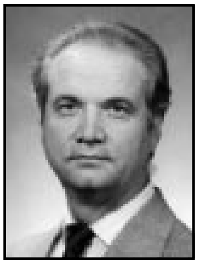

Advice & Counsel

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

Treating EN Waste

**Dear Advice & Counsel,
What methods are available for treatment of spent electroless nickel plating solution?**

Signed, Ed Ta

Dear Mr. Ta,

First, treating a spent electroless nickel plating solution can be a dangerous process, because it involves decomposition (plate-out) of the solution, which, if not done very carefully, can result in eruption of the solution because of released hydrogen gas. You must proceed with utmost caution and exercise a high degree of chemical safety, wearing full protection at all times when you are near the process.

I'll be borrowing rather heavily from an *AESF Illustrated Lecture* written by Dr. Robert Wing in 1980, so I'll start by giving Dr. Wing credit for a job well done in working on treatment of complexed wastes.

Assuming your electroless nickel plating solution is proprietary, it is difficult to know what complexing agents are part of the formulation, so the following treatment schemes must be bench-tested to see which one or which combination works best. The following are treatment schemes with which I am familiar:

Scheme #1

Most EN platers start by carbon-filtering the spent solution to remove some of the organics that tend to complex nickel metal. With carbon filtration, the final treated solution contains about half as much dissolved nickel as a solution that has not been carbon-filtered. Heat the solution to 180–200 °F, and raise the pH to 8–10 with sodium hydroxide. Add 8–10 g/L of sodium hypophosphite. If the solution does not decompose, add 0.5 mL (12%) sodium borohydride for each gallon of solution. Allow three hours for the reaction to go to completion, then allow the waste to sit undisturbed for two or three days.

Scheme #2

Load the spent solution (at room temperature) with a high-surface-area material (*e.g.*, steel wool) that will cause plate-out of the bulk of the nickel (usually ~ 1 oz/gal in concentration). As the plate-out subsides, the temperature of the spent solution is increased slowly, to keep the plating going, until it eventually reaches the boiling point of the solution. Addition of 8–10 g/L of sodium hypophosphite as the reaction proceeds sometimes helps the process go to completion.

Scheme #3

Raise the pH to 12 with calcium oxide. Allow to settle 16 hr. The whole process may take several hours, after which the treated solution will still contain ~ 25–50 ppm of dissolved nickel. This is usually the case, no matter which of the treatment schemes you follow. Assuming one of the schemes has been successful, the spent solution now is at the point at which Dr. Wing's work comes in handy.

There are several treatment schemes that Dr. Wing developed or evaluated to treat and remove that last 50 ppm or so of dissolved nickel. Simple pH adjustment won't work, because the nickel is complexed with organics. You need to find a way to destroy the organic or precipitate the nickel, despite the presence of the complexing agent.

Sulfide Precipitation

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 forms of sulfide addition are: 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* for wastes that do not require removal of hexavalent chromium. The process can even reduce hexavalent chromium to

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trivalent, and precipitate metals simultaneously (the chromium is precipitated as the hydroxide). Use of sulfides other than ferrous sulfide or thiocarbamates is discouraged from a safety standpoint.

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.

Because of the instability of ferrous sulfide, it must 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.

When the pH is maintained between 8.5–9, the liberated iron will form a hydroxide and precipitate as well. The unreacted ferrous sulfide is filtered or settled out with the metal sulfide precipitate, while the effluent is practically sulfide-free. Anionic polymers aid settling of metal sulfide precipitates. The sludge is easily dewatered by conventional techniques.

The table provides a comparison of solubilities for metals when they are precipitated as the hydroxide vs. sulfides. Note that nickel, as the sulfide, has about 20 orders of magnitude less solubility than the hydroxide.

Removing Dissolved Metals With Insoluble Starch Xanthate

Insoluble starch xanthate (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. Sodium chloride concentrations up to 10 percent do not hinder metal removal. It is effective for removal of non-complexed metals over the pH range of 3–11. For chelated metals, optimum removal occurs at pH 3–5. ISX can be slurried and metered-in for large-volume, continuous-flow operations or precoated on diatomaceous earth-type filters to allow metal removal.

Metal Precipitate	Ksp
ZnS	$1.2x10^{-23}$
$Zn(OH)_2$	$1.7x10^{-6}$
$Zn_3(PO_4)_2$	$3.1x10^{-7}$
$Cr(OH)_3$	$1.2x10^{-8}$
PbS	$3.4x10^{-28}$
$Pb(OH)_2$	$6.7x10^{-6}$
CdS	$3.6x10^{-29}$
CuS	$8.5x10^{-45}$
NiS	$1.4x10^{-24}$
$Ni(OH)_2$	$6.3x10^{-3}$

Dr. Wing has written many papers on the manufacture and use of ISX, many published in *P&SF.*

Sodium Dithiocarbamate

The use of dithiocarbamates (DTC) 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 is often added as a "polishing" operation after dissolved metals have been converted to metal hydroxides. Stoichiometric amounts of DTC will lower metal concentrations to 1 mg/L, while a 10-percent excess of DTC will reduce metal concentrations to 0.2 mg/L or less. Effective metal removal is obtained over the pH range of 3–10. Cationic polymer (1–2.5 mg/L) aids in flocculation and sludge-settling.

The major disadvantage only applies to stream dischargers. DTC is usually supplied commercially as a 40-percent solution of the dimethyl or diethyl derivative. One gallon would contain 3.33 lb of DTC, which would remove from 0.5 to approximately 4.5 lb. of dissolved heavy metal, depending on the type of metal and the wastewater matrix.

Treatment with Sodium Hydrosulfite

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 < 5.0, and an automatic temperature controller maintains a temperature range of 60–71 °C (140–160 °F). Hydrosulfite is metered-in to maintain an excess concentration of 200–500 ppm sodium hydrosulfite. A five-percent lime slurry is then added to maintain a pH above 9. The waste is then clarified.

Because chelating agents are still present in the overflow from the clarifier, the treated effluent goes directly to the final pH adjustment sump, by-passing the general rinse-water system completely, and avoiding a reaction between the chelates and any other heavy metals.

Many complexed metals respond well at room temperature with hydrosulfite. Increasing temperature greatly improves the settling ability and dewatering ability of the sludge. In certain cases, the sludge must be removed quickly from chelate-containing supernatant water; otherwise, re-dissolution of the metal will result. The above procedure can be modified to accommodate flow-through treatment systems.

Sodium hydrosulfite treatment of chelated wastes offers the advantages of good removal/treatment of chelated metals at relatively low chemical cost. The sludge formed upon neutralization is easily de-watered, and the heavy metals can often be reclaimed by a high-temperature metals reclaimer.

The major disadvantage of the process is the energy cost and the practicality of heating a waste stream to the high temperature required.

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 power to reduce six pounds of nickel from waste.

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 and elevated.

Borohydride may react with other compounds (*i.e.*, organics) in wastewaters, thereby reducing its availability for metal ions. Most users, therefore, 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. The wastewater must first be adjusted to pH 8–11 before borohydride addition. This adjustment will precipitate some of the metals as hydroxides; borohydride, however, is a strong enough reducing agent to slowly convert hydroxides into "solid" metal.

After pH adjustment, the calculated amount of sodium borohydride is metered into the effluent to reduce the metallic contaminant to the elemental state. Because of the normally low level of dissolved metal ions in wastewaters to be treated, efficient mixing of the borohydride is essential. The resulting mixture is held for at least five minutes to ensure complete reaction. Temperature is not critical. The precipitated metal is then recovered by clarification, followed by filtration. Flocculants, such as magnesium salts or commercial organic flocculants, may be used if required to facilitate settling of the precipitated metal. If necessary, the residual metal and borate level may be lowered even further 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.

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