# ENFINITY ELECTROLESS NICKEL OPERATIONS


**ABSTRACT**

This paper describes a new electroless nickel process chemistry that eliminates the need to dispose of the solution after 8 to 10 MTOs due to build up in by-products. This technology provides for a chemistry which is free of Sodium and Sulfate ions and continuously removes Ortho-phosphite and other unwanted by-products. This paper will also provide a review of operations of a 500 gallon high phosphorus process utilizing this technology in continuous operations for over 5 years and 100s of MTOs.


## INTRODUCTION

Ever since the first commercialization of the process, a desire of electroless nickel operators and formulators has been to have an electroless nickel plating process which could be continuously regenerated and not require waste treatment and disposal. This desire has increased in recent years with the mandate to install waste minimization programs and waste reduction by POTWs.

Our original goal was to develop a process which could be recovered and reused after 6 to 10 MTOs. The effort soon turned to a continuous treatment process which eliminated the need to treat the entire volume of electroless nickel solution.

There were several benefits to having a continuous and infinite electroless nickel process. These are:

### *Benefits to Infinite Operations*

- ***Improve Quality of the Deposit***
- ***Elimination of Waste Treatment of EN***
- ***Reduction of Overall Cost***
- ***Source Reduction of Nickel***

In 1986 a team was formed to produce an electroless nickel process which would provide these benefits. The project was started with a complete search of available technology. In addition, laboratory logs from 1963 covering some aspects of the process were assembled. The team consisted of Dr. Hal Cooper, Richard Stapleton, Diane Mills and Phillip Stapleton with regular review.

Over a period of 18 months the technical feasibility of the process was demonstrated. Several mechanical and chemical issues were studied with the intent of having a product.

## EARLY DEVELOPMENTS

There are several by-products and contaminants which collect in the electroless nickel process and ultimately cause waste treatment and disposal of the solution. These materials can be summarized as follows:

## *Contaminants in the Electroless Nickel Process*

- ***Sodium sulfate***
- ***Ortho-phosphite***
- ***Nickel phosphide***
- ***Iron***
- ***Zinc***
- ***Aluminum***
- ***Chlorides***
- ***Organics***

The means of removing these contaminants from the process is varied and includes filtration, ion exchange, electro-dialysis and crystallization. Some of these techniques are costly and complex and require secondary treatment to reduce the quantity of waste nickel generated.

Early work by Gutzeit in this area utilized a chiller to crystallize the Sodium sulfate from the aged solution while removing the Ortho-phosphite by precipitation with lime. Their patents reported using sulfuric acid to lower the pH after lime treatment. The sulfate was then removed in the next lime treatment as Calcium sulfate.

A practical problem with their method was the crystallization of Nickel sulfate along with the Sodium sulfate producing a salt cake which contained nickel. This condition produces a hazardous waste which is difficult to treat and render non-hazardous. While these early efforts were attempting to resolve the issue of eliminating the by-products in the solution they produced many more questions and in the end were not embraced.

One of our prime objectives was the development of a balanced chemistry system which would eliminate the need for extra ions being added to the process. This was accomplished through the use of a nickel salt which contained the reducing agent. This material provided for the elimination of the sodium and sulfate ions by using nickel hypophosphite.

### EXPERIMENTAL WORK

The initial lab work involved building several solutions using standard production formulations and the reducing nickel salts. These were compared against standard nickel sulfate and sodium hypophosphite solutions. The physical properties were compared included hardness, corrosion and wear resistance along with ease of use, stability and costs.

A major concern was the removal of trace elements and contaminants which generally are the cause of premature disposal. Studies were conducted using 4 liter solutions for up to 20 MTOs for zinc, aluminum, iron, lead, cadmium and other elements to determine the efficiency of the purification. These tests showed that all major contaminants are removed with the purification treatment.

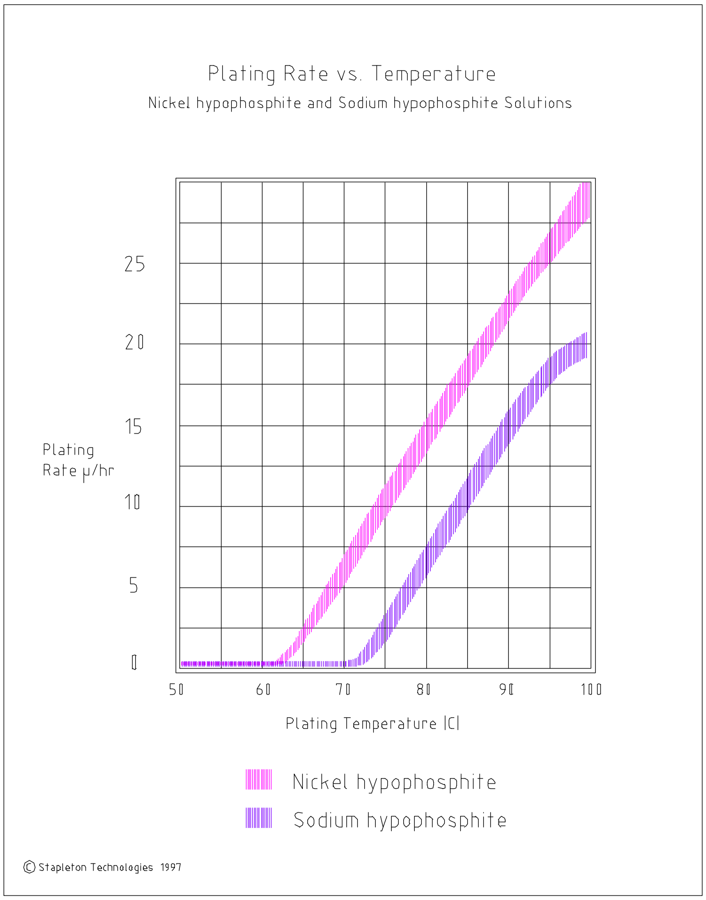
Extensive tests on solubility's of solution constituents with both magnesium and calcium were performed. These were needed to select the most efficient purifier and carboxylic species.

Initial laboratory studies also focused on the manufacture of the raw materials used in the process. This was a primary concern since some ingredients had high cost.

From these efforts, several benefits were realized. These benefits included increased phosphorus in the alloy, faster plating rates and lower internal stress.

## *Benefits of Nickel hypophosphite Chemistry*

- ***Higher Plating Rate at equivalent conditions***
- ***Higher Phosphorus in Alloy at equivalent conditions***
- ***Lower Internal Stress in the deposit.***




### PLATING RATE

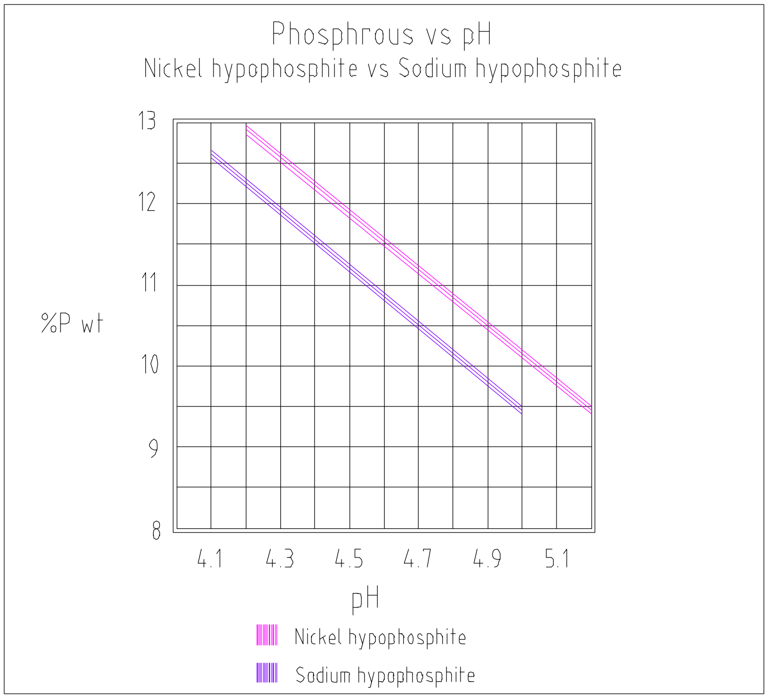
A series of rate verses temperature tests were performed using a standard mid-phosphorus complex. It was discovered that the deposition of nickel from hypophosphite proceeds at an average rate of 0.2 mils per hour faster than the deposition from Nickel sulfate. In the graph on the following page the plating rate verses temperature is plotted. There is little benefit in operating at lower temperature since a significant evaporation is required to make room for additions. There is a benefit however to the higher plating rate: the lowering of the pH without reducing the plating rate, which causes an increase of the phosphorus in the alloy.

This can be an important consideration in selecting a high phosphorus deposit on thick deposits. A 60% increase in plating rate on a 3 mils (75 micron) requirement will reduce the processing time from 12 hours to 7.3 hours making several applications far more productive.

It was also possible to produce sustained plating rates in excess of 1.3 mils per hour with high speed mid phosphorus process chemistry. While this feature may be of interest the usefulness is questionable.

## HIGHER PHOSPHORUS ALLOY

Another benefit is the increase in phosphorus in the alloy. This was realized by plating several test specimens at various conditions and then alloy analysis by ICP. This series of tests showed that the phosphorus content was significantly higher at the same operating conditions as conventional Sodium hypophosphite solutions




This condition provides for faster plating rates with equal phosphorus contents or higher phosphorus contents in the alloy. In either case these nickel hypophosphite salt processes provided greater flexibility and increased function.

## LOWER INTERNAL STRESS

Another benefit which is related to the deposit alloy is the internal stress. Stress analysis of high phosphorus deposits showed that they were more compressively stressed than conventional electroless nickel. This condition is directly dependent on the higher phosphorus content in the alloy and is an important feature for some metallic optics applications.

## OTHER BENEFITS

There are several other benefits to the infinite process. A significant advantage is the consistent low solution concentration. This aids in increasing the performance of the deposit by improving adhesion on aluminum, reducing rinsing questions and controlling deposit stress due to high Ortho-phosphite.

## MATERIAL BALANCE

The most significant element of this infinite electroless nickel process is the maintenance of an absolute material balance. What this means is all ions added to the process are either plated onto the part or removed through treatment. This is accomplished by incorporating new chemistry and equipment into a process system to achieve this balance.

## *Elements of a Material Balance*

***Continuous Additions of Nickel***
***Continuous Additions of Reducer***
***Continuous Removal of Reduction Reaction By-Products***
***Continuous pH adjustment***
***Continuous removal of contaminants***

As in conventional electroless nickel processes the nickel concentration can be used to determine the additions. The nickel concentration in the infinite electroless nickel process is maintained in the 6 to 6.6 g/l range. An ICP was used to measure the nickel as well as all other trace elements during the laboratory development. In the field both Photometric and X-Ray analysis for nickel are used.

When a 5% reduction in nickel occurred a fixed 5% addition was made to the process. The reduction reaction of electroless nickel produces several effects within the process. These are all dependent on the consumption of nickel and therefore can be controlled by the nickel. The primary process conditions effected by the reduction reaction are:

## *Process Conditions effected by Reduction*

- ***Reduction of nickel concentration***
- ***Reduction in hypophosphite concentration***
- ***Increase in Ortho-phosphite concentration***
- ***Reduction in process pH***

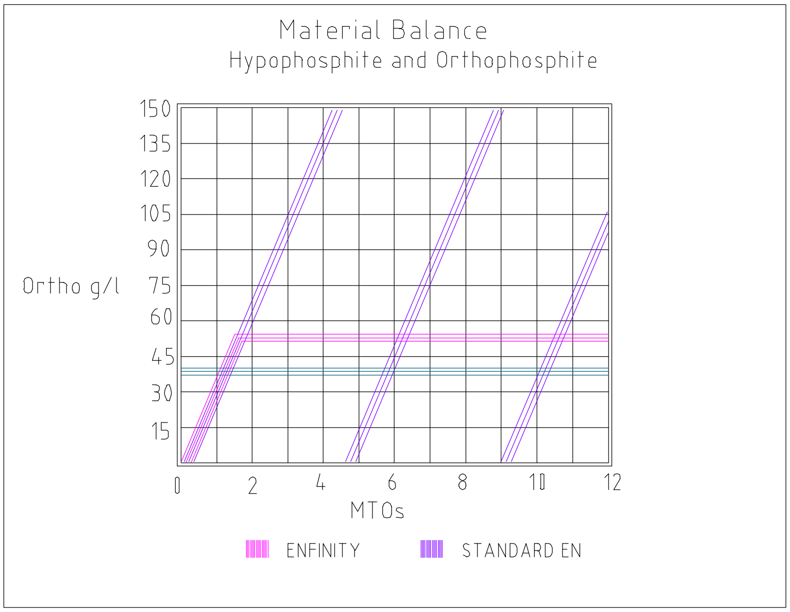
To maintain the material balance these conditions must be returned to the initial point or the electroless process will not be infinite. By using a 5% trigger of nickel the operator can make the adjustments for all conditions at one time and return the process to its original condition.

The Ortho-phosphite increases as a direct result of the reduction of nickel. In the infinite process a small off-line batch processor is used to treat the Ortho-phosphite for 5% of the working volume.

This removed solution is reacted with a proprietary purifier and then agitated for 5 minutes. The pH will rise due as the exothermic reaction precipitates the Ortho-phosphite. After digestion the reacted material is filtered.

As the filtration process is completed the filter cake is rinsed with a small amount of deionized water which removes the remaining nickel in the cake. The filtrate is returned to the plating tank and the filter cake becomes non-hazardous waste.

## *Material Balance of Infinite EN*




In the graph on the left, the concentration of Ortho-phosphite and Hypophosphite ions are plotted. The blue lines which cross the upper regions of the graph show the Ortho-phosphite without treatment in the conventional process while the ENFINITY process is being maintained at less than 60 g/l orthophosphite.

The initial operation of the infinite electroless nickel process proceeds as a conventional process. Once the process gets to beyond 2 MTOs the purification process is started. With consistent processing the Ortho-phosphite in the manner described the Ortho level can be controlled to any point. When the level goes to below 1 MTO or 30 g/l the treatment becomes less efficient and treatment should be stopped. Once back up to 40 to 60 g/l the treatment should resume.

The pH of the process is reduced by the reduction reaction. The amount of acid produced is equivalent to the amount of Ortho phosphite produced. Consequently when the Ortho is removed by precipitation the filtrate that is returned to the working solution will cause the pH to return to the initial control point.

The use of carbonates, or high solubility Sodium and Potassium hydroxides to adjust the pH is not possible as in conventional electroless nickel. These ions have high solubility's and can't be removed by precipitation. Their addition will ultimately cause the process to become saturated and require disposal.

The laboratory investigation of this technology studied all major properties of nickel deposit. Aside from the improvements in plating rate and phosphorus content at equivalent conditions the deposits produced have the same properties.

### LABORATORY OPERATIONS

The laboratory evaluation of this technology was performed in a 15 gallon process tank. The tank was made of natural poly-pro and heated with electric immersion heaters. A pump and bag filter was used to remove solids and improve heat transfer.

Working solution was removed before each 5% nickel addition was made. The removed solution was allowed to collect until there was 4 gallons to treat. This material was cooled by natural means and the reaction was started at a temperature below 35 ©. A fixed amount of purifier was added for each 4 gallons and the batch was allowed to digest for 5 minutes. The reacted solution was filtered with a Buchner filter. A Deionized water wash was performed just prior to the last liquid being visible on the filter. The treated solution was used to adjust the pH and replace the liquid volume of the removed solution for the next quarter of a MTO.

This 15 gallon solution was operated for over 70 MTOs in the laboratory using these procedures. Typical solution use per day was 50% requiring over a half year of tank time to demonstrate the principles.

The need to have an automated filter unit was evident from the beginning. The filtration requires a 25 to 30 "Hg vacuum. If the vacuum is less, a wet hazardous filter cake is produced.

Using Deionized water rinse and a strong vacuum on a Buchner filter the cake can be filtered to about 50% solids. Studies were made on several different designs of filters with various filter cloths. The most efficient were with shark skin and at 30 "Hg. By slurring and triple rinsing the cake the amount of nickel was below the TCLP and WET limits.

## EQUIPMENT

An integral part of the implementation of this technology is the filtration equipment which removes the Ortho-phosphite. There were several different designs considered. The function of the equipment is:

### *FUNCTION of INFINITE PURIFICATION EQUIPMENT*

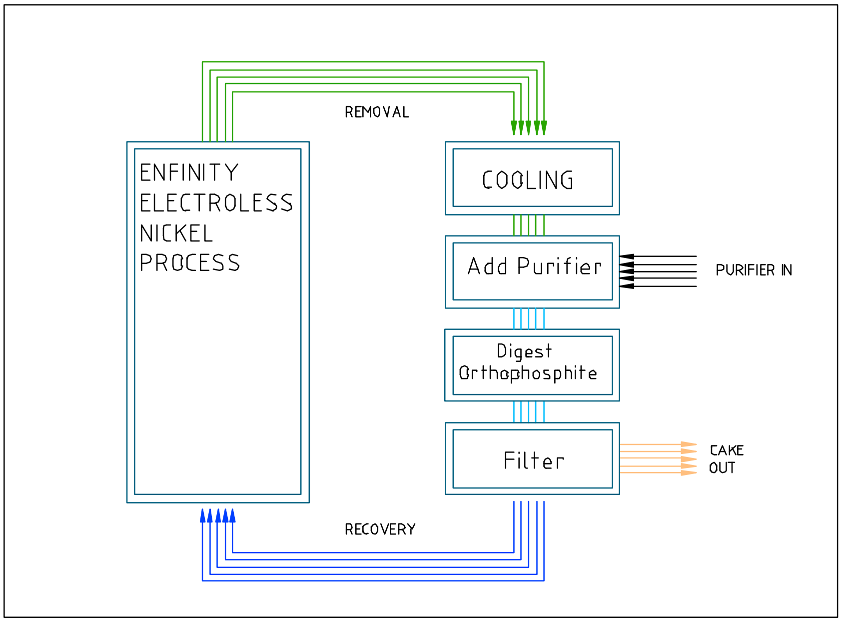
***Maintain the Material Balance***
***Remove Ortho-phosphite from the Process***
***Make Additions of Maintenance Materials***
***Adjust the pH of the Working Solution***


Figure 1, PU2 Unit at MSI

From these functions several designs have been made and field tested. There were many mechanical issues which had to be resolved including control of the reactor, determination of a dry filter cake and software to control overlap processing.

The purification function if organized into four segments. They are described in the following chart. Each of these functions are controlled by a microprocessor using pneumatic pumps and valves.

### *Infinite EN Purification Equipment*




All of these functions have been incorporated into a modular, skid mounted unit that in addition adds the maintenance chemicals. The initial designs did not included an analyzer to test for nickel. This feature has now been added.

## BETA SITE TESTING

The initial filter unit was designed, built and delivered directly to the Embee Inc. for completion. The computer, sensors, pumps and other equipment were installed at the Embee beta site. The software was written after the hardware installation had been completed. The beta site installation required 3 months.

The first unit was installed on a 300 gallon electrically heated poly-pro tank. The first solution was operated to 5 cycles with sulfate being added. While the filter removed the sulfate along with Ortho-phosphite the amount of time to treat became very long. It was decided that a new solution be made up and no sulfate be added.

This solution was started and operated to 10 MTOs in production. The process was able to maintain the Ortho at around 60 g/l which is an equivalent to 1.7 MTOs while running completely automatically.

During the Beta Site phase the software modifications were accomplished, sensor designs modified and other design considerations made. These upgrades became an important aspect of the future design.

## PRODUCTION

After the Beta Site work was completed these modifications were incorporated into the next generation of units. The economics were also an important consideration and developing a smaller and more compact unit became a priority.

This new unit was built, programmed and installed within 14 weeks. The unit has the same capacity as the first unit.

The second unit, PU2, was installed at Metal Surfaces Inc. on a 500 gallon tank and has been running continuously since July 1, 1992. The process is operated in a poly-pro tank with external heat exchanger. The original solution and is providing a high phosphorus alloy on a wide range of base materials and applications. The initial solution was operated to 145 MTOs at which time the organic components of the solution became to concentrated. A second solution has been made up and in 1997 this solution is approaching 50 MTOs. The next major milestone will be when this solution goes over 300 MTOs.

Trace metal analysis of the solution show that the Iron, Zinc, Aluminum, and Magnesium are each being maintained constant at around 30 ppm while other trace materials like Lead, Cadmium remain less than 1 ppm. After going over 50 MTOs there has been no evidence of organic contamination or pitting.

## FIELD OPERATION

The PU2 is very simple to operate. It has been designed to have little maintenance and can be serviced if necessary by the operator. The PU2 has four buttons for the operator. These are:

## PU2 OPERATOR CONTROLS

5% ADDITION
TREAT BATCH
UNLOAD FILTER
RETURN FILTER

The operator presses the 5% ADDITION button and the PU2 removes 25 gallons of working solution, replenishes the process with nickel by 5% and replaces the removed solution with 27 gallons of purified solution. Level sensors tell a microprocessor that the correct volume has been moved and the pneumatic pumps are halted.

After the reactor cools the removed solution to below 35 © a light on the panel of the PU2 indicates to the operator that a batch is ready to treat. The operator places a pre weighed amount of purifier into the reactor and starts the treatment function by pressing the TREAT button.

The batch is cooled, reacted, digested, transferred and filtered automatically within the PU2 by the control of the microprocessor. Signals are sent to a pneumatic manifold where air is used to operate pumps, valves, motors and pneumatic cylinders.

When the filter cake is ready to be removed from the PU2 a light on the panel tells the operator to unload. The operator checks to see if the tote is in position and presses the UNLOAD button. This causes the filter of dump the load and by pressing the RETURN button the filter returns to rest.

The filtrate which was produced from the initial filtration is placed into a holding tank and is used for the next 5% addition.

## DoD & BATTELLE

In 1993 the DoD through the Armstrong Research Center contracted with Battelle Memorial Institute to study electroless nickel at the DoD facilities. After a complete review by Battelle the Stapleton ENFINITY process was selected and a demonstration site selected at Tinker AFB.

The process was tested successfully and demonstrated that the ortho-phosphite could be maintained at a constant level during the life of the solution. Parts were plated to thickness of 60 mils to demonstrate electroless nickel as a chrome replacement. These tests required that the process operate continuously for over 80 hours to produce the desired high phosphorus coating.

In 1994 the ENFINITY process was submitted for consideration for a R&D100 Award. This award recognizes the top 100 inventions during the year and includes the ABS braking, the CD and many others. Stapleton Technologies received the award for the ENFINITY process along with Battelle and Armstrong for sponsoring the demonstration of the process.

## PU3

The next generation of purification equipment utilizes a continuous treatment during the production cycle and a pressure filter instead of a vacuum filter. The equipment called the PU3 operates automatically when the solution needs to be replenished. The advantage of this design over the PU2 is the operator has less involvement in the treatment. The PU3 is designed for operations where several people are responsible for the solution and multiple shifts make training more complex.

## ECONOMICS

The overall cost of the infinite electroless nickel process is lower than conventional electroless nickel when considering waste treatment, disposal and quality. The chemistry is slightly more than conventional electroless nickel at $2.30 - $2.50 per mil square foot with the capital equipment cost in the range of $30K. These economic factors must be analyzed against current and future costs in order to measure the value.

## *ECONOMIC FACTORS for INFINITE EN PROCESS*

Increase in Quality
Corrosion Resistance
Adhesion
Solderability
Phosphorus Content
Reduction of Deposit Stress
Deposit Consistency

Elimination of Hazardous Waste
Source Reduction of Nickel.
Reduce Liability of Waste Disposal
Reduce the Storage and Accounting functions

Elimination of Waste Treatment

***Reduce Waste Treatment Operator functions***

Reduce Permitting Requirements
Reduce Liability of Treatment Operations

These benefits must be analyzed for each specific facility and the cost vs the benefit analysis made.

## SUMMARY

In conclusion it is our belief that the infinite electroless nickel process will be fully embraced when deposit quality, and environmental responsibility become the driving forces in the market. Organizations that have this vision will continue to use the infinite process and lead the industry into the next century.

This paper was originally presented at the EN93 Conference produced by Product Finishing and has been expanded and updated as required.

**RETURN**