



Don Baudrand, *Don Baudrand Consulting*, e-mail: domwb@tscnet.com

Abstract
Treatment and Disposal of Spent Electroless Nickel Plating Solutions

Don Baudrand, Consultant, Poulsbo Washington
David Crotty, PhD., MacDermid, Inc. New Hudson Michigan

Electroless nickel: How shall I treat thee? Let me count the ways. Elizabeth Barrette Browning would be overwhelmed by the number of ways to treat electroless nickel, as are we. There are many different approaches to treating and disposal of spent electroless nickel solutions. This paper will discuss many of the methods that have been used with varying degrees of success in terms of the amount of nickel left after treatment. It is often wise to combine treatments, one following another. Examples include plate-out with palladium salts, plate-out with steel wool, borohydride induced plate-out, nickel dust plate-out, Precipitation of metals using various precipitants, ion exchange, electrowinning, reverse osmosis and electrodialysis. Which one should I use? How do they compare? Some of the pros and cons of each process will be noted.

Introduction

When Elizabeth Barrett Browning wrote her famous poem "How Do I love Thee" which starts "How do I love thee, let me count the ways" she had never heard of electroless nickel. When electroless nickel plating was introduced to the world in about 1947, most of us had never heard of the strict regulations in treatment and disposal of electroless nickel plating solutions and rinse water. Today we are faced with many choices for the treatment and disposal of these plating solutions and the rinses necessary for the process. How do you choose the right process or combination of processes for your circumstances? A major input the decision making process is being aware of the choices available. What are the choices today? Let us consider some of them.

Table I

Waste Treatment of Water Rinses

Caustic soda (Sodium hydroxide) or magnesium hydroxide precipitation.

Lime (Calcium oxide) or slaked lime (Calcium hydroxide and calcium carbonate). Sulfide or thiocarbamate precipitation

High pH chelate break up and precipitation Ion exchange

Electrowinning

Reverse osmosis

Table II

Waste Treatment of Spent Solutions

Caustic soda (Sodium hydroxide) or magnesium hydroxide precipitation. Lime (Calcium oxide) or slaked lime

(Calcium hydroxide and calcium carbonate). Sulfide or thiocarbamate precipitation.

High pH chelate break up and precipitation. Ion exchange.

Electro winning.

Reverse osmosis.

Electrodialysis.

Haul Away.

Sodium Borohydride.

Plate out.

Solution Life Extension.

Before discussing the individual treatment process, I want to emphasize the importance of good rinsing and water conservation. It is essential for quality work that good rinsing and efficient use of water is practiced. Counter flow rinse systems using three rinses produce nearly ideal rinsing conditions, and can use up to 90% less water than a single rinse tank producing the same quality of rinse water. Sometimes spray rinses over the tanks improve rinsing. The combination of spray and immersion rinsing is usually best. Treatment and reuse of rinse waters has advantages. The reuse or reclaim of nickel is also possible and is good practice. It is important to be aware that electroless nickel solutions contain chelators (complexing agents) such as citrate, gluconates, glycolates, malates, lactic acid, and ammonia, that will tie up other metals making them difficult to waste treat. Therefore, separating the effluent stream after nickel removal is necessary. The effluent containing chelators should not be combined with any other waste streams unless the other effluents have been treated for metal removal. Sending the chelate containing waste stream directly to the sewer may be acceptable if phosphorus, sulfate and the bio oxygen demand (BOD) and chemical oxygen demand (COD) requirements are met. The remaining ingredients in the effluent are bio degradable unless fluorocarbon wetting agents are used, or other non biodegradable constituents are added, usually not found in most proprietary electroless nickel chemicals.

Rinse water treatment

Referring to table I, each treatment listed, or combination of treatments can produce acceptable results. The choice is based on the availability of equipment, space, costs, ease of operation, convenience, time of processing and federal and local regulations that may exceed federal standards.i

Caustic soda, magnesium hydroxide or lime treating.

Caustic soda, magnesium hydroxide or lime treatments are done at pH 12.[2.] Slow additions are required due to the large amount of heat generated by the neutralization reaction. Flocculating agents are usually added and coagulation and settling times are long, typically 16 hours or more. The costs are low. The sludge generated is large, compared with other treatment systems, especially if lime (the lowest cost material) is used. After settling the supernatant liquid can be decanted and the sludge removed. Or the effluent can be filtered collecting the sludge on the filter cake. The sludge should be dewatered as much as possible. The sludge is hazardous waste that must be hauled to an approved hazardous waste land fill. Or if possible, reclaim the nickel for reuse.

Sulfide or thiocarbamate precipitation

Sulfide removal of nickel produces less sludge than alkaline precipitation, but results in an even more hazardous sludge due to the nickel sulfide. Most land fill facilities will not accept this waste material. Diethylthiocarbamate and similar proprietary products can reduce the nickel level to very low values fairly quickly. The thiocarbamate treatments are usually reserved for polishing the effluent after most of the nickel is removed by other treatment methods. Ferrous sulfide and sodium sulfide are a little less effective, but less expensive. Ferrous sulfide produces a larger volume of sludge than other sulfide or thiocarbamate treatments.[2.]

High pH chelate break up

High pH break up is done to free the nickel from the chelates (complexing agents) so that nickel can be easily precipitated as nickel hydroxide more efficiently and more completely than using lime or other hydroxide treatments alone. Chelates hold tightly onto nickel at lower pH (4-6). The higher the pH, the more nickel would be released to precipitate. Destroying the chelate allow more nickel to precipitate and at a faster rate. Chelates are organic compounds subject to oxidation by several processes. Included are ozone, potassium permanganate and chlorine, or sodium hypochlorite. Ozone is three oxygen atoms tied together and provide a powerful oxidizing (destroying) agent. Ozone generators are available and not too expensive to purchase and operate. Potassium permanganate in an alkaline solution is another strong oxidizing agent. It produces manganese sludge and cause purple stains on most anything it contacts. Alkaline chlorination as used to treat cyanide waste can also be used to destroy chelators. It takes a longer time and more chlorine or hypochlorite to complete the destruction of the chelators compared with the destruction of cyanide.

Ion Exchange

Ion exchange can remove nickel and other metal ions from the rinse waters. If done properly, the water can be reused for rinsing. Both cation and anion exchange resins must be used to remove both metals and non metals. Ion exchange can be supplemented by reverse osmosis or electro dialysis. Another ion exchange process called "Starch Xanthate",[3] is an insoluble material that can be added to a filter or to the water in a retention tank. It exchanges sodium for nickel. The removal is almost instant and leaves little residual heavy metals. It can be used for batch or continuous flow systems by pre- coating a filter.

Electrowinning

Electrowinning is a term used to describe plating metal from a solution for recovery purposes. The water containing nickel is introduced to a plating cell with many anodes and cathodes. DC current and voltage is applied and nickel is deposited on the cathode. The cathodes may be stripped of nickel from time to time, and the nickel reused. Sulfuric acid/peroxide is often used for stripping. The current efficiency is low, therefore the cost of electricity is a factor.

Reverse Osmosis

Reverse osmosis is a process that can concentrate nickel solutions. It works by applying a pressure on a salt solution (nickel salts such as nickel sulfate) in the presence of a semi permeable membrane. Pure water is forced through the membrane leaving concentrated nickel salts behind. The concentrated nickel can be returned to the plating tank. Multi pass cells are an efficient way to utilize reverse osmosis.

Sodium borohydride

To treat waste rinse water, maintain the pH between 8 and 11. Add the sodium borohydride solution slowly. The amount of borohydride to remove 1 gram of nickel is theoretically 1.1 grams. However the borohydride reacts with other metals and some organics thus requiring about two times the expected amount. The sodium borohydride is added as a 12% solution in 43% sodium hydroxide. Additional sodium hydroxide is often needed to maintain the pH between 8-11. The advantages are low cost, good efficiency , and good removal from chelating agents. The disadvantages include poor settling, often requiring filtering, and the redissolving of some of the metal after 1 hour.

Waste Treatment of Spent Electroless Nickel Solutions

Referring to table II, all the same treating processes used for waste treating rinse waters can and are being used for treating electroless nickel plating solutions. The difference is the amount of materials to handle, high concentration of all the materials in the solution and most importantly the chelators (complexing agents) and impurities that accumulate in the plating solution. The most common are zinc, aluminum and iron. Waste treatment equipment may be different in capacity and design.

Caustic soda magnesium hydroxide and lime treatments

Caustic soda (sodium hydroxide) magnesium hydroxide and lime are effective for treating spent plating solution. However, a large amount of sludge is generated. The sludge should be dewatered. Using lime some of the phosphorus compounds are also precipitated. Flocculating materials are added to increase the size of the precipitated particles of metal hydroxides and speed settling. Even so settling takes a long time. Metals such as zinc and aluminum are soluble in alkaline solutions, thus will not be removed. The effluent usually contains enough nickel and soluble metal compounds that a polishing step is reused to meet the regulations. Polishing is done by diethylthiocarbamate, ion exchange, reverse, or osmosis .

Ferrousulfide and Diethylthiocarbamate

Ferrous sulfide and diethylthiocarbamate treatments of the spent plating solution can be done, but is usually expensive and produces hazardous sludge in quantity. Removal of nickel and all other heavy metals that may be present is effective leaving little behind. Most of the regulation can be met. Note, however, that as in other treatments the effluent after removal of metals will contain chelating agents that can combine with other metals if the effluent is mixed with other metal containing waste streams. It is best to discharge the effluent from nickel removal separately from all other waste streams in some cases further treatment (oxidation of the organics) to meet BOD and Sulfide sldges are COD requirements unacceptable in most land fills.

Electrowinning

Electrowinning can be used to plate out the nickel from spent electroless nickel plating solution. The cells must be of larger capacity then for treating waste rinse waters. The principle and procedures are the same.

Reverse Osmosis

Reverse osmosis as described under waste rinse water treatment works the same for plating solution. It is likely to be more cost effective when it is used to extend the life of the plating solution.

Electrodialysis

Electrodialysis is capable of removing the salts that build up during the use of an electroless nickel solutions, including orthophosphite, and sulfate. It also removes some of the important solution constituents. The electrodialysis machine consists of multiple cells of membrane pairs. Each cell has a cation and anion membrane. The spent electroless nickel solution and a 5g/L, sodium sulfate solution are circulated through the membrane layers. A DC potential is applied across the membrane stack. The anions such as orthophosphite and sulfate from the spent electroless nickel solution migrate toward the anode, passing through the anion membrane and entering the sodium sulfate waste stream. They are prevented from re-entering the spent electroless nickel stream by the cation membrane. The cations such as sodium and nickel migrate in the direction of the cathode. The cation membrane allows smaller size cations to pass through into the waste stream. A minimum amount of nickel can pass through, thus most of the nickel is retained in the electroless nickel bath. When electrodialysis is used on the spent electroless nickel solution, analysis and adjustment of both major and minor constituents is necessary. Electrodialysis can be used to treat spent nickel solutions, but it is likely to be more cost effective if it is used to extend the life on the electroless nickel solution by removing the accumulated by products of the plating reaction.[4],[5]

Ion Exchange

Ion exchange alone is not usually used to treat spent electroless nickel plating solutions. However, Roger Anderson and Wayne Neff have developed a process for extending the life of a plating solution which could be adopted to waste treating as well. Ion exchange is used to remove nickel and sodium. The nickel is reclaimed by removing the sodium from the resin bed using dilute sulfuric acid, then eluting the nickel from the bed to be returned to the plating solution. The sulfate is precipitated using a two stage calcium treatment then the orthophosphite is precipitated using magnesium oxide. The remaining effluent after filtering is returned to the plating solution.

Plate out of nickel

Catalytic Materials

Plate out of nickel by catalytic materials is a common practice. Adding clean Steel wool, or iron filings, to a spent solution starts the process. The temperature is gradually raised to above the normal operating temperature. While raising the temperature, the pH is adjusted with sodium hydroxide. Additional sodium hypophosphite is added and sometimes a little stabilizer to keep the reaction from going too fast. *Caution*, the reaction can be rapid at high temperature. Ramping the temperature prevents over reaction that could cause enough gassing to spill solution over the tank.

Plate out by the addition of other catalytic materials such as small amounts of palladium chloride works well following the same general procedure as for iron filings or steel wool. A patented process (patent II 4,260,493) uses colloidal catalyst.

The nickel plated steel wool or iron filings, and the powdered nickel from catalytic reduction are, at present, considered non hazardous material and can be stored to accumulate enough that it can be sold as nickel scrap. The solid volume is small compared with the amount of sludge produced by other methods.

Conclusions

Plate out using sodium borohydride Sodium borohydride is a powerful reducing agent capable of reducing many metal ions to metal. Caution, the reaction can be very fast. The solution temperature should be from 45-50C and the pH adjusted to 11 or 12 using a dilute solution of sodium hydroxide before the sodium borohydride is added. It is available as a solution containing about 12 % sodium borohydride in 40% sodium hydroxide. A small further dilution of this reagent makes additions more conservative. Nickel is precipitated quickly. The pH and temperature can be raised toward the end as the reaction (gassing) slows to complete the nickel removal.

Haul away

There are a number of commercial waste treatment facilities that will take spent electroless nickel solutions. Costs range from \$.75 per gallon to \$3 per gallon. There is also a charge for analysis of each container to be sure that no other materials were added to the spent electroless nickel that would interfere with treatment procedures. The nickel is sometimes recover in a way that it can be recycled.

Plating solution life extension

Extending the life of the electroless nickel plating solution can be done in several ways. The use of nickel hypophosphite instead of nickel sulfate has the potential of extending solution life by 50% or more by limiting the amount of sulfate accumulation. This is especially important for plating onto aluminum substrates.

Treatment of the electroless nickel plating solutions to remove sulfates and orthophosphite and returning the treated solution to the plating tank has been proposed. Several successful installations have been made. A number of not so successful installations also have been made. The process technology is new and improvements need to be made. However, these processes hold great promise for solution life extension to many regenerations of the nickel content. Combining the techniques of electro dialysis, reverse osmosis, ion exchange or combinations of these and perhaps some precipitation treatments with the use of nickel hypophosphite holds promise.

There are many ways to treat electroless nickel solutions at present. The future holds more and perhaps better methods. One of the best treatments for spent electroless nickel is extending the bath life. This results in less nickel bearing waste to treat. Combined with good and efficient use of rinse waters offer the greatest gains. Of the methods included in this paper, it is the authors opinion that electro dialysis holds promise. Combinations of treatments may offer good results. The use of Nickel hypophosphite in combination with continuous treatment processes seems to be valid. The use of nickel hypophosphite can be an immediate bath life extender until treatment equipment can be purchased and installed. Now we need a supplier of nickel hypophosphite to offer it in quantity and at a reasonable price.

References

1. *Duncan, Ronald N., EN 95 Conference, 1995, Gardner Publications, Cincinnati*

2. *Parker, K., Plating & Surf Fin Vol. 70(2) 52, 1983*

3. *Wing, dl' Bonk, R. R. Metal Finishing 41(12) 23, 1987*

4. *Belelinare, R., EN Conference, 97, Gardner Publications, Cincinnati, Dec. 1997*

5. *Crotty, D., Proceedings AESF SurFin '99*