Electrodialysis of Electroless Nickel Process Solutions: A Comparison of Life Extension Strategies

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Abstract

Electroless nickel deposits have found wide acceptance in a number of industries. The electroless nickel processes are different from most electroplating processes in that salts build up during plating that limit the useful bath life. This presents a large waste treatment load for the plating shop. Several approaches are being used to extend the useful life of an electroless nickel plating bath. One of these approaches is the use of electrodialysis.

Electrodialysis is capable of removing the salts that build up during bath life, most notably the sulfate and orthophosphite salts, but it also removes important bath constituents. This paper will present data obtained from studies of the electrodialysis of commercially used electroless nickel plating baths and the results of rebuilding the baths to working condition. The results of these studies will be used to discuss the pros and cons of electrodialysis in terms of plating concerns and economics.

Introduction to Electroless Nickel

To understand how life extension strategies operate it is necessary to know why the life span of electroless nickel baths is limited in the first place. The basic chemical constituents of an electroless nickel bath are as follows:

1. A source of nickel ions (nickel sulfate, nickel chloride, nickel sulfamate, etc.)
2. A reducing agent (sodium hypophosphite, sodium borohydride, hydrazine, etc.)
3. Complexors/chelates (typically organic acids, such as lactic acid and citric acid)
4. Stabilizers (heavy metals, divalent sulfur compounds, etc.)
5. pH buffers and pH control agents
6. Brighteners (cadmium, some sulfur compounds, certain metals, etc.)
7. Water

The nickel solution is the source of nickel for the deposition reaction. The reducing agent is the driving force for the reduction of the nickel ions to nickel metal. The complexors hold the nickel ions in a chemical complex which provides some of the control of the deposition process. Stabilizers are catalytic poisons to the deposition reaction that are used to prevent plating on undesired objects (like the tank) as well as controlling the rate of deposition. The pH buffers are necessary to maintain the pH of the reaction in the operating range of the system. Brighteners are added to some electroless baths to improve the deposit appearance. There are many types of electroless nickel baths, but for this discussion we will focus on acid nickel sulfate/sodium hypophosphite baths.

One commonly accepted mechanism for the reduction and deposition of nickel in a hypophosphite reduced bath is as follows:[1]

$$\mathrm{NiSO_4+H_2O \rightarrow Ni^{++}+SO_4^{=}+H_2O} \qquad (1)$$

$$\mathrm{NaH_2PO_2+H_2O \rightarrow Na^{+}+H_2PO_2^{-}+H_2O} \qquad (2)$$

$$\mathrm{Ni^{++}+H_2PO_2^{-}+H_2O \rightarrow Ni^{o}+H_2PO_3^{-}+2H^{+}} \qquad (3)$$

$$\mathrm{H_2PO_2^{-}+H_2O \xrightarrow{(CATALYST)} H_2PO_3^{-}+H_2\uparrow} \qquad (4)$$

Equations (1) and (2) simply show the dissociation of the nickel salt and sodium hypophosphite in water. Equation (3) shows the reduction of the nickel ion by hypophosphite to form nickel metal and an orthophosphite anion. Equation (4) shows a parallel reaction of hypophosphite with water to form orthophosphite and hydrogen gas. There are other mechanisms that explain the deposition reaction, but in every case *the reactions have by-products as* highlighted below:

$$\mathrm{NiSO_4+H_2O \rightarrow Ni^{++}+}\mathbf{SO_4^{=}}\mathrm{+H_2O} \qquad (5)$$

$$\mathrm{NaH_2PO_2+H_2O \rightarrow }\mathbf{Na^{+}}\mathrm{+H_2PO_2^{-}+H_2O} \qquad (6)$$

$$\mathrm{Ni^{++}+H_2PO_2^{-}+H_2O \rightarrow Ni^{o}+}\mathbf{H_2PO_3^{-}}\mathrm{+2H^{+}} \qquad (7)$$

$$\mathrm{H_2PO_2^{-}+H_2O \xrightarrow{(CATALYST)} }\mathbf{H_2PO_3^{-}}\mathrm{+H_2\uparrow} \qquad (8)$$

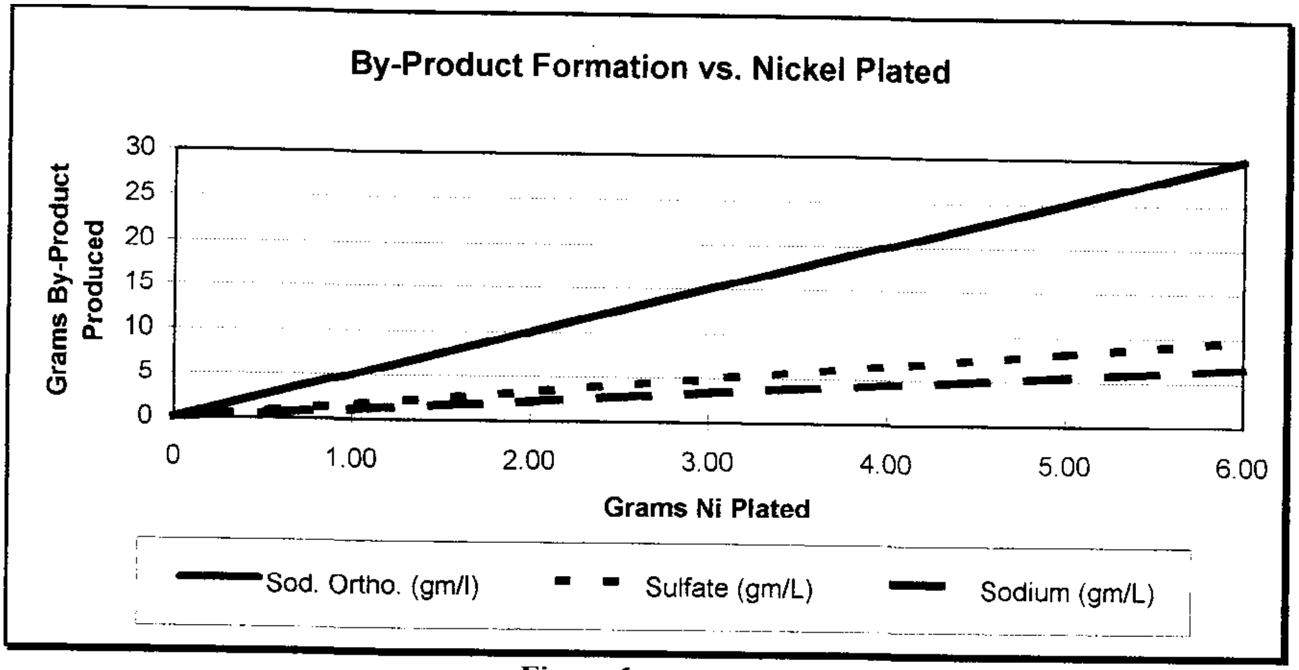

Figure 1

The build-up of these major by-products over the course of the bath life is the major reason that electroless nickel is a *self-limiting* process. The increase in the orthophosphite concentration causes it to compete with the complexing agents for the nickel ions. This results in the formation of sparingly soluble nickel phosphite. The formation of nickel phosphite is familiar to many electroless platers as "white out" or "milking out" of the bath. Precipitated nickel phosphite in the plating bath causes roughness, porous deposits, and decreased plating rates. Increased levels of orthophosphite have also been linked to increased deposit stress.[2,3]

The hypophosphite will undergo side reactions that limit the efficiency of the nickel reduction reaction. Typical values for the efficiency of the hypophosphite range from 20% to 40%.[1] Theoretically, three moles of hypophosphite are required to reduce one mole of nickel, as illustrated below:[4]

$$Ni^{++}+H_2PO_2^-+H_2O \xrightarrow{(CATALYST)} Ni^0+H_2PO_3^-+2H^+ \quad (9)$$

$$H_2PO_2^-+H_2O \xrightarrow{(CATALYST)} H_2PO_3^-+2\,H \quad (10)$$

$$H_2PO_2^- + H \rightarrow P + OH^- + H_2O \quad (11)$$

In theory, three moles of the orthophosphite anion, one mole of sulfate, and three moles of sodium are produced for every mole of nickel deposited.[5] However, the hypophosphite decomposes independently and in practice it is not uncommon for the ratio of hypophoshite to nickel to be close to 3.36:1. This means that for every gram of nickel metal plated, 3.9 gm of orthophosphite ion (5.0 gm as sodium orthophospite), 1.64 gm of sulfate, and 1.1 gm of sodium are produced, and remain in the plating bath (Figure 1). As the bath ages these materials increase in concentration and eventually render the bath unusable.

The production of hydrogen during the deposition reaction causes the solution to become more acidic, and some form of alkaline material must be added to maintain the bath at operating pH. Examples of some typical alkalis used are ammonium hydroxide, potassium hydroxide, potassium carbonate, and ammonium carbonate, all of which add to the increase of salts in the bath..

In addition to orthophosphite, sulfate, sodium, and alkali by-products, there are numerous common contaminants that will limit the life of an electroless nickel bath. Examples of these common contaminants are iron, zinc (from zincated aluminum), copper, nitrates, chloride, oils, calcium, sodium, and other hard water salts. All of these undesirable species contribute to the limited life of the electroless nickel plating solution.

Strategies to Extend Bath Life

There are three fundamental approaches to extend the useful life of electroless nickel baths:

1. Eliminate the potential of forming the by-products by changing the formulation of the plating bath.
2. Develop methods to purify the used plating bath.
3. Bleed and feed of conventional chemistry.

Bath Formulation Changes The type and amount of chemical by-products formed by the electroless nickel deposition reaction can be manipulated by altering the basic chemistry of the plating bath. Several investigations into altering the basic chemical constituents of the plating bath have been attempted, with varying degrees of success. Condensing the chemical reactions listed previously, the overall reaction can be expressed as follows:[6]

$$NiSO_4+3NaH_2PO_2+3H_2O \rightarrow Ni^{o}+3NaH_2PO_3+H_2SO_4+2H_2 \quad (12)$$

If an alternate source of nickel was used the reaction would change. Consider the use of nickel hypophosphite

$$Ni(H_2PO_2)_2+2H_2O \rightarrow Ni^{o}+2H_2PO_3^{-}+2H^{+}+H_2\uparrow \quad (13)$$

Equation (13) demonstrates the use of nickel hypophosphite, thus eliminating the sulfate from nickel sulfate and the sodium from sodium hypophosphite. The orthophosphite is still generated by the deposition reaction.

It was noted above that overall the ratio of hypophosphite used to nickel plated is typically about 3.36:1. Equation (13) only provides a 1:1 ratio. Thus, for each mole of nickel hypophosphite used, some 2.36 moles of hypophosphite ion must be obtained from some other source. Despite this fact, laboratory tests and field experience have shown that this type of approach can at least double the life of a plating bath.

One drawback with the extended life formulations to date has been the economics. Nickel sulfate is available commercially in high volume and high purity. Materials like nickel hypophosphite are not available in bulk and thus the economy of scale is not in effect, making nickel hypophosphite is more expensive.

Another problem has been the introduction of impurities into the plating bath. Electroless nickel is very sensitive to contamination. A relatively small amount of certain contaminants can have a devastating effect on the electroless bath. Under 5 mg/L (PPM) of lead, cadmium, chrome (+6), tin, mercury, antimony, or palladium can kill a bath. Under 100 mg/L of nitrates can damage an electroless nickel bath, as can 200 mg/L of iron, and 100 mg/L of zinc. More care must be taken when using extended life formulations to prevent contamination of the plating bath, and premature end of the solution.

Conclusion for Bath Formulation Extended life formulations work, and have been used successfully in the field for years. While the economics of the systems are not generally competitive with conventional electroless nickel, they do offer benefits such as reduced down time, reduced waste, and longer plating life on certain substrates such as aluminum. The ability to obtain or manufacture raw materials of sufficient purity necessary for the extended life systems is a critical prerequisite for the optimum performance of these products. A major consideration is the introduction of contaminants to the plating bath. Impurities will harm an extended life bath just as they harm a conventional bath, and therefore limit the useful life of the bath. Extended life formulations may not suitable for every shop, and a careful evaluation should be made prior to using these formulations. In the proper environment, extended life formulations seem to be a logical approach to the problem of extending the useful life of an electroless nickel bath.

Precipitation Method The basic premise behind chemical precipitation is familiar to most platers who use similar strategies in their waste treatment systems. A common example is metal precipitation by the addition of hydroxides. By selectively precipitating the impurities formed in the electroless nickel bath and filtering out the precipitate, the life of the bath may be extended.

Methods exist to purify the solution by removing the orthophosphite. Konrad Parker investigated several methods to remove orthophosphite, and found that calcium salts effectively removed the orthophosphite by precipitation and filtration.[4] The effect on the hypophosphite concentration was minimal, since calcium hypophosphite is soluble in the plating bath.

It is critical to realize that calcium is an impurity in the electroless nickel bath. Excess calcium in the bath can have numerous detrimental effects, including deposit roughness, "white out" or precipitation of salts, incorrect nickel metal titration results, dull deposits, depressed plating rate, poor corrosion protection of the deposit, and poor adherence of the deposit. The absence of sulfate in the bath chemistry would eliminate the formation of calcium sulfate, and dramatically increase the calcium tolerance of the plating bath. Thus the calcium precipitation method is best used on extended life formulations that use an alternate source of nickel that does not contain sulfate.

Proprietary precipitation agents have been developed, primarily for use on extended life formulations. These agents selectively precipitate out the orthophosphite from the plating solution with little effect on the other components in the plating bath. Using the extended life formulation in conjunction with the precipitation, the life of the electroless nickel bath has been increased to a reported 70 metal turn overs.[7]

The basic method of precipitation treatment is as follows:

1. A portion of the plating bath is removed for treatment at a predetermined point, generally around 4 to 5 MTOs.
2. The removed solution is allowed to cool to room temperature.
3. The necessary amount of precipitation agent is calculated.
4. The calculated amount of the precipitation agent is added to the cool plating solution and mixed for several hours, usually around 4 hours.
5. The treated solution is then circulated through a filter press to remove the precipitate.
6. The treated solution is transferred to a holding tank.
7. De-ionized water is circulated through the filter press to dissolve any entrapped nickel and hypophosphite.
8. The solution is checked for nickel, hypophosphite, orthophosphite, plating rate, deposit appearance, and pH. Adjustments are made to the solution as needed.
9. The solution is held in the holding tank until needed.

The precipitation procedure is an involved process, and it requires both technical skills and dedicated equipment. Typically, three separate process tanks are used in addition to the filter press. The size of the tanks depends on the amount of bath to be treated. There is also filtration, pumps, and plumbing to consider.

Mayes reports the following results obtained when treating an electroless nickel solution with a proprietary precipitation agent:

	Before (gm/L)	After (gm/L)	Decrease (%)
Nickel	5.58	5.40	3.2
Hypo	25.85	22.68	12.2
Ortho	93.28	29.73	68.1
pH	4.90	4.93	

The reduction in the orthophosphite level is significant, and hypophosphite and nickel losses are small. However, the table also shows that the chemistry is not altered uniformly. After treatment, the bath needs to be analyzed for all critical parameters, so that adjustments to the bath chemistry can be made.

Conclusion for Precipitation Method

The benefits of precipitation regeneration are numerous. The necessary equipment is much less expensive than other regeneration equipment, such as dialysis units. The precipitation is quite selective in the removal of the orthophosphite, having a minor effect on the hypophosphite and almost no effect on the nickel metal. When used in conjunction with extended life formulations, a life of 70 MTOs has been reported in actual production applications.

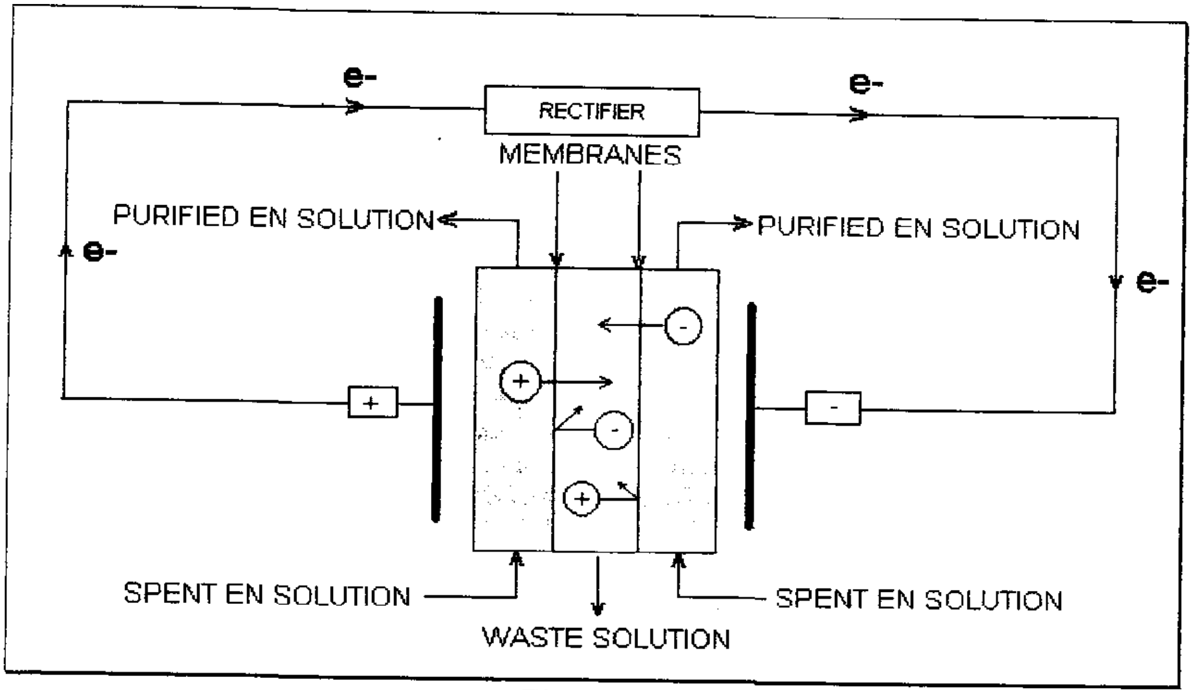

Figure 2

While this is exciting technology, there are several drawbacks to precipitation regeneration. There are equipment costs to consider in both capital investment and maintenance, and valuable floor space is needed for the equipment. The build-up of commonly introduced contaminants to the bath is a major concern since the longer life of the bath provides more opportunity for contamination. In addition a considerable amount of analysis work is required from skilled personnel.

Of course, the precipitation method produces a considerable amount of precipitate (sludge) and disposal costs must be considered.

Electrodialysis Electrodialysis is a method designed to purify electroless nickel plating baths by using a semi-permeable membrane *in conjunction* with electromotive force to selectively remove undesirable species from the plating bath. Hackh's Chemical Dictionary (fourth edition) defines dialysis as "Microfiltration by a semi-permeable membrane, which separates (molecules) from colloids of ultramicroscopic size." The term electrodialysis indicates that a direct current is applied across the cell to increase ion mobility through the membrane. A cathodic membrane selectively allows a cation to pass, and an anodic membrane allows anions to pass. A single cell of an electrodialysis unit is shown in Figure 2.[8]

The Electrodialysis Process A membrane stack of perhaps 40 to 80 separate cells, as diagrammed in Figure 2, is used to electrodialyze the EN solution. The EN solution is pumped through the EN side of each cell and a conductive "ortho" waste solution is *pumped through the waste side of each* cell. A DC current is applied across the membrane stack. Cations in the EN

Table 1
Electrodialysis of an Electroless Nickel Bath[8]

	New Bath	3 MTO	6 MTO	Dialysis to 1.5 MTO	Component Losses
Nickel (gm/L)	6	6	6	5.4	10%
Hypophospite (gm/L)	30	30	30	9.5	69%
Orthophosphite (gm/L)	0	90	180	43	76%
Sodium Sulfate (gm/L)	17.4	70	122	50	59%
Complexor (%)	100	105	110	60	45%
Zinc (ppm)	0		49	23	53
Iron (ppm)	0		86	28	67

stream are driven to the cathode (negative) side. If the cations meet a cationic membrane they are allowed to pass. If they meet an anionic membrane they are not allowed to pass. Similarly, anions are driven toward the anode (positive) side. If they meet an anionic membrane they are allowed to pass through. If they meet a cationic membrane they are not allowed to pass through. The two types of membranes are placed strategically so that, for example, a cation like sodium is allowed to pass through a cationic membrane into the waste stream but is prevented from re-entering the EN stream in the next cell by the presence of an anionic membrane.

The cationic membrane is designed to have pores that are large enough to allow sodium to pass but small enough so that nickel cannot easily pass.

In practice the unit will have the volume of electroless nickel solution in one tank and the "ortho" waste tank will have about half of this volume of water with some sodium sulfate to provide conductivity. As the electrodialysis progresses the volume of the EN side will drop and the volume of the "ortho" waste side will increase. The volume change is proportional to the time of operation.

Bellemare[8] has provided a set of example results obtained from the electrodialysis of an EN bath, Table 1.

Table 1 shows the results of reducing the "age" of a bath by 4.5 MTO based on the removal of orthophosphite. The amount of nickel metal ions that were lost during this electrodialyis is small compared with other losses. The hypophosphite and orthophosphite are lost at about the same rate, about 70%. The loss of sodium sulfate is slightly smaller at 60% and the loss of complexor is about 45%.

During the typical electrodialysis and rebuild cycle, some 10% of the nickel, 70% of the hypophosphite and 45% of the complexor package must be replaced.

One benefit claimed for electrodialysis is the reduction of liquid complexed wastes. From Table 1 it can be seen that some nickel and some complexor are in fact transferred to the "waste" side of the

Table 2
Electrodialysis of Bath From Shop A

ED time	Vol. Gal.	Nickel gm/L	Ortho gm/L	Hypo gm/L	%CA	%CB	Pb PPM	Cd PPM	Zn PPM
0	340	4.9	207	28	141	182	0.49	0.85	127
24	295		154	19	110	135			
48	240	3.9	93	10	88	86			
68	200	3.5	40	4	65	60	0.36	0.65	99

Note: All concentrations corrected to 340 gallons

dialysis unit. About 40% of the volume of the EN bath is also transferred to the "waste" side of the dialysis unit when bath age is reduced 4-5 MTOs. These factors affect costs which will be discussed later.

Finally, the example in Table 1 shows that the loss of zinc and iron during the electrodialysis is not as great as the loss in orthophosphite. While losing about 76% of the orthophosphite, only about 50% of the zinc was removed. This is important because one of the major factors regarding bath life when plating aluminum substrate is the zinc concentration. It appears from this example that the zinc concentration could climb with repeated electrodialysis treatments, and may reach a level where it interferes with the bath performance.

Electrodialysis Investigations

In our investigations of electrodialysis, we worked with two midwestern shops that were using the same proprietary mid phosphorus electroless nickel plating process. One had the electrodialysis equipment on site, the other did not. The shop that had the electrodialysis equipment, Shop A, processes a large proportion of aluminum work. The electroless nickel bath is used primarily with the aluminum work until the bath no longer provides good adhesion, and then the bath is used to plate steel. The bath is used until it has been regenerated to about 6-7 MTO's and then is sent to be treated by electrodialysis. The plating baths from this operation typically are contaminated with zinc, from the zincates, and a very small amount of iron. Shop A uses stainless steel tanks with anodic protection.

The second shop, Shop B, plates various types of steel including a large amount of castings. The electroless nickel baths are generally contaminated with iron, and the level of iron is usually very high due to the roughness of the castings processed. The electroless nickel baths are used until they have been regenerated about 10 times and then discarded. Shop B uses polypropylene tanks. Samples of the electroless nickel plating baths were taken from Shop B and treated in our laboratories using our own electrodialysis unit.

Electrodialysis of Shop A Electroless Nickel Baths. The data from a typical electrodialysis run at Shop A is shown in Table 2. In this run 340 gallons of bath were treated for 68 hours, during which time the volume in the EN tank dropped to about 200 gallons. The volume of the Ortho waste tank started at about 150 gallons and increased to about 290 gallons. Table 2 lists the concentrations of materials as the electrodialysis progressed, assuming the volume of the EN bath was returned to the original 340 gallons. Table 2 also includes the concentrations of two complexors, CA and CB. The complexor concentration is presented as the percentage of these complexors in a freshly prepared EN bath.

This EN bath was treated with electrodialysis for 68 hours, reducing the "age" of the bath from about 6.6 MTO to about 1.3 MTO based on orthophosphite concentration. Table 3 lists the component losses during treatment of this bath.

Table 3
Component Losses
Treatment of Bath from Shop A

Bath Component	% Loss 68 hours	%Loss per MTO
Nickel	28	5.3
Orthophosphite	81	15
Hypophosphite	85	16
Complexor M	54	10
Complexor L	67	13
Zinc	22	4

This bath was reconstructed using enough nickel, hypophosphite, complexors and stabilizers to bring these components to 100% of normal starting concentrations and the bath was returned to the plating line. This bath was able to plate aluminum for only 0.7 MTO before adhesion failure was observed. It was continued to be used with steel until it reached a little over 6 MTO.

The solution life of a bath processing aluminum is an important factor for Shop A. It is known that a high level of zinc in the bath contributes to the poor performance with aluminum work. Other baths that started with less zinc lasted longer. For example, one bath contained about 120 PPM of zinc which was reduced during the electrodialysis to about 60 PPM. This bath worked well with aluminum for about 3 MTO of plating, at which point adhesion failure was observed and the bath work was switched to steel. However, as noted in Table 2, the high zinc level in the bath did not drop low enough to avoid adhesion problems with aluminum. For this reason the performance over aluminum was poor and the run was considered at least partially a failure due to this factor.

Sometimes a shop might be tempted to dilute a bath that is contaminated rather than send it to disposal processing. This may seem to be a good solution to this problem but it leads to a proliferation of plating baths in the shop's inventory and in the long run is not a good approach. A contaminated bath should be designated to be disposed.

The stabilizer concentrations in the baths of Shop A were very low as received from the plating shop because the anodic protection method used in Shop A electrolytically "dummies" the lead and cadmium from the solution. On top of this, the electrodialysis of this bath removed about 25% of the stabilizers, so that significant additions of a stabilizer package is required on rebuild of the plating bath.

Electrodialysis of Shop B Electroless Nickel Baths. Samples of the EN plating bath were obtained from Shop B

Table 4
Electrodialysis of Bath From Shop B

ED Hours	Vol. Gal	Ortho gm/L	Hypo gm/L	%M	%L	Pb PPM	Cd PPM	Fe PPM
0	9.0	170	34	134	154	1.09	1.92	380
2	8.8	156		112	133			
17	7.5	90		104	108			
23	6.8	66		98	97			
25	6.5	56	12	98	92			
30	6.2	40	10	84	87	0.72	1.77	211

at various MTO points in the bath life. For this example a bath sample was taken at about 5.6 MTO and treated with electrodialysis down to about 1.3 MTO. Table 4 lists the data obtained from this run. As with the example from Shop A, the concentrations of bath components have been adjusted as if the bath volume were returned to the original volume.

Table 5 lists the component losses from this example run. Note that the iron concentration was reduced about 44% in this example.

If the treatment of the bath from Shop A (Table 3) and the bath from Shop B (Table 5) are compared we see that the % loss of materials per MTO is approximately the same. Thus the treatment in the industrial sized electrodialysis unit that is installed in Shop A compares well with treatment in the laboratory sized unit.

Table 5
Component Losses
Treatment of Bath from Shop B

Bath Component	% Loss 30 hours	%Loss per MTO
Orthophosphite	76	17
Hypophosphite	71	16
Complexor M	37	8.5
Complexor L	44	10
Iron	44	8

Waste Volume Considerations. During the electrodialysis of the bath from Shop A, that was detailed in Tables 2 and 3, the ortho waste side of the electrodialysis unit grew in volume from about 150 gallons to about 290 gallons due to the transfer of 140 gallon of water from the EN side into the waste stream during the reduction of bath age from 6.6 MTOs to 1.3 MTOs.

Shop A returns the EN bath to the electrodialysis unit whenever the concentration of orthophosphite reaches about 200 gm/L (6.5 MTO). The electrodialysis process is used to reduce the orthophosphite concentration down to about 45 gm/L (1.5 MTO). Each time this process is repeated the ortho waste side of the unit contains about 290 gallons of solution, a combination of the original 150 gallons of fresh water with some sodium sulfate as a conductivity salt plus the 140 gallons that were transferred by the processing.

At the end of a processing run the 290 gallons in the "ortho" tank will contain about 195 gm/L of orthophosphite, 28 gm/L of hypophosphite, about 1.6 gm/L

Table 6
Log of Waste Generation
Normal Operation vs. Electrodialysis

MTO	Standard Waste	Dialysis Waste	MTOs	Standard Waste	Dialysis Waste	MTOs	Standard Waste	Dialysis Waste
1	0	0	11	0	0	21	340	0
2	0	0	12	0	240	22	0	240
3	0	0	13	0	0	23	0	0
4	0	0	14	340	0	24		0
5	0	0	15	0	0	25	0	0
6	0	0	16	0	0	26	0	0
7	340	240	17	0	240	27	0	240
8	0	0	18	0	0	28	340	0
9	0	0	19	0	0			
10	0	0	20	0	0	**Total**	**1360 gal**	**1200 gal**

of nickel metal ions and the 40% of complexors from the bath chemistry.

Not all of the 290 gallons of solution from the "ortho" side needs to be sent to waste treatment after each dialysis cycle because a heel of solution can be left in the tank to provide conductivity. However, if only the 140 gallons that is transferred during the process is pumped off each time, eventually the heel would be a very concentrated solution. In practice, of the 290 gallons present in the "ortho" side, about 50 gallons are allowed to stay in the tank and the remaining 240 gallons are sent to waste treatment.

Table 6 provides a log of wastes that would be generated during normal production of this 340 gallon bath vs repeated electrodialysis for about 28 MTO's. The bath in question works well for about 7 MTO so normally it would produce 340 gallons of waste every 7 MTOs. The dialyzed bath will first be taken to 6.5 MTOs then reduced 5 MTO's to 1.5 MTOs. After that each time 5 MTOs (150 gm/L orthophosphite) has been added to the bath age the bath is returned to the electrodialysis unit. After about 28 MTO the normal operation would generate 1360 gallons of waste. After about 27 MTO total electrodialysis operation would generate about 1200 gallons of waste.

The type of waste generated by these two scenarios are different. The waste from normal operation contains 5-6 gm/L of nickel, 25-30 gm/L hypophosphite and 130-140% of the startup complexor concentration. The electrodialyzed operation waste contains only 1-2 gm/L of nickel, along with 28 gm/L of hypophosphite and the 40% of the chelators from the bath.

Many platers begin the waste treatment of EN baths with a plate out operation to reduce nickel metal concentration. This type of operation can require considerable additions of hypophosphite which adds expense to the plate out operation. However, the waste from the electrodialysis has almost enough hypophosphite to plate out the nickel present. The plate out operation of this type of waste stream would be a bit more economical.

Table 7
Costs of Materials

Material	Usage Assumptions	Cost ($/gal)
Component A	6%	$9.89
Component B	15%	$14.47
Chelator Pkg.	15%	$7.00
Sodium Hypophosphite	30 gm/L (0.25 lb/gal)	$1.60/lb

Costs. The costs of the two scenarios described for the electrodialysis of Shop A's 340 gallon bath can be made using the material costs given by Bellemare and making a few assumptions about their usage. Table 7 lists the costs of all the materials that will be needed.

For the dump and dialysis schedule described in Table 6 we can calculate the costs of bath make up or rebuild. We can ignore the costs of each MTO because they will be the same for each scenario.

For a 340 gallon tank make up costs are:

Component A	20.4 gal	$201.75
Component B	51.0 gal	$737.97
Total Cost		$939.72

To rebuild the bath each time it is electrodialyzed (adding 28% of nickel, 65% of chelators, and 85% of hypophosphite) the costs are:

Component A	5.7 gal	$56.37
Chelator Pkg.	33.2 gal	$232.40
Hypo	72 Lb	$115.60
Total Cost		$404.37

Table 6 shows that during 28 MTOs the bath is made up fresh four times for a total cost of $3758.88. For the dialysis scenario the bath is made up fresh once for $939.72 and rebuilt four times for a total of $2557.20. This amounts to a savings of about $42.89 for each MTO for the 340 gallons or $12.60 per MTO for a 100 gallon tank. If zinc and iron buildup can be avoided the bath can be treated with electrodialysis more than four times and the savings can improve over this.

The cost of waste treatment varies by location. For example, it is possible in large cities like Detroit to have electroless nickel solutions hauled away by a recycler for well under $1.00 per gallon. At that price onsite waste treatment is impractical and the suggestion that the electrodialyzed waste could be electrolessly decomposed might not be the most cost effective treatment.

For those shops that normally use electroless decomposition as a step in the waste treatment process, the introduction of electrodialyzed ortho waste would surely present an less costly waste stream to treat.

Assuming that the EN waste is hauled away and recycled for $1.00 per gallon there would be a savings of about $160 over 28 turnovers for a 340 gallon bath, or about $1.68 per turn over for a 100 gallon bath.

The average electrodialysis unit capable of handling 340 gallons costs about $80,000. With the modest savings detailed here in waste treatment and chemical costs it would take a long time to break even, and this does not consider the labor involved with the electrodialysis and analysis.

It can be suggested that treatment schedules other than the one detailed here might have advantages. For example, with Shop A performance over aluminum is very important. Thus it might be best to run the bath to 5 MTO and dialyze to 1 MTO. This is a good approach. However, a workup for the costs of this scenario is very similar to the costs presented above.

Discussion of Results. The results of our investigations into the effects of electrodialysis of baths from Shop A and Shop B have shown that electroless nickel baths can be rebuilt rather simply if the amounts of orthophosphite, hypophosphite, stabilizers and contaminants (like zinc and iron) have been analyzed. The contaminant levels should be the first indicator as to the health of the bath. If the contaminants are high the bath should be discarded.

The major advantage of electrodialysis is that the plating bath can be maintained in a condition where the work is consistent. The traditional problems of the deterioration of bath operation and deposit properties toward the end of bath life are dramatically minimized This in itself is a significant advantage.

The electrodialysis does reduce the stabilizer concentrations about 10-20%. However, the amount of the stabilizer package required for a rebuild will be different depending on the operation of each shop. It has been noted here that anodic protection systems for stainless steel tanks can "dummy" out the electroless nickel bath stabilizers and this factor figures strongly in the amounts of stabilizer package needed on a bath rebuild. Other factors in shop operation may also affect the approach needed to rebuild the stabilizer package. Thus, it is important to have an analysis background knowledge of the stabilizer concentrations for each shop.

The analysis of costs presented here suggest that cost is not a major advantage of electrodialysis when all costs are taken into consideration.

The complexor package passes through the membrane with the orthophosphite. Some loss of the complexors is desired to avoid a buildup of complexors, but care must be taken to return the bath to at least 100% of fresh make-up concentrations. While the complexor loss seems to parallel the loss of orthophosphite, it is a good idea to have a background history of complexor concentrations for a shop that is about to use electrodialysis. Once this history is understood, a table like Table 8 can be set up for that shop.

Table 8
Complexor Package Needed on Bath Rebuild

Orthophosphite Removed By Dialysis	Complexor Package Required
Less than 90 gm/L	Replenish Nickel and Hypo as if a normal replenishment.
90-130 gm/L	3.1% by volume
130-160 gm/L	6.3% by volume
Above 160 gm/L	9.4% by volume

Note that the Complexor Package at 12% provides 100% of fresh make-up.

The strategy for rebuilding a bath includes the following steps:

1. Analysis of the contaminates from the work must be done to determine if the bath can be electrodialized and rebuilt. If the contaminants (i.e. zinc or iron) are above a set limit the bath should be discarded.
2. After electrodialysis replenish hypophosphite as required by analysis with purified liquid hypophosphite solution.
3. Replenish the complexors for a particular proprietary process with a complexor package based on experience of losses of complexors vs. losses of orthophosphite. Table 8 lists the strategy for the particular mid phosphorus process used in this study.
4. Replenish the stabilizers with a proprietary stabilizer package. The amount required should be based on analysis of the stabilizers. However, once some experience is gained concerning the operation of a particular shop it is likely that a specific routine addition would be possible.
5. Adjust nickel concentration by analysis.
6. Filter the rebuilt plating solution and adjust pH.

Conclusions

Electrodialysis has several benefits, including the extension of the bath life, and the creation of a "steady state" environment for the users. Electrodialysis is well suited to environments where predictable deposit properties and plating rates are desired, and is perhaps the best feature of the process. Frequent electrodialysis of a bath, perhaps keeping the bath in the range of 1 to 5 MTO, would be ideal in this regard.

Today, electrodialysis operations do not produce a cost savings when compared to conventional electroless nickel operations when all costs are taken into account. The costs of rebuilding a bath are significant. A supplier and the customer may make an agreement on how these costs might be distributed, but in the end someone must pay for the materials needed to rebuild the EN bath.

Waste volumes are not really minimized to any significant extent. However, most of the nickel metal ions do remain in the electroless nickel bath. The nickel, complexors and hypophosphite that are present in the waste may present an opportunity to treat the nickel by electroless decomposition using the waste hypophosphite rather than using expensive fresh hypophosphite.

Since the cationic membrane of the dialysis unit is designed to prevent the migration of nickel into the waste stream, the system is inherently susceptible to metallic contamination. The level of zinc, which has a higher molecular weight than nickel, has been seen to rise in baths so that shops that plate aluminum must exercise some care to avoid zinc buildup. Iron is also not removed significantly so that shops with rough castings or other types of work that add iron to the bath must also exercise more care. The electrodialysis example chosen for these discussions did not remove enough zinc from the bath to obtain good performance over aluminum.

After a bath is dialyzed it needs to be analyzed and adjusted and this requires skilled personnel.

Acknowledgments
The authors would like to thank MacDermid Inc. for supporting this work. We also would like to thank Pure Cycle Inc. of Palmer, Mass. for providing the lab electrodialysis unit used in some of these studies.

References

1. Mallory, G., "The Electroless Nickel Plating Bath", EN Conf. III, Gardner Publications, 1979.
2. Baldwin, C., Such.,T., *Trans. Inst. Met. Fin.*, **46**, 73 (1968).
3. Mallory, G, Altura, D., *SAE Technical Paper 830693*, 1983.
4. Parker, K, *Plat. Surf. Fin.*, **76**(3),48 (1980).
5. Richtering, W., et al, EN Conf. 97, Gardner Publications 1997.
6. Riedel, W., "Electroless Nickel Plating", Finishing Publications Ltd., 1991, pg 17.
7. Mayes, R., Reno, Y., EN Conference 97, Gardner Publications 1997.
8. Bellemare, R., EN Conference 97, Gardner Publications 1997