,700	$65,450	18,700	$28,611
3 g/l Savings	56.1	$449	56.1	$777	232	$462	2,300	$18,550	2,300	$3,519

Water and sewer cost ($8.00/Kgal) based on actual cost. WWT costs ($13.85/Kgal) and sludge generation (4.14 lbs/Kgal treated) based on industry averages from PRIM survey. EN solution cost is $4.00/gal for 6 g/l bath and $3.50/gal for 3 g/l bath.

The projected overall cost savings for the 3 g/l system is $23,757 per year.

Additional Information

This project focused on certain potential P2 benefits of a low nickel EN bath. Coventya Chemicals Company has conducted other testing related to the production aspects of the technology. A useful article written by Coventya Chemicals Company, entitled *Reduced Ion Electroless Nickel to Meet a Sustainable Future* is available at no cost on the Surface Technology Environmental Resource Center (STERC) at http://www.sterc.org/subs/rinseman.php.

[6] EN baths at this facility are replenished continuously and therefore when spent, the bath contains the normal operating concentration of nickel (i.e., 3 or 6 g/l Ni).

References

[1] Barnstead, Mike and Morcos, Boules; Electroless Nickel Plating, Products Finishing, Feb., 2011.

[2] USEPA, Extending Electroless Nickel Bath Life Using Electrodialysis.

[3] Zinkus, Glenn A. and Klink, Kevin; Air Emission Factors for Metals Finishing Operations, AESF/EPA Conference for Environmental & Process Excellence, 2003.

[4] Schaffer, Ambrose; Reduced Ion Electroless Nickel to Meet a Sustainable Future, Surface Technology Environmental Resource Center (STERC), Technical Articles, Nov. 2018.