Advice & Counsel

Frank Altmayer, CEF • AESF Technical Director
Scientific Control Laboratories, Inc. • 3158 Kolin Ave. • Chicago, IL 60623-4889
E-mail: mfconsutant@msn.com

P2 for Electroless Nickel (continued)

We continue answering the question from last month:

Water Quality Issues

In general, a purification system for water used in the electroless nickel solution should include the following:

- A one-micron pre-filter ahead of the ion exchange system to remove particulates that can foul the IX resin.
- A carbon filtration system to remove chlorides and hydrocarbons from the water.
- A final 0.5-mm filter to remove silicate particles that may be discharged from the DI system. Such particles have produced rough deposits and short solution life in some installations.

Level Control

Installation and maintenance of level controls is an important part of any pollution prevention program. Electroless nickel solutions can yield evaporative losses of up to one inch of liquid per hour, especially if air-agitated. Some form of level control may be desirable, but these can often cause solution losses or tank fires, as a result of failure. Float controls, for example, are often fouled by solid residues that build up from mists condensing on mechanical components. Electronic/optical sensors may be mounted outside the tank wall to avoid fouling by solids, but are frequently affected by volume fluctuations due to parts entering or leaving the tank. Ultrasonic level sensors are available, but I have not seen them used in EN installations. The best answer is frequent inspection and cleaning.

Over-temperature Sensors

Electrically heated tanks should have over-temperature sensors to shut down in an over-temperature condition, even if level controls are employed.

Solution Maintenance

Auto-Analyzers/Replenishers

With auto-analyzers and replenishers, the analysis of the solution is performed continuously, and a series of pumps add replenishing solutions as they are required. Solution chemistry is typically controlled within ±2 percent. These automated systems can reduce labor and improve solution life and the quality of the deposit by assuring consistent chemical content. They do require careful calibration and a significant amount of maintenance.

In the absence of automated analytical control, the EN solution should be analyzed for nickel, hypophosphite, and pH at a frequency that yields a variation of ±2 percent of the nominal recommended concentration values. SPC charting is quite helpful in monitoring and controlling the process.

The EN supplier should provide information on the stabilizer(s) used so that the plater does not inadvertently add an excess, slowing down the process and shortening its life.

Operational Practices

Good operational practices that should be employed in any EN plating operation include:

1. Use of drip trays between tanks to reclaim dripped solutions.
2. In-tank filtration wherever possible, to prevent solution leakage outside the tank.
3. A collection system for capture and return of chemical spills originating from external filters, and solution holding tanks.
4. A leak detection/alarm system to alert operators of a possible tank rupture, leak, or liner rupture.
5. Filtration of all liquids through a one-micron filter **before** the liquid is added to the plating tank.
6. Complete dissolution of all solids before they are added to the plating tank.
7. Use of the EN plating tank only for EN plating, not for electroplating.
8. Employment of electrolytic recovery prior to waste treatment of any nickel-bearing concentrates.
9. Immediate retrieval of dropped parts using a plastic net (or other) system.
10. Use of timers for all processing steps.
11. Electroplating (with nickel) any substrates that contain significant amounts of lead, cadmium, iron, or aluminum on the surface, as these are contaminants to the EN process and shorten the life of the solution.
12. High rinse rates after nitric acid dips to avoid transfer of nitrates to the EN process, as nitrates are also a contaminant that can shorten the life of the solution.

The maximum level of commonly encountered impurities, as defined by the supplier, must be maintained. Below are suggested levels found in the literature. You can follow these if you don't have manufacturer's recommendations:

Impurity	**Maximum ppm**
Lead	2
Cadmium	2
Iron	150
Aluminum	300
Palladium	1
Cr^{+3}	15
Cr^{+6}	1
NO_3	50
H_3PO_3	150

Tank Loading

Low tank loading (below 0.25 ft^2 /gal) can shorten the solution life and affect the quality (phosphorus) content of the deposit.

Treatment of Spent EN Solutions

Electroless nickel plating solutions employ chelating agents to keep nickel ion activity at a controlled concentration (keep nickel dissolved). Once the plating solution becomes “spent,” it must be batch treated to reduce the dissolved nickel below regulated limits.

Treatment methods employed include those mentioned/described previously, and autocatalytic plate-out, which has been described in the literature and by suppliers of EN processes:

1. The room temperature solution is loaded with a high-surface-area substrate. Steel wool is a cheap, readily available, high-surface-area substrate.
2. The solution temperature is slowly raised and the level of gassing is monitored. As gassing subsides, the temperature is further increased until the boiling point is approached. No further increase in temperature beyond the boiling point is feasible.
3. Additional reducing agent is added in small amounts until further additions result in no further gassing. At this point, the nickel has plated out to a dissolved nickel content of about 5–50 ppm.
4. The remaining dissolved nickel is precipitated using any of the procedures described in this lecture, including starch xanthate, DTC, sodium hydrosulfite, or sodium borohydride, based on bench testing in the laboratory to discover the most successful treatment technique.

An alternate autocatalytic decomposition procedure follows:

1. Carbon filter
2. Heat to 180-200 °F
3. Raise pH to 8–10 with NaOH
4. Add 1.5 oz/gal sodium hypophosphite
5. If solution does not decompose:
6. Add sodium borohydride 0.5mL (12%)/gal
7. Reaction may take 2–3 hr
8. Settle for 2–3 days

The resulting solution contains 20–50 ppm nickel, and must be chemically treated to produce a compliant treated waste water.

A third method of treatment for spent nickel-bearing wastes can utilize displacement of the nickel with calcium (added as the oxide). The treatment is rather time consuming, but is effective on a variety of wastes. Either lime (calcium hydroxide) or sodium hydroxide can be used to raise the pH to 12, prior to the addition of 1.5–2.0 g/L of calcium oxide. Settling is typically very slow (16–24 hr). The resulting treated solution will contain between 1 and 50 mg/L of dissolved nickel, and further chemical treatment is often necessary.

Additional treatment schemes can be found in the literature, but the best treatment is no treatment. At least one supplier, for example, takes back spent EN solutions for reprocessing/recycling.

Chemical Treatment of Dilute EN Wastewater & Treated Wastes

Chemical treatment options are:
1. Add DTC
2. Ferrous sulfide
3. Starch xanthate
4. Sodium hydrosulfite

Dithiocarbamates (DTC)

The use of dithiocarbamates as a metal scavenger has gained acceptance by metal finishers who must meet very low heavy metal discharge standards. DTC has a fairly low toxicity and is reported to degrade rapidly upon discharge into the environment. It has, however, been involved in at least one major fish kill, so do **NOT** discharge this chemical at high concentrations into the sewer system!

Stoichiometric amounts of DTC can lower nickel concentrations to 1 mg/L, while a 10-percent excess of DTC will reduce nickel concentrations to 0.2 mg/I or less. Effective metal removal is obtained over the pH range of 3-10. Cationic polymer (1-2.5 mg/L) normally aids in flocculation and sludge settling.

Ferrous Sulfide

In sulfide precipitation, the metal ions are converted to metal sulfides, which generally are lower in solubility than metal hydroxides (except for trivalent chromium). The sulfide can be introduced in several ways, but because sulfide-bearing chemicals can be dangerous to handle, the most common form of sulfide addition is ferrous sulfide, which has low solubility, but enough to precipitate metal hydroxides without introducing dangerous levels of free sulfide and thiocarbamates, which are too expensive to use for bulk treatment and are almost always used as a “polishing” operation.

Ferrous sulfide is available as a proprietary process.* The process can even reduce hexavalent chromium to trivalent, and precipitate metals simultaneously (the chromium is precipitated as the hydroxide).

The system for precipitation of insoluble metal sulfides from ferrous sulfide involves three stages: A two-stage lime neutralization system is used to adjust the pH of the raw wastewater containing the dissolved metals to pH 8.5–9.5. The wastewater is then routed to a mixing tank, where ferrous sulfide slurry and polymer are added. The wastewater then is routed through a clarification system.

Due to the instability of ferrous sulfide, it has to be generated on-site from sodium sulfide and ferrous sulfate. The sulfide is released from ferrous sulfide only when other heavy metals with lower equilibrium constants for their sulfide form are present in solution.

Insoluble Starch Xanthate (ISX)

ISX is an ion exchange material (1.5–1.8 meq metal ion/g capacity) that instantaneously removes heavy metal ions by exchange with sodium or magnesium. It differs from most ion exchange systems because it is selective for heavy metal ions. It is effective for removal of non-complexed metals over the pH range of 3 to 11. For chelated metals, such as EN wastes, optimum removal occurs at pH 3–5. ISX can be added as a solid for batch treatments to remove heavy metals from wastewaters. It can be slurried and metered-in for large volume, continuous flow operations or precoated on diatomaceous earth-type filters to allow metal removal. The ISX-metal sludge that forms in these operations de-waters very easily to greater than 30–40 percent solids.

**Permutit SUIfcXT11, Div. of USFilter.*

Sodium Hydrosulfite Treatment

Sodium hydrosulfite is a strong reducing agent effective for metal removal from chelated systems on a batch basis. The chelated waste is adjusted to a pH of less than 5.0, and an automatic temperature controller maintains a temperature range of 60–710 °C (140–1600 °F).

Hydrosulfite is metered in to maintain an excess concentration of 200–500 ppm sodium hydrosulfite. A 5-percent lime slurry is then added to maintain a pH above 9. The waste is then clarified.

Sodium Borohydride

Sodium borohydride is a water-soluble reducing agent that will reduce metal ions to a lower valence state or to the free metal. A distinct advantage of borohydride is its high chemical efficiency. One pound of sodium borohydride has the reducing power to recover six pounds of nickel from wastewaters.

For most efficient metallic ion reduction, the pH must be maintained between 8 and 11. Below pH 8, hydrolysis of the borohydride produces hydrogen gas; above pH 11, the reduction decreases. Because hydroxide ion is consumed in the reduction, the pH must be monitored/controlled. The pH adjustment will precipitate some of the metals as hydroxides; however, borohydride is a strong enough reducing agent to slowly convert hydroxides into free metals.

Borohydride may react with other compounds (*i.e.*, organics) in wastewaters, thereby reducing its availability for metal ions. Therefore, most users find a 100-percent excess of borohydride generally ensures rapid and complete metal reduction. The borohydride is added as a 12-percent solution in 43-percent caustic, and should be handled like neutralizations with 50-percent caustic. After pH adjustment, the calculated amount of sodium borohydride is metered into the effluent to reduce the metallic contaminant to the elemental state. Vigorous mixing is essential. The resulting mixture is held for at least five minutes to ensure complete reaction. Temperature is not critical. The precipitated metal is recovered by clarification, followed by filtration. The residual metal and borate level may be lowered even further, if necessary, by treatment with activated carbon and/or a suitable ion exchange resin.

The precipitated metal must be removed from the treated wastewater quickly (<1 hr), because redissolving of the metals can occur.

Note on Waste Treating EN-bearing Solutions

Because chelating agents are still present in the treated waste from any of the above procedures, it goes directly to the final pH adjustment sump, bypassing the general rinse water system completely. This is to avoid the chelates resolubilizing any heavy metals before they can be separated in the main clarifier.

High Turnover EN Processes

At least one supplier has developed an EN process that provides a high number of turnovers (75–150 have been claimed) by precipitating the orthophosphite from the EN solution using proprietary chemicals. P&SF