

Extending the Life of Electroless Nickel Solutions

By R.K. Mayes

Methods to extend the solution life of electroless nickel continue to draw interest from the electroless nickel consumer. The opportunity to obtain more metal turnovers per solution make-up and reduce waste treatment requirements has cost-savings incentives. The development of a proprietary salt additive composed of nickel metal and hypophosphite ions for the make-up and replenishment of the electroless nickel solution has distinct advantages over conventional electroless nickel formulations. The operation of a production plating bath using the salt will be reviewed.

Electroless nickel plating has gone through many stages of evolution since its modern conception by Brenner and Riddell¹ in 1946. The original nickel/hypophosphite process has developed into a variety of processes yielding distinct deposit characteristics and application benefits.

- Acid, Low Phosphorus, 1-5 pct/wt
 - high as-plated deposit hardness
 - excellent wear resistance
- Acid, Mid-phosphorus, 6-9 pct/wt
 - corrosion resistance
 - wear resistance
 - decorative finishes
- Acid, High Phosphorus, 10-13 pct/wt
 - excellent corrosion resistance
 - non-magnetic deposit
 - compressively stressed deposit
 - Composite deposition
 - wear resistance: diamond
 - silicon carbide
 - lubricity: PTFE
- Alkaline, Low Phosphorus 3-4 pct/wt
 - low temperature: plating on plastic
 - strike bath: plating on aluminum
 - plating on zinc diecast
- Ternary Alloys
 - nickel-cobalt-phosphorus
 - nickel-iron-phosphorus
 - nickel-tungsten-phosphorus
 - nickel-rhenium-phosphorus
 - excellent shelf-life solderability

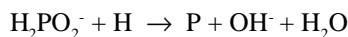
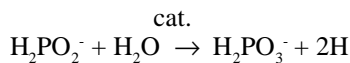
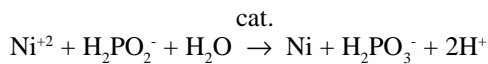


Filtration set-up on EN tank at Epner Technology to allow salt addition to working solution.

diode-bonding
electrical resistance
magnetic or non-magnetic

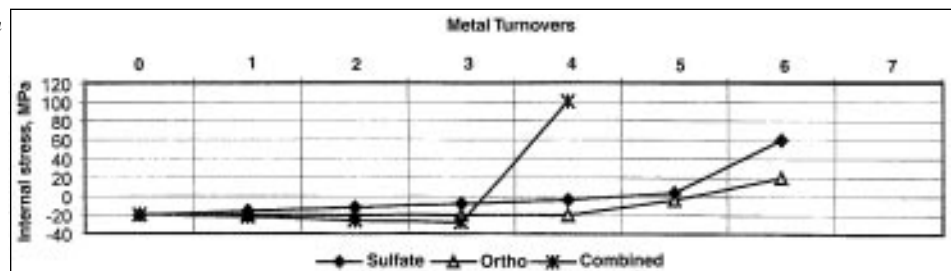
An enigma associated with all of these electroless nickel solutions is the limited solution life of the process. As the process operates, nickel metal plates out of solution (ideally on the desired substrate) and reaction by-products are generated.

The chemical reactions that occur when nickel is reduced and the sodium hypophosphite is oxidized in electroless nickel plating can be summarized as follows:



Replenishment of chemicals is required to keep the optimum concentrations available to maintain the autocatalytic

Fig. 1—Effect of salt additions on deposit stress.



MTO	[SO ₄ ⁻²]	[HPO ₃ ⁻²]	[Na ⁺²]	[K ⁺]
	0.1	0	0.6	0
1	0.2	0.27	0.9	0.2
2	0.3	0.54	1.2	0.4
3	0.4	0.81	1.5	0.6
4	0.5	1.08	1.8	0.8
5	0.6	1.35	2.1	1.2
6	0.7	1.62	2.4	1.2

reaction. Ultimately, accumulation of the reaction by-products reduces the effectiveness of the process (depressed rate of deposition) and alters the deposit characteristics (increasing tensile stress, loss of desired appearance, and porosity of the deposit; see Figs. 1 and 2). Plating on aluminum will experience blistering of the deposit. The solution will no longer be productive and must be taken off-line.

Table 1 illustrates the increase in salt concentration with each metal turnover (MTO) of nickel (MTO represents the addition of nickel replenishment salts equal to the concentration of nickel in the initial solution make-up) in a nickel/hypophosphite plating bath.

The spent solution must be removed from the process tank and properly discarded. There is a variety of options for the waste treatment of spent electroless nickel solutions; however, they are not the object of this paper. New chemistry is made up to continue electroless nickel production. The limited life span of the electroless nickel process is expensive in operational chemical costs and in spent solution treatment or disposal costs.

This paper will investigate the various regenerative approaches taken to obtain longer life from the electroless nickel solution through practice and treatment. It is the next step to take in the development of electroless nickel formulations. The proprietary electroless nickel solutions available on the market have solved the early problems of poor formulations, instability, and inconsistent deposit quality. The next generation of electroless nickels are coming out of the laboratory and onto the production floor.

Extending Electroless Nickel Bath Life

There have been many investigations into methods to improve the working life span obtained from an electroless nickel solution. Jankowski² reported the case study of "bleed and feed" processing. A 450-gal solution achieved 35 metal turnovers through monitoring and controlling the specific gravity of the operating bath. As the bath is operated, the specific gravity increases (Table 1 reveals the cause). When

the solution obtains a predetermined specific gravity, a set portion of the bath is removed and replaced with fresh solution. The specific gravity is effectively reduced, enabling production to continue. The "bleed and feed" process would be repeated as the predetermined specific gravity is again reached in solution. This process provides the operator a means for bath life extension, uniform bath operation and uniform deposit characteristics. It does not eliminate the need for treatment of the waste "bleed" solution. The bath can remain effective through this practice until an imbalance occurs, rendering the solution non-productive. Jankowski reported an approximate 20-percent reduction in make-up costs. Hajdu, in a similar investigation,³ found similar operational benefits from an electroless nickel solution, but concluded that the "bleed and feed" practice may not show economic benefits.

Parker^{4,5} experimented with chemical precipitation and ion exchange to remove the reaction by-product orthophosphite. In the precipitation experiments, a variety of salts was tested for efficiency in removing the orthophosphite from a spent proprietary solution. The selection of the test salts was determined by orthophosphite solubility, availability and cost. Parker's conclusion found chemical precipitation of orthophosphite possible but that further refinement is required to perfect the process.

As for ion exchange, the results appeared more encouraging. Parker determined that a weak-base anionic resin offers an effective method for orthophosphite removal. The treatment of 380 L (100 gal) of spent solution requires 0.1 m³ (3.5 ft³) of the weak-base anionic resin material. The passage of spent solution through the ion exchange resin removes 13.6 kg (30 lb) of orthophosphite (0.4 mol/L). Nickel (5-10%) and hypophosphite ions (0.1 mol/L) are also depleted and would require replenishment to the treated solution. Again, Parker feels that further work is required to perfect the process.

Anderson and Neff⁸ describe the treatment of spent electroless nickel through the application of ion exchange, followed by chemical precipitation to remove reaction by-products. The solution is processed through ion exchange resin to remove nickel ions and sodium ions. The solution is then treated by a two-stage chemical precipitation, the first removing sulfate anions and the second removing orthophosphite anions. The nickel ions are recovered from the ion exchange resin and returned to the final treated solution. The plating solution has been cleansed of its contaminants and put back together. This treatment has been laboratory proven and awaits implementation of the operation at production levels.

Bellemare⁶ suggested the use of electro dialysis as a viable alternative to the traditional dump and remake of electroless nickel solutions. The electro dialysis unit is a series

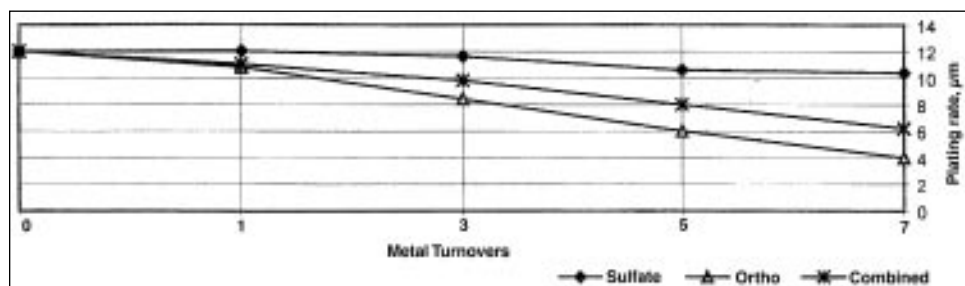


Fig. 2—Effect of salt additions on plating rate.

Table 2
Bath Analyses Before and After Dialysis

	0 MTO	3 MTO	6 MTO	Dialysis to 1.5 MTO
Ni metal	6	6	6	5.4
NaH ₂ PO ₂	30	30	30	9.5
NaH ₂ PO ₃	0	90	180	42.5
NaSO ₄	17.4	69.6	121.8	49.5
Chelate	100%	105%	110%	60%
Zn, ppm	0	---	49	23
Fe, ppm	0	---	86	28

of membranes with an alternating electrical charge applied. The spent electroless nickel solution is circulated through one set of alternating membranes while a second conductive solution (5.0 g/L sodium sulfate) is circulated between the membranes containing the electroless nickel. The circulation of solutions and the application of current create a flow of anions and cations. The process removes material from the electroless nickel solution and places it in the conductive solution. The membranes are designed to allow the passage of particles in only one direction. The material, a combination of orthophosphite, hypophosphite, nickel and chelators, would be considered as waste. The rate of removal is dependent upon the concentration and mobility of the ions in the electric field.

Table 2 shows data derived before and after treatment by electro dialysis. At six MTO, the aged electroless nickel was passed through the electro dialysis unit. The solution was regenerated to a reusable 1.5 MTO condition. The data reveal that a chelator package, electroless-nickel-grade nickel sulfate and sodium hypophosphite must be added to replenish the bath to operating concentrations. Regular treatment of the electroless nickel will provide consistent deposit characteristics and will reduce some chemical costs. There are, however, economic and environmental costs to be considered with production-scaled treatments.

Both Barnstead and Richtering^{7,8} have suggested the use of nickel hypophosphite as a substitute for nickel sulfate and sodium hypophosphite, and as having distinct benefits in electroless nickel solutions. In a working electroless nickel solution, the specific gravity increases as a result of the accumulation of reaction by-products. The fact that sodium ions and sulfate anions are not present in the replenishment chemistry of a nickel-hypophosphite system leads to a slower aging electroless nickel solution. Testing performed by Duncan (Figs. 1 and 2),⁹ has shown the significant effect that the accumulation of sulfate anions can have on the stress in an electroless nickel deposit. Elimination of the sulfate improves the deposit characteristics obtained from the solution. The electroless nickel formulation with nickel hypophosphite will provide extended solution life compared to conventional electroless nickel.

Stapleton¹⁰ presented the development of a high-phosphorus formulation utilizing nickel hypophosphite along with a chemical precipitation procedure to remove orthophosphite continuously from the working solution. The purification equipment was designed to withdraw aged solution automatically and replenish with treated solution. The system was also designed to replenish the electroless nickel chemistry and provide pH control, as required. The concentration of orthophosphite in the working electroless nickel solution was maintained at a level of 60 g/L. The second production installation of this technology used a 500-gal solution, successfully plating a wide range of substrates over a solution life of 50 MTO.

Schaefer¹¹ presented a case study of a mid-phosphorus formulation offering a similar regenerative chemistry and a chemical precipitation process. Schaefer further reported that the regenerative electroless nickel (REN) obtained 75 MTO from a 200-gal solution.

The chemical precipitation treatment Schaefer described is a semi-continuous, off-line process. The orthophosphite is controlled through monitoring the specific gravity or by back titration with sodium thiosulfate. When the working solution reaches the target level of the orthophosphite anion, a portion of the aged solution is removed from the tank and replaced with regenerated solution (similar to the "bleed and feed" process). The aged solution is placed in the Ortho Removal System (ORS) and the appropriate amount of precipitating agent is added to the solution. The solution is mixed, allowing the reaction to take place. The treated solution is then separated from the insoluble precipitate by passing it through a filter press. The solution is analytically rechecked for future use and held until needed.

The ORS equipment is not automated as is Stapleton's purification unit but is simply three tanks, several mixers, an air-driven pump and a filter press. The ORS equipment would be designated solely for the regeneration process to prevent contamination of the electroless nickel solution (Fig. 3).

Epner Technology, Brooklyn, NY, the jobshop described by Schaefer, is still using the REN chemistry and the ORS. Since the first bath make-up in 1993, Epner has made only two new solutions of the REN. The current bath has over 230 MTO (as of 2/99) with no end in sight. The REN solution is providing consistent operation and deposit characteristics.

The author presented a case study¹² of the same REN chemistry at an installation at C.J. Saporito Plating, Cicero, IL. The installation of REN chemistry and ORS equipment was on a much larger scale than at Epner, but employing the same principle in treatment. Saporito recently (2/99) obtained 131

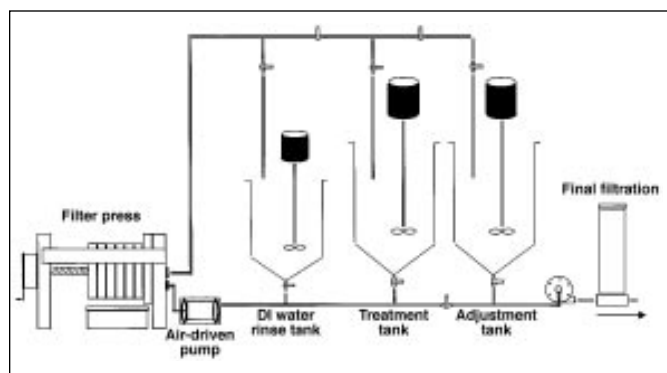


Fig. 3—Ortho Removal System.

MTO in its 500-gal tank. Table 3 shows the before (B) and after (A) analysis of ORS treatment as obtained by C.J. Saporito.

The concept of the use of nickel hypophosphite as a component chemical for an electroless nickel solution has been proven in the laboratory and in production. Its use eliminates the replenishment of sodium ions and sulfate anions in the working solution. It provides a longer solution life than conventional nickel sulfate/sodium hypophosphite systems. However, there are also limitations. In the case of a liquid nickel hypophosphite formulation, the nickel and the hypophosphite are found in the same component. The solution concentrations are limited to 30 g/L of nickel metal and 130 g/L of hypophosphite. This raises solubility issues. This solution cannot be as concentrated as an electroless-nickel-grade, liquid nickel sulfate or a 200 g/L sodium hypophosphite solution.

There are plating applications that the use of REN chemistry would not provide benefit due to the low concentration of chemicals:

- *High loading barrel or rack plating operations.* The REN operation could experience volume growth because of the rapid consumption of nickel.
- *EN equipment setups where evaporation is not promoted.* The memory disc drive industry utilizes EN tanks with covers to minimize the introduction of particulates into the solution. This setup minimizes evaporation and REN would probably experience volume growth.

New Technology

In an effort to overcome this liability, the nickel hypophosphite is now packaged in solid form and the replenisher component has been further concentrated to 2X strength. The limitations above no longer hold because this packaging has reduced the bulk volume of the chemical additions to the working solution. The solid nickel hypophosphite has been tested and is extremely soluble in warm water. This allows the salt to dissolve easily in the 88 °C (190 °F) working REN solution. Laboratory trials have shown no problems in making salt additions directly over work in the tank; however, this is not the recommended procedure, which is to introduce the salt to the working solution at operating temperature and allow the solution to be filtered prior to re-entering the production tank.

The repackaged REN chemistry is currently supplied to two industrial jobshop platers. The first is Queens Plating Company Inc., Long Island City, New York. Queens Plating has a dual tank electroless nickel set-up with 165-gal capacity. At the time of the installation, the production throughput was consistent loads for barrel plating of brass parts requiring 0.00015 in. of nickel. Queens Plating is operating the REN chemistry without the ORS option.

Queens Plating's line is a manual barrel hoist with manual replenishment of the chemistry. The plating tank is constructed with three drains in the floor of the tank, connected by CPVC piping leading to a circulation pump. The pump discharge leads to a steam heat exchanger and into a 5- μ m filter bag. The filter bag is suspended in a polypropylene box located at the head of the tank. The REN solution falls through a slot in the bottom of the polypropylene box, into the working solution.

The tank set-up required a slight modification to imple-

Table 3

Gal/ORS	Nickel g/L	Hypo g/L	Ortho g/L
370 B	5.6	25.8	93
A	5.4	22.7	24
280 B	6.5	25.2	112
A	6.0	23.1	37
370 B	5.4	26.2	126
A	5.3	22.8	23
370 B	5.8	28.2	112
A	5.4	24.7	25
390 B	5.7	26.3	100
A	5.6	25.5	25
370 B	6.1	28.0	115
A	5.9	25.2	33
540 B	5.9	29.0	86
A	5.3	24.8	15
540 B	5.2	30.0	107
A	5.2	24.5	18

ment a suitable, safe, and "idiot proof" method to facilitate salt additions: The filter bag was removed. A large filter bag was designed to fit the polypropylene box. A small polypropylene box was fabricated to fit inside the larger box to act as a small reservoir of REN solution. A quick-connect on a CPVC pipe extension directed the returning REN solution into the small box, constantly supplying hot solution into the small box. The REN solution overflows the small box and passes through the filtered large box, through the slot and into the tank. At the start of each shift, the operator titrates the nickel concentration of REN solution and makes necessary adjustments. He makes three subsequent titrations during the day. In production, REN chemical additions are made following every three barrel loads. The required additions of the salt are made into the large filtered box with the small box reservoir. The salt quickly dissolves, flowing into the working solution. The required liquid replenisher addition is made over the side of the tank directly to the REN solution.

Queens Plating has been operating with the manual salt replenishment for seven months. The packaging of the chemistry minimizes the floor space required for storage. The operator works with smaller quantities per each REN addition compared to the previous liquid-replenished chemistry. The management of Queens Plating is satisfied with the operation, the performance and the cost of the REN chemistry.

The second jobshop to work with the salt package is Epner Technology, Brooklyn, NY. Epner had been working with the REN solution for five years and was eager to try the salt. Epner has a history of being the shop to take on the difficult jobs and they have always looked to new technology to make their work easier.

Epner's tank modification was a simple adjustment made

to their piping set-up. The REN solution was returned to the tank via discharge into a 5- μ m filter bag suspended 3/4 in the working bath. The CPVC piping was cut prior to the bag connection and new connections were made, supplying two filter bags and a ball check valve. During normal flow, the valve is closed, and solution enters one filter bag to the tank. When the chemical addition is to be made, the salt is placed in the filter bag, connected to the piping, and immersed 3/4 into the working solution. The valve is partially opened, allowing the hot REN solution to flow to both filter bags. The salt is allowed to dissolve in the hot operating solution and is filtered before entering the tank.

The REN salt package has been in use at Epner for six months, providing satisfactory performance. The maintenance of the bath chemistry is easier for the operator because there is less material to add. The bath concentration of 75 g/L of orthophosphite is monitored and maintained by the use of the ORS. As mentioned earlier, the REN bath has passed 230 MTO of solution life.

The next investigation is the development of the best physical form to supply the salt. The use of automatic chemical controllers for the maintenance of solution chemistry is mandatory for specific operations. The salt material must be free-flowing for proper addition to the tank. This investigation is underway.

Summary

The goal of the new substitute chemistries is to allow the user to operate with "greener" environmental advantages than

the former methods of operation. In the early 1980s, the use of non-cyanide zinc solutions grew as formulations improved and operators became more familiar with controlling the process. The cyanide-free chemistries are more complicated to operate and maintain than the old tried-and-true cyanide baths. For the new chemistries to operate successfully, old work habits must be abandoned and new ways accepted.

Suppliers of electroless nickel chemistries are investigating new methods to benefit the finisher. There is the opinion, "don't fix what ain't broke," and there is the option to investigate new technology. Options are offered for the ways finishers can work to extend the solution life of their electroless nickel baths. The requirement of all life extension chemistries or procedures is a commitment by the finisher to work more intelligently. Actions must be taken throughout the plating facility for a new process to be successful. Control of the chemical process line is mandatory. While the pretreatment chemistry may be the least expensive chemistry on the line, it plays a vital role in determining the accept/reject tag during final inspection. The training of operators is of paramount importance because the work is in their hands. The operators are the ones on the line, and it is their knowledge or lack of it that affects the operation. They check for water break cleaning, they see if parts on a rack are not gassing when they should be, they see that the filter pump is not running. The operator plays an integral role in the plating cycle. The operator must be trained to know the process line and to raise a flag when something is not correct.

Implementing control and training results in minimizing

the introduction of contaminants down the process line. Reduced contamination in the electroless nickel solution results in extended life. The process of treating a regenerative solution is more effective with less contamination present. Longer life derived from the electroless nickel solution provides more profit from product produced and less cost to reduced waste generation and waste treatment. Electroless nickel is developing into a "green" chemical process.

Editor's note: *This paper is an edited version of a presentation at SUR/FIN® '99, Cincinnati, OH.*

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