U.S. Environmental Protection Agency Region 9
Pollution Prevention Program

Extending Electroless Nickel Bath Life Using Electrodialysis

INTRODUCTION

This pollution prevention (P2) project was conducted under a partnership between U.S. Environmental Protection Agency (EPA) Region 9; the Arizona Department of Environmental Quality; the City of Phoenix; the American Electroplaters and Surface Finishers Association; and Metco Metal Finishing, Inc. (Metco). This partnership was created to promote P2 techniques and technologies, identify P2 technology needs, and accelerate P2 technology transfer within the metal finishing industry. Technical support for this project was provided by Tetra Tech EM Inc. The project was funded by EPA Region 9.

ELECTROLESS NICKEL PLATING

Electroless nickel (EN) plating is a nonelectrolytic process that uses chemical oxidation and reduction reactions to produce a nickel deposit on parts. EN plating is the most common type of nonelectrolytic plating performed and has the following advantages over conventional nickel electroplating: (1) a uniform coating is produced on parts, even those with complex shapes; (2) EN deposits are typically less porous, providing excellent wear and corrosion resistance; (3) nonconducting surfaces can be nickel-plated; and (4) racking may be simpler because no electrical contact is needed between parts and the rack.

EN baths are successfully operated over 15 regenerations using electrodialysis; annual cost savings at one facility are $50,570 from reduced EN chemical use, liquid waste disposal, and rejection of parts.

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Electroless Nickel Plating Chemistry

Ni^{+2}	+	NaH_3PO_2	+	buffers, complexors	=>	(Ni + P)	+	H_2	+	NaH_3PO_3
Nickel ion		Hypophosphite				Nickel deposit		Hydrogen gas		Orthophosphite

The main constituents of an EN bath include nickel ions, hypophosphite, buffers, and complexors. The nickel ions, often added to the bath as nickel sulfate, combine with phosphorous during the plating process to form the nickel deposit. Hypophosphite, typically present as sodium hypophosphite, is the reducing agent that catalyzes chemical reduction of nickel ions. Buffers maintain the pH of the bath, and complexors maintain the nickel ions in soluble form; both stabilize the bath and help maintain a steady plating rate.

BY-PRODUCTS AND CONTAMINANTS

During EN plating, by-products of the chemical reaction, including orthophosphite, sodium sulfate, and ammonia, build up and decrease bath performance. Orthophosphite, which is produced when hypophosphite is oxidized during the plating reaction, is the most significant by-product. As the concentrations of by-products increase, the nickel deposition rate decreases. EN bath use is measured in metal turnovers (MTO); one MTO is defined as plating onto parts the amount of nickel equivalent to that in a single new bath. During production, chemicals are added to the bath and multiple MTOs are produced from a single bath. As the EN solution ages, the deposition rate of the bath plating decreases (see Figure 1). In addition, the nickel plating becomes more porous and tensile-stressed, and its appearance becomes less lustrous. Physical properties such as magnetics and solderability may also be adversely affected.

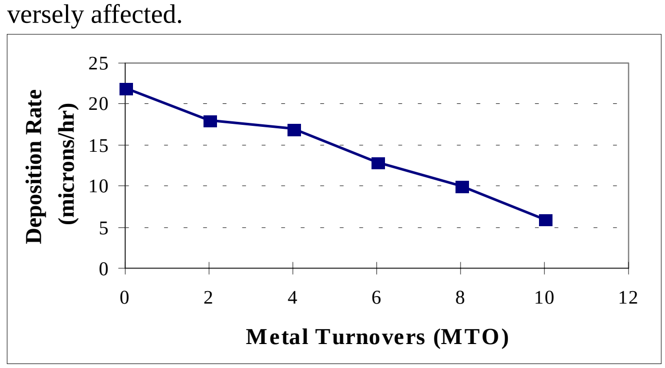

Figure 1. The EN deposition rate decreases by 40 percent after six MTOs. In most commercial applications, EN baths average five MTOs for aluminum parts and seven MTOs for ferrous parts before they are spent.

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Metals from parts being plated, such as aluminum, zinc, and copper, and dragin contaminants may also accumulate in the bath and negatively affect bath quality and stability. Eventually the nickel deposit no longer meets specifications or the deposition rate reaches a level that does not meet production requirements, resulting in the need to dump the spent bath.

Frequent bath make-ups result in significant operating costs from high EN process chemical purchases. In addition, the large volume of highly concentrated spent EN solution generated requires expensive treatment and disposal. Spent EN baths must be treated separately from other waste streams because the complexors can interfere with traditional metal precipitation processes. On-site treatment of spent EN solution typically involves nickel plate-out using caustic and other chemicals and bleeding the treated solution into a wastewater treatment system. Some facilities ship their spent EN baths off site to a treatment facility that reclaims and recycles the nickel.

ELECTRODIALYSIS

Electrodialysis can be used to regenerate spent EN baths by selectively removing orthophosphite and other contaminants. An electrodialysis unit consists of a stack of semipermeable, cation- and anion-selective membranes arranged in alternating order with a cathode and anode at either end of the stack (see Figure 2). During electrodialysis operations, spent EN solution is pumped into the "concentrate" compartments of the unit, and deionized (DI) water is pumped into the "diluate" compartments. A rectifier creates an electrical potential across the membranes, causing anions to migrate toward the anode and cations to migrate toward the cathode. Anion-selective membranes allow only undesirable anions such as orthophosphite and sulfate to flow into the diluate compartment of the unit while retaining the hypophosphite in the concentrate compartments. Cation-selective membranes allow sodium and other cationic contaminants ions to pass through the membrane into the diluate compartments while retaining the larger nickel ions in the concentrate compartments. In this way, desirable EN bath components are retained in the concentrate, which is reused in the EN process bath, and undesirable components accumulate in the diluate, which is removed for disposal.

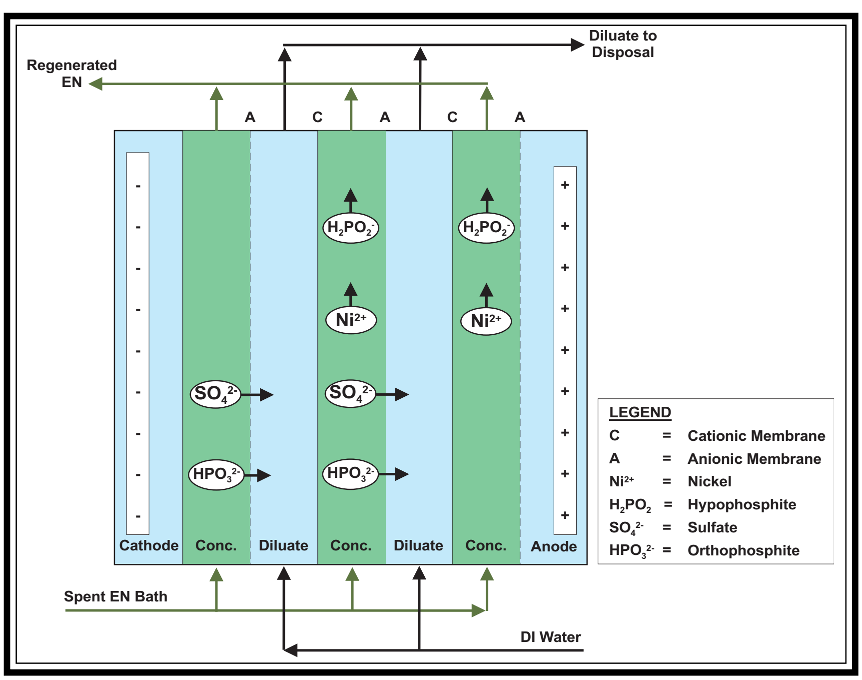

Figure 2. Cross section of electrodialysis unit

Electrodialysis is a batch process, and the regeneration rate depends on the size of the electrodialysis unit and the volume and concentration of influent spent solutions. The electrodialysis unit has a meter that monitors the total dissolved solids (TDS) or conductivity of the EN solution. As the concentrations of orthophosphite and other by-products decrease in the EN bath, TDS levels and conductivity decrease proportionately. Orthophosphite concentrations can also be directly measured using titration methods.

Electrodialysis Membranes

- Membrane size depends on the bath volume, dump frequency, and bath concentration.
- The total membrane surface area typically ranges from 35 to 190 square feet.
- The maximum temperature rating of a membrane is typically about 110 °F; therefore, baths must be cooled before electrodialysis.
- The membrane life expectancy ranges from 1 to 7 years.
- Fouling can be minimized by filtering the solution before electrodialysis.

The electrodialysis process typically produces a regenerated bath with 60 percent of the original bath volume. Most of the volume lost in the electrodialysis process is dissolved salts and water, but small amounts of desirable components, such as nickel, hypophosphite, buffers, and complexors, are also lost to the diluate stream. After bath regeneration, replenishment chemicals are added to the bath in order to restore the chemical concentration and balance, and DI water is added to restore the original bath volume. The diluate waste stream is generated at a rate of about 40 to 60 gallons per 100 gallons of EN bath regenerated, part of which is DI water. The diluate contains a low concentration of nickel and small amounts of active chelators, and it can usually be bled into a conventional wastewater treatment system, or disposed of off site

CASE STUDY:
METCO METAL FINISHING, INC.

Metco is a medium-sized metal finishing job shop in Phoenix, Arizona. Metco has five primary process lines: (1) copper, tin, and EN plating; (2) zinc plating; (3) anodizing and conversion coating; (4) zinc phosphate; and (5) bright nickel.

On the copper, tin, and EN plating line,

Typical Maintenance Requirements for Electrodialysis Unit

- ✓ ***Pretreatment filters*** - The frequency of changing pretreatment filters varies depending on the amount of suspended solids, oil, and grease in the bath.
- ✓ ***Membrane cleaning and replacement*** - The membranes require periodic cleaning to prevent fouling and may need to be replaced every 1 to 7 years.
- ✓ ***Cathode stripping*** - During electrodialysis, a small amount of nickel may be plated onto the cathode. The cathode is made of stainless steel and can be stripped in dilute nitric acid.

Metco has three 170-gallon EN plating tanks; while two tanks are being used for plating, the third is used for bath storage or is cleaned. Metco uses Fidelity 9002 bath chemicals supplied by OMG Fidelity, Inc., that provide a bright, 7- to 9-percent phosphorous (mid-phosphorous) nickel deposit.

Before using electrodialysis, Metco made up 71 new EN baths per year; used 9,120 gallons of EN plating solution per year; and spent $37,630 for new bath make-up chemicals and $43,380 for chemical additions. The average EN bath at Metco was operated for five to six MTOs before disposal. Metco shipped spent baths off site for treatment and disposal at a cost of $31,740 per year.

ELECTRODIALYSIS TRIAL

In cooperation with EPA Region 9, Metco identified electrodialysis as a technology with the potential to reduce its waste by recovering nickel and hypophosphite from spent EN baths for reuse. To determine the effectiveness of this technology, Metco performed a 3-month trial with a demonstration electrodialysis unit manufactured by Zero-Discharge Technologies, Inc., for OMG Fidelity, Inc. The demonstration unit had the capacity to reduce the contaminant level of a 100-gallon bath used for five MTOs to a level corresponding to one MTO in 48 hours. During the trial period, Metco regenerated and reused an EN bath six times with no degradation in bath or plating quality. The EN bath was used for four or five MTOs between regenerations, or for a total of over 28 MTOs. Each regeneration of a spent EN bath reduced its orthophosphite concentration from an average of 140 to 28 grams per liter.

Figure 3. Full-scale electrodialysis unit at Metco

FULL-SCALE ELECTRODIALYSIS IMPLEMENTATION

Based on the performance of the demonstration unit, Metco decided to implement a full-scale electrodialysis unit manufactured by Zero-Discharge Technologies, Inc. (see Figure 3). The unit has a total of 30 diluate and concentrate compartments and was designed with a regeneration capability of reducing the contaminant level of a 100-gallon bath from a six-MTO equivalent to a one-MTO equivalent in 48 hours. The unit requires 21 ampere of electrical current and 380 watts per hour of electrical power.

After a 3-month shake-down period, Metco is using the electrodialysis unit to operate EN baths through 15 regenerations and five MTOs between regenerations, for a total of over 75 MTOs per bath. Metco maintains four EN baths — two in operation, one in storage, and one undergoing electrodialysis — to ensure the availability of regenerated EN baths for production.

Reject rates on the EN line have decreased by about 50 percent, and reject costs have decreased from an average of $1,700 to $523 per month. Metco attributes most of this change to the more consistent plating quality provided by dialyzed EN baths.

Because of the increased EN bath life, Metco estimates that it will have to prepare only three new baths per year compared to 71 baths per year without electrodialysis. Moreover, because of EN bath regeneration, EN process chemical purchases have decreased by 25 percent.

The electrodialysis unit has also improved process efficiency at Metco by significantly decreasing the "break-in" time for EN baths. Line operators prefer using EN baths processed by electrodialysis because they provide the desired plating quality almost immediately, whereas new EN baths achieve the desired quality only after one MTO.

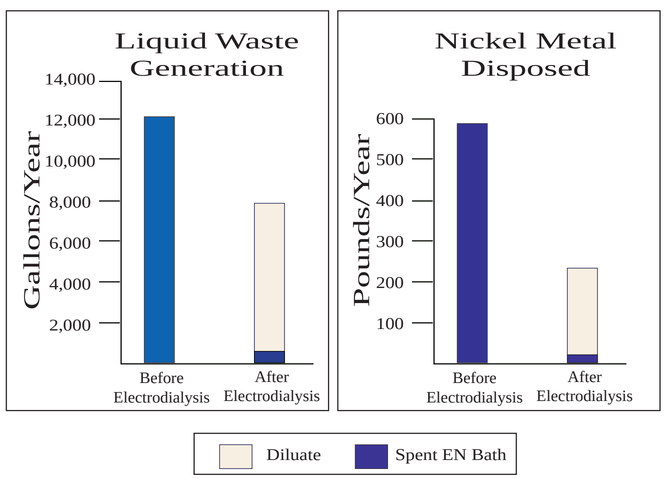

Figure 4. Total EN liquid waste disposal has been reduced by 33 percent.

Figure 5. Total nickel mass disposed has been reduced by 56 percent.

EN bath regeneration generates about 100 gallons of diluate waste solution per 170 gallons of spent EN bath regenerated. Despite the new diluate waste, Metco has reduced the total volume of its EN liquid waste streams by 3,860 gallons per year using electrodialysis (see Figure 4). Based on the nickel concentrations in the spent EN bath and diluate waste streams, the total mass of nickel disposed of has decreased by 321 pounds per year (see Figure 5). Total EN process chemical use has decreased by 25 percent, and EN liquid waste generation has decreased by 33 percent.

Total EN process chemical use has decreased by 25 percent, and EN liquid waste generation has decreased by 33 percent.

Metco ships the diluate waste stream off site for treatment at a unit cost of $0.77 per gallon compared to the $2.63 per gallon paid for disposal of spent EN solution. Therefore, Metco has realized a 77 percent reduction in the total liquid waste disposal cost associated with EN. Other facilities may realize even greater savings by treating the diluate on site in a conventional wastewater treatment system. For example, the typical operating cost for a conventional wastewater treatment system is $0.15 per gallon of wastewater. Metco is currently evaluating and testing on-site treatment options for the diluate to further reduce the disposal cost; however, Metco's current ion exchange wastewater treatment system may have difficulty in handling the high TDS content of the diluate.

The capital cost of the 30-compartment electrodialysis unit is $28,000. A total of 4.5 hours of Metco staff labor was required to install the unit. **The payback period for the unit is about 7 months.**

Operation and Maintenance

- Each EN bath regeneration takes 60 hours and 2.5 hours of staff labor.
- The full-scale unit uses 1-micron pretreatment filters that are changed every 3 months.
- Membranes are cleaned every 3 months using nitric acid, requiring 2 hours of staff labor.
- Three months of shakedown time was required for the full-scale unit.
- Solid, plastic fittings and plumbing should be used to avoid small leaks associated with flexible fittings and hoses.
- Electrodialysis effectiveness is monitored by performing nickel, hypophosphite, and orthophosphite analyses using on-site titration methods.

ELECTRODIALYSIS CASE STUDY RESULTS

BEFORE - WITHOUT ELECTRODIALYSIS

EN Bath O&M	Unit Cost	Annual Cost[a]
New EN Bath Make-ups	$530/bath	$37,630
EN Chemical Additions	$611/bath	$43,380
Spent EN Solution Disposal	$447/bath	$31,740
Labor - Make-ups	$25/bath	$1,780
EN Rejects - Cost	$1,700/month	$20,400
		Total = $134,930

AFTER - WITH ELECTRODIALYSIS

EN Bath O&M	Unit Cost	Annual Cost
New EN Bath Make-ups	$530/bath	$1,590[b]
EN Chemical Additions	$542/bath	$43,380[d]
Regeneration Additions	$202/regen	$15,550[c]
Spent EN Solution Disposal	$447/bath	$1,340[b]
Labor - Make-ups	$25/bath	$75[b]
EN Rejects - Cost	$523/month	$6,280
		Total = $68,220

Electrodialysis Unit O&M	Unit Cost	AnnualCost[c]
Diluate Disposal	$77/regen	$5,930
Labor - Regeneration	$125/regen	$9,630
Labor - Membrane Cleaning	$100/cleaning	$400
Electricity	$13/month	$160
		Total = $16,120

Total Savings = $50,600/year
Electrodialysis Unit Capital Cost = $28,000
Installation Labor = $225
Total Capital Cost = $28,225

Payback Period = 7 months

[a] = Based on 71 new bath make-ups per year
[b] = Based on three new bath make-ups per year
[c] = Based on 77 regenerations per year
[d] = Chemical additions during bath operation remained the same.

For more information on the Metco case study or other EPA Region 9 P2 projects, please contact the following individuals:

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Assistance for this fact sheet was provided by Tetra Tech EM Inc.