UCRL-ID-120612

Electroless Nickel Recycling Via Electro-Dialysis

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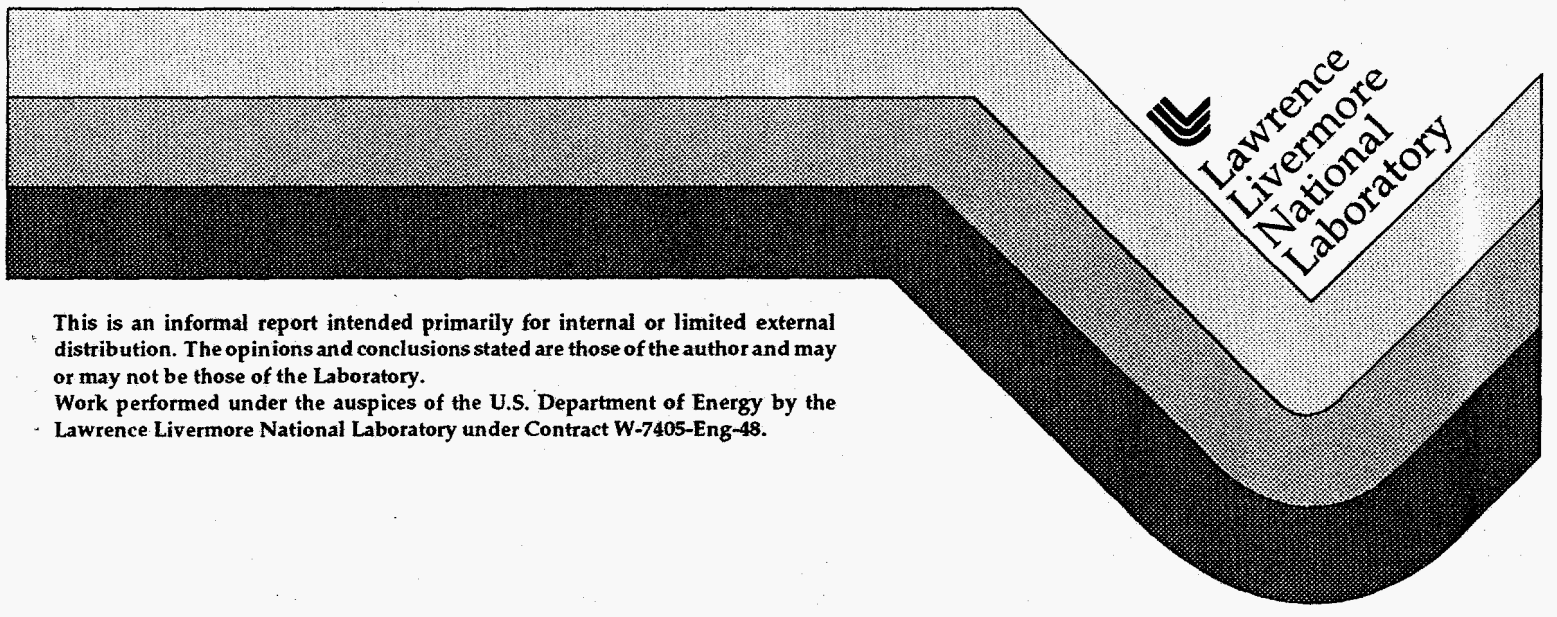
April 1995



Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Electroless Nickel Recycling
Via Electrodialysis

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Electroless nickel is widely used in the metal finishing industry as a coating. It plates evenly on a variety of surfaces and replicates or enhances the surface finish. It has high hardness and good corrosion resistance and machinability. However, its bath life is limited and it has a tendency to spontaneously plate out on the tank and associated equipment. These problems add to the cost per unit component plated. Also, expensive waste treatment is required before users can dispose of the spent solution.

Electroless nickel's limited bath life is inherent in its chemical make-up. Using hypophosphite as the reducing agent for the nickel ion generates by-products of nickel metal and orthophosphite. When the level of orthophosphite in the solution reaches a high concentration, the reaction slows and finally stops. The bath must be disposed of, and its treatment and replacement costs are high. Metal salts have a tendancy to plate out because of the dissolved solids present, and this also makes it necessary to discard the bath.

Lawrence Livermore National Laboratory (LLNL) has conducted a study of an electrodialysis process that can reduce both chemical purchases and disposal costs. Electrodialysis employs a membrane, deionized water, and an electromotive potential to separate the orthophosphite and other dissolved solids from the nickel ions. With the aid of the electromotive potential, the dissolved solids migrate across the membrane from the process solution into the water in the recycling unit's holding cell. This migration lowers the total dissolved solids (TDS) in the process solution and improves plating performance. The dialysis process makes it possible to reuse the bath many times without disposal.

Testing

The first trials of the recycling technology were performed on an electroless nickel solution that had been used for 40 days. This bath, initially at a metal concentration of 7 grams per liter (g/l) had 5 metal turnovers (in other words, it had been replenished with a total of 35 grams of nickel), and its deposition rate had dropped from 0.0006

inches per hour to less than 0.0002 inches per hour. We measured the total dissolved solids (TDS) content, which was 165,000 parts per million (ppm). The nickel metal concentration was still at 6.8 gm/l and the hypophosphite was at 40 gm/l.

After filling the recycling unit's holding cell up with de-ionized water, the unit was plumbed to the tank and the recirculating pumps activated. De-ionized water was circulated past the membrane at a rate of 6 gallons per minute, and the plating solution on the other side of the membrane was circulated at 4 gallons per minute. The dc power supply was adjusted to 15 amps and 3 volts. While the amperage remains constant, the voltage varies depending on the conductivity of the process solution. The more TDS removed from it, the lower its conductivity and the higher the voltage.

After 22 hours of operation, the voltage had increased to 12 volts, and the liquid in the holding cell had turned slightly green. The TDS in the plating solution had decreased to 70,000 ppm, the level typical of a new bath. After replenishing the hypophosphite in the plating bath and adjusting the nickel to the correct operating concentration, the bath was heated to 92° C, and a test panel was plated. The plating rate increased to almost 0.001 inches per hour. This bath was then used for another 5 metal turnovers and retreated with equally successful results.

This bath has now been operated for many metal turnovers and recycled through the dialysis unit numerous times. The only problem occurs when the nickel plates out on the tank and has to be stripped. We are planning to install a small anodic dc current to the tank and heater to minimize nickel reduction and plating out, but this addition is still in the planning stage. In theory, this bath could run indefinitely with dialysis and chemical replenishment.

We next investigated nickel recovery in a low-phosphorous bath. The plating rate of a new bath is 0.001 inches per hour. This decreases with use. The bath had been used for plating aluminum and had plated out on the heater and tank walls several times during its operation. Plating out was probably caused by the dissolved zinc from zincating prior to plating. At the time of recycling, the bath had a TDS of 225,000 ppm. It was connected to the dialysis unit in the same way as described above, and operated for 26 hours until the TDS had been reduced to 80,000 ppm. The hypophosphite and nickel were replenished and the bath heated to 90° C. The plating rate from the recovered bath was almost that of a new bath. The bath was very stable and operated for 2 turnovers before it started to plate out on the heater. The tank and heater were stripped, and we continued to use the solution until the TDS increased to 200,000 ppm. The bath is presently drummed up and awaiting reuse when the low-phosphorus deposit is again requested.

Several other chemistries were tested with the successful results. These chemistries included MacDermid Elnic 100, Enthone Niposit 85, Macdermid EN-MAC, and Stapleton Stabuff 850. Only one chemistry, Attotech (formerly Shipley) Niculoy 22 presented a problem. That chemistry had a very rapid plating rate of 0.0016 inch per

hour after recovery, and solution plated out spontaneously on the tank walls and heater. No matter what changes we made, the bath continued to plate out. It may not be possible to recover this chemistry with electrodialysis. We hypothesized that the stabilizer had been removed from the bath during dialysis, and this caused the spontaneous plating out problem. However, the manufacturer declined to sell the stabilizer separately from the nickel concentrate so we could not determine if this was the case.

The cost savings from adding nickel recycling to the plating process can be high, depending on the cost of treatment chemicals and waste disposal. Table 1 shows a savings of $495 per 100 gallons of process solution with electrodialysis recycling. The table compares costs with and without recycling for a 100 gallon batch plating process.

Table 1. Process costs per 100 gallon bath

	a. without recycling			b. with dialysis recycling		
Plating chemicals	**unit cost**	**quantity used /100 gal bath**	**cost per bath**	**unit cost**	**quantity used /100 gal bath**	**cost per bath**
Nickel						
Initial bath chemistry	**22.50/gal**	**20 gal**	450.00	**22.50/gal**	**20 gal**	450.00
Makeup over lifetime of bath	22.50	50	1,125. 00	22.50	50	1,125.00
Replacement after bath disposal	22.50	20	450.00			
Makeup after recycling				22.50	1	22.50
Hypophosphite						
Initial bath chemistry	25.00	3.3	82.50	25.00	3.3	82.50
Makeup over lifetime of bath	25.00	25	625.00	25.00	25	625.00
Replacement after bath disposal	25.00	3.3	82.50			
Makeup after recycling				25.00	1.5	37.50
Disposal cost of solids	**1.85/lb**	**12 lbs**	22.50			
Total operating costs			2,837.50			2,342.50
Savings per 100 gal through recycling						$495

In both scenarios the bath is used until its TDS gets to approximately 225,000 ppm. During its use, the bath makeup of nickel and hypophosphite is added each time concentrations drop to 90% of initial values.

In scenario (a) the spent bath goes through treatment consisting of flocculation, precipitation, and filter pressing to separate solids from water. The water is sewered or reused while the solids are disposed of at $1.85 per pound. Afterwards, a new bath is made up.

In scenario (b) the spent bath is subjected to dialysis recycling, which lowers TDS levels. Most of the bath chemicals are recovered, and this avoids the cost of having to make up a new bath. Disposal costs are also avoided.

The electrodialysis recycling unit costs $15,000. Payback is achieved after approximately 30 bath recyclings. Payback time can vary markedly depending on bath use, area of work plated, thickness of the plate, substrate, and other factors. One of many possible scenarios might be to use a 100 gallon bath to plate 0.001 inch of nickel on 50 square feet of steel substrate per day. At this rate, the 100 gallon bath would have to be disposed of or recycled every 2.5 work days (assuming an 8-hour-long work day). In this case, payback would be achieved in about 3.5 months.

Conclusion

The cost of the electrodialysis equipment is quickly recovered by the reduced purchase of chemicals. The electrodialysis operation is simple and runs unattended except for maintaining the proper liquid level in the recycling unit and monitoring TDS in the bath. The process was used successfully in a variety of electroless nickel chemistries. The recycling unit appears to offer the user significant economic as well as environmental benefits.