Electrochemical Treatment of Spent Electroless Nickel Solution

By Rudy Macko & Tom Mason

Electroless nickel (EN) coatings are widely used in the manufacture of automotive parts, providing uniform coating, corrosion protection, wear resistance and lubrication. In contrast to EN plating benefits, the disposal and treatment of waste solutions can cause many difficulties. The use of electrochemical treatment technology greatly improves the operation of the main wastewater treatment process and reduces operation costs. A new, state-of-the-art jobshop in the Chicago area that provides EN plating for the automotive industry has installed a large separated electrolytic cell for the treatment of spent EN solution (from dumps and wastewater). The waste/wastewater is handled by the separated electrolytic cell, batch treatment system, filter press and neutralization station. The implementation of modern electrolytic technology and auxilliary equipment provides an effective waste treatment process that meets environmental compliance criteria.

This article is an edited version of a Poster Paper featured at the AESF/EPA Conference for Environmental Excellence, held during AESF Week 2000 in Orlando this past January.

Electroless Nickel Overview

Electroless nickel (EN) plating is a relatively young plating method compared with other metal plating. The advantage of EN plating is its ability to coat interior surfaces of pipes, valves and other parts, along with applicability on a variety of materials, such as metal, plastic, glass and ceramics. Electroless nickel plating provides uniform coating, corrosion protection, wear resistance and lubrication.

In contrast to EN benefits, the disposal and treatment of waste solution can cause many difficulties. Nickel is a regulated metal and, therefore, needs to be removed from spent EN solution or rinsewater prior to discharge.

Traditional Approach

The traditional treatment approach, which precipitates nickel from wastewater/waste solutions and then separates it from water as sludge, is a relatively difficult process. The EN bath formula contains stabilizers, brighteners, inhibitors and buffering organics, which produce complex metals and interfere with the metal precipitation techniques. Large dosages of treatment chemicals, such as sulfides, carbonates, carbamates or reducing agents (hydrazine, borohydride) need to be applied in order to remove nickel to compliance levels.

EN rinsewater is typically directed to the main wastewater stream and processed by in-house wastewater treatment processes for precipitation and separation of nickel.

Ion exchange (IX) technology is another option for the removal of nickel from EN rinse streams. Ion exchange rinses are regenerated with acid upon saturation with nickel. Spent IX regeneration solutions containing a few grams of nickel per liter need to be treated. It can be batch or electrolytic treatment for removal of nickel, or it can be hauled away for off-site disposal.

Disposal and treatment approaches of spent EN bath solutions vary. EN dumps can be metered to plant wastewater streams and treated in wastewater treatment systems. Other alternatives are batch or electrochemical treatment or hauled off-site by licensed haulers.

Innovative Treatment Of EN Waste Solution

The market research indicated that the Chicago, IL, area had limited EN plating capacity. A number of EN plating works was performed by platers in other states. The result of this fact was the opening of a new plating shop, North American EN, Inc. (NAEN), in Elk Grove Village, IL, in September 1998. NAEN focused on applying a state-of-the-art plating process to meet customer requirements, along with effective modern waste management, to comply with and exceed environmental criteria.

NAEN runs high- and mid-phosphorus electroless nickel bath solutions and operates lines that can process rack or barrel plating.

EN plating operations generate two types of liquid waste: rinsewater and spent bath solution. A few treatment alternatives of generated waste solutions were evaluated.

Selection Criteria

The considered criteria for selection for treatment approach were:

- Space
- Effective process requiring low labor, energy and chemical consumption
- Reasonable capital cost.

Selected waste management operation employs a combination of in-house treatment process and service program.

Overall wastewater treatment setup consists of ion exchange, batch treatment with filter press, electrolytic separated cell and effluent neutralization (final pH adjustment).

Rinsewater from the EN plating operation is handled by serviced ion exchange. IX canisters are replaced and regenerated at the servicing IX company after saturation with nickel. Spent concentrate solutions (*e.g.*, cleaners) and floor spills are handled by batch treatment for removal of regulated metals, which are precipitated and separated by filter press.

Spent electroless nickel bath solution is handled by separated electrolytic cell and batch treatment.

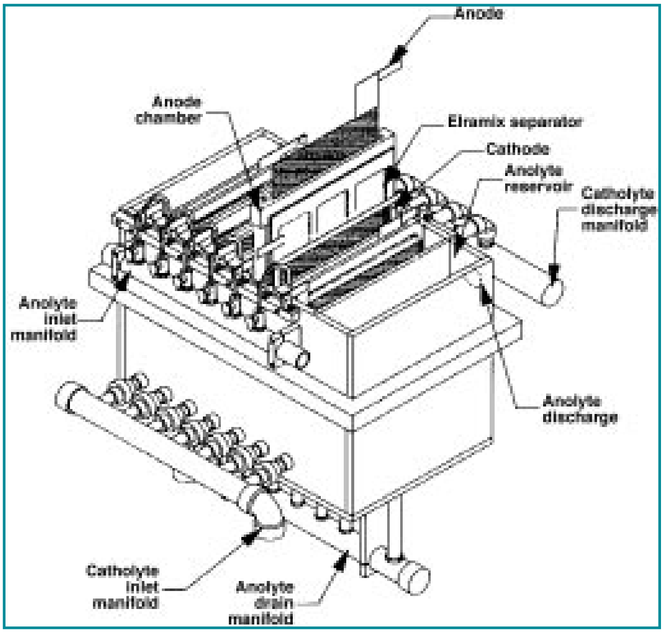

Fig. 1—Electrolytic recovery cell.

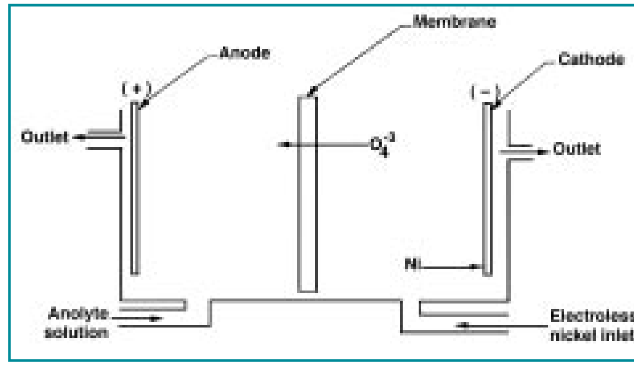

Fig. 2—Electroless nickel recovery.

Electrochemical Treatment Of Spent EN Bath Solution

Electrodialysis and electrowinning technologies are suitable to remove nickel from spent EN solution. These electrochemical treatments for nickel removal and recovery are seldom used.

Standard electrowinning process using regular electrolytic cell for depositing of nickel on the cathode is exhibiting low current efficiency. Improvements and development of a new generation of electrolytic cells, however, enable recovery of metal from difficult metal plate-out solutions and significantly improve and economize the electrolytic process.

Separated Electrolytic Cell

The separated electrolytic cell is a proven technology for treatment of spent EN solutions. This cell employs membrane separators placed between anode and cathode, which divide components of solutions in two compartments (anolyte, catholyte) based on their ionic nature (anionic, cationic). The principle of this process is that electric energy segregates chemical species that migrate to cathode and anode. The membrane isolates anionic and cationic groups and reduces interference with metal deposition on the cathode. The spent EN solution is introduced to the catholyte compartment of the electrolytic cell. Negatively charged (anionic) species, such as phosphites, phosphates, etc., are transported through the membrane separator to the anolyte chamber, which contains diluted mineral acid or even waste solution. Cationic metal species remain in the catholyte chamber.

Also, if nickel is present in the anolyte solution, it is transported through the membrane to the catholyte chamber. Nickel is reduced to elemental metal and is deposited on the cathode. Other metal contaminants, such as iron, are converted to hydroxide form and precipitate from the solution. The catholyte solution flows by gravity to a specially designed clarifier that removes precipitated residual metals. Further metal recovery enhancement is achieved by applying a high surface cathode. Overall, the separated electrolytic cell operates at higher amperage than a traditional electrowinning cell.

NAEN Operation

The North American EN operation generates about 1,500 gal of spent EN solution per month. NAEN treats its spent EN solution in batches of 3,000 gal. The collected spent EN solution in a 4,500-gal tank is processed by separated electrolytic cell. The cell is equipped with 26 reticulated (high-surface) cathodes and 25 anodes separated by a diaphragm and porous, polymeric membranes, which creates two chambers—catholyte and anolyte. Anodes and cathodes are connected to separate bus bars located on the opposite side of the cell. The cell contains an air-sparging system, maintaining adequate mixing of solution and preventing accumulation of solids (such as metal hydroxide) in the cell.

Two pumps that provide circulation of anolyte and catholyte solution are part of the separated electrolytic cell. The auxiliary equipment consists of anolyte solution (diluted EN solution) and catholyte (spent EN bath) holding/circulation tanks, rectifier and small clarifier for separation of suspended solids from the spend catholyte loop (EN solution).

The typical nickel concentration of spent EN solution is about 5,500 mg/L. The pH of the solution is adjusted and maintained in the range of 8–10 with ammonia hydroxide. The cell operates at electric current of 5 volts and ~500 amps. Nickel content in the catholyte loop is monitored on a regular basis. Collected samples are analyzed by an atomic absorption spectrophotometer. The nickel plate-out process runs around the clock for a few days, until the concentration of nickel in the spent bath solution declines to a range of 10–250 ppm. Then the electrolytically treated solution is transferred to batch treatment for polishing treatment prior to discharge. Residual nickel as a primary contaminant is precipitated in batch treatment by ferric chloride and dithiocarbamate (DTC) and separated by filter press.

Separated electrolytic cells utilizing reticulated cathodes are capable of plating out nickel from spent bath solutions to a level of 1 ppm. Reduction of nickel concentration to single-ppm levels is not practical because of poor current efficiency at low metal level in the solution. A batch treatment stage in the treatment of spent EN bath solution, therefore, was implemented to enhance time and economics of the treatment process.

The cathodes loaded with nickel are removed and sold to a local metal reclaimer as scrap metal. The market value of nickel is around $1.80/lb. The mass of nickel metal deposited on a single cathode ranges from 5–7 lb. Cathodes deposited with nickel to its full capacity are replaced with new reticulated cathodes.

The electrolytic treatment separates and accumulates phosphoric acid in the anolyte solution. NAEN plans to reuse this acid in its manufacturing operations.

Economics of The Electrolytic Process

The current efficiency of nickel plating from spent EN solution ranges from 0.25 to 0.35 grams/amp-hr. Calculated cost of EN electrochemical treatment is shown below.

	Per gal
Electrical cost	$ 0.027
Chemical cost	
pH adjust	$ 0.120
Batch treatment	$ 0.100
Labor cost	$ 0.290
Total	**$ 0.540**

The labor cost is related to handling of EN solution (*e.g.*, emptying of cell), change of cathodes, batch treatment and maintenance.

Conclusion

The combination of serviced ion exchange for the handling of electroless nickel rinse streams, separated electrolytic cell for treatment of spent EN bath solution, and nickel recovery—along with batch treatment for processing of remaining bath solutions—is an effective treatment process that meets environmental discharge criteria in shop with limited available space and minimum labor requirements.

The use of separated electrolytic technology for treatment of spent EN solution provides a few benefits:

- Reliable process for handling of difficult-to-treat solution
- Sludge-free process
- Metal recycling—nickel recovery
- Economical operation cost
- Elimination of long-term liability occurring during sludge generation or hauling of waste for off-site disposal P&SF

About the Authors

Rudy Macko has been with USFilter Memtek Products (28 Cook St., Billerica, MA 01821) for the past 15 years, and currently is manager of Process Technology. His responsibilities concern wastewater treatment, water recycle, heavy metal recovery, acid purification and recovery, utilizing microfiltration, reverse osmosis, ion exchange, electrolytic and gravity settling technologies. He has a BS in chemistry and an MS in fermentation technology from Slovak Institute of Technology, Bratislava, Slovakia.

Tom Mason handles inside sales for North American EN's high- and mid-electroless nickel processing.