The EDEN System for Electroless Nickel Bath Life Extension and Consistent Quality

Peter Longfield, Atotech USA Inc., Rock Hill, SC & Graham Orgill, Atotech UK Ltd., West Bromwich, UK

Electroless nickel coatings have many unique properties making them preferred for many industrial applications. However the process operation is difficult because of a relatively short bath life and variations in deposit quality during the bath life. A process has been developed which overcomes these obstacles by continuously regenerating the bath with a custom tailored electro dialysis system. It allows EN plating under consistent process operating conditions, producing consistent deposit properties and, in principle, a "never-dump" EN bath. The process has been in production for the deposition of low, mid and high phosphorus deposits. The paper will describe the new technology, concentrating on experiences from large EN platers, one of whom has attained more than 2,000 metal turnovers with consistent deposit quality.

For more information, contact:
Peter Longfield,
Atotech USA Inc.
1750 Overview Drive,
Rock Hill, SC29730
USA.
Phone +1 (803) 817 3542
Fax +1 (803) 817 3624
E mail: plongfield@atousa.com

Or
Graham Orgill
Atotech UK Ltd.,
William Street,
West Bromwich
West Midlands B70 0BE
England.
Phone +44 (0) 121 606 7777
Fax +44 (0) 121 606 7230
E mail: graham.orgill@atotech.com

Introduction

The autocatalytic deposition of nickel from aqueous electrolytes containing reducing agents like sodium hypophosphite, sodium borohydride or dimethylamineborane is generally referred to as Electroless Nickel. While various binary or ternary alloys (NiP, NiB, NiCoP, NiWP, etc.) may be obtained by this method, the binary Nickel-Phosphorus alloys are by far the most technically used alloys with a market share of some 98%. The Electroless deposition of nickel was first developed in 1946 by Brenner and Riddell [1,2]. Over the past 59 years, the process technology has improved substantially and is well established in many industrial areas. The applications vary from decorative uses (e.g. in the plating on plastics) to mainly functional applications providing both wear and corrosion protection. The physical properties of the deposits, uniformity of coating even on complex shaped components, corrosion and wear resistance and magnetic properties, are superior to electroplated Nickel. Today it is the most important autocatalytic plating process with an annual growth rate of 4 – 6 % in recent years [3]. Depending on the deposition parameters and plating bath composition, nickel-phosphorus alloys with 2 – 13 %w/w phosphorus can be deposited.

The single largest application of high-phosphorus (> 11 % w/w) Electroless Nickel coatings is currently plating on rigid memory discs (RMD) for storage in electronic data processing [4]. The aluminium-alloy substrates require a perfectly flat, non-magnetic, corrosion resistant coating, which can be polished and finally sputtered with the magnetic storage medium.

The remaining market is distributed over many applications in chemical industry, automotive, printing, electronics, oil & gas, aerospace and general machinery.

In general terms, all Electroless Nickel coatings can be grouped into four types according to their phosphorus content in the alloy.

	P- content in %w/w	Market share
Low – P	1-3	3%
Low-mid P	3-6	12%
Mid-P	6-10	60%
High-P	>10.5	25%

The mechanism of Electroless deposition of Nickel-Phosphorus alloys involves many different reactions and can best be described by the following simplified reactions:

$$NiSO_4 + 3\ NaH_2PO_2 + 3\ H_2O \rightarrow Ni + 2\ H_2 + H_2SO_4 + 3\ NaH_2PO_3 \quad (1)$$

$$3\ NaH_2PO_2 \rightarrow NaH_2PO_3 + 2\ P + 2\ NaOH + H_2O \quad (2)$$

$$NiSO_4 + 6\ NaH_2PO_2 \rightarrow Ni + 2\ P + 2\ H_2 + Na_2SO_4 + 4\ NaH_2PO_3 \quad (3)$$

The detailed mechanism has been subject of discussions [5,6]. The most widely accepted mechanism is given by Zeng and Zhou:

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^{2-} + 2H^{\cdot}_{ads}$$
$$Ni^{2+} + 2H^{\cdot}_{ads} \rightarrow Ni + 2H^+$$
$$H_2PO_2^- + H^{\cdot}_{ads} \rightarrow H_2O + OH^- + P$$
$$2H^{\cdot}_{ads} \rightarrow H_2$$

It is evident from equations (1) to (3), that during the Electroless deposition the concentrations of metal ions and reducing ions is decreasing and the reaction by products (sodium orthophosphite and sodium sulphate) are increasing in concentration. To maintain the reaction under steady state conditions, nickel sulphate and sodium hypophosphite have to be replenished frequently. Under industrial production conditions this is achieved by either manual or automatic addition of highly concentrated solutions containing nickel sulphate and sodium hypophosphite.

The generally used term to describe the " age " of a plating solution is the so-called metal turn over (MTO). One metal turn over (or MTO) has passed, when all of the nickel originally present in the bath has been plated and replenished

The frequent addition of replenishment products leads to a continuous increase in the concentration of by-products. The following example shows this effect for a typical industrial Electroless nickel bath containing:

Ni	6 g/l	=	0,10 M
$NaH_2PO_2.H_2O$	30 g/l	=	0,28 M

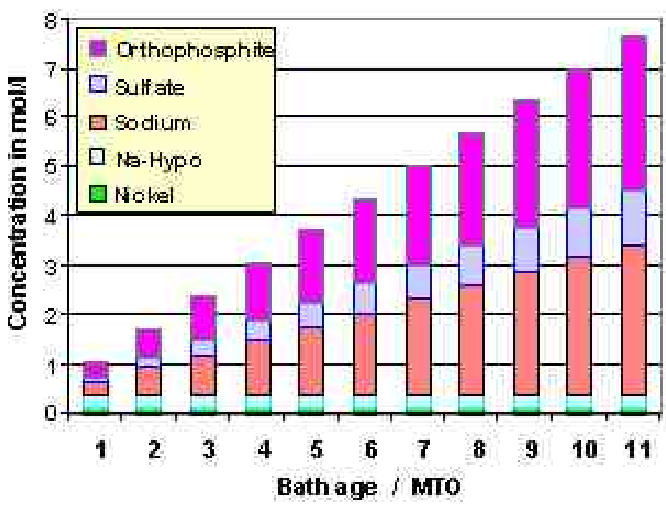
For each mol of deposited Nickel, 3 mol of Na^+ and 1 mol of SO_4^{2-} remain in the bath and approximately 3 mol of HPO_3^{2-} are formed [7].

For 1 metal turn over or 6 g/l Ni deposited:

Na^{+}	increases by	7,0	g/l	=	0,30M
SO_4^{2-}	increases by	9,6	g/l	=	0,10M
HPO_3^{2-}	increases by	24,0	g/l	=	0,30 M

The concentrations of the individual species as a function of the bath age calculated from these figures are shown in fig. 1. Under practical conditions, the actual figures may be slightly lower due to solution drag-out effects. However the fundamental increase of solution density with time is not significantly reduced.

Fig. 1:
Theoretical increase of reaction products in mol/l as a function of bath life in metal turn over (MTO).



The accumulation of by-products leads to a decreasing plating rate and deterioration of deposit quality (higher internal stress, lower corrosion resistance) until the process is no longer technically and economically acceptable. The complete bath solution has to be discarded and a new bath has to be made-up [8, 9]. Compared to typical electroplating solutions Electroless nickel solutions have a very short operating life. Depending on the process and deposit quality requirements, Electroless nickel electrolytes have to be discarded after 7 – 12 MTO. It is obvious, that this is a severe disadvantage of Electroless nickel-plating technology causing both ecological and economical concerns and limitations. In addition, over a complete bath life of an industrial process solution, all process parameters are varying continuously which has an influence on coating properties and quality – a fact that is not acceptable for modern production philosophies.

The shortfalls of standard Electroless plating processes can be summarised as:

- Short bath life
- Fluctuations of process parameter (plating rate, temperature, pH)
- Variations of deposit quality (internal stress, P-content, corrosion resistance, magnetic properties).
- Frequent new bath make-up and resultant down time

Technology concepts for bath life extension

The extension of Electroless nickel bath life has been the subject of many development projects in the past. Various concepts have been considered to date:

1. Use of sodium and sulphate free chemistry, i.e. nickel hypophosphite
2. Selective chemical precipitation of by-products
3. Selective ion exchange
4. Direct cathodic reduction
5. “Bleed and Feed”
6. Electrodialysis (standard batch treatment concept)

The first method is based on the fact, that replacing nickel **sulphate** and **sodium** hypophosphite by nickel hypophosphite reduces the introduction of foreign ions considerably and slows the increase of total salt concentration and hence increases bath-life. This is shown in fig. 2

However, the formation of orthophosphite is not affected and the bath life extension can only be expected to reach a factor of 2. The high cost of Nickel Hypophosphite and its limited solubility have restricted the commercial use of this concept.

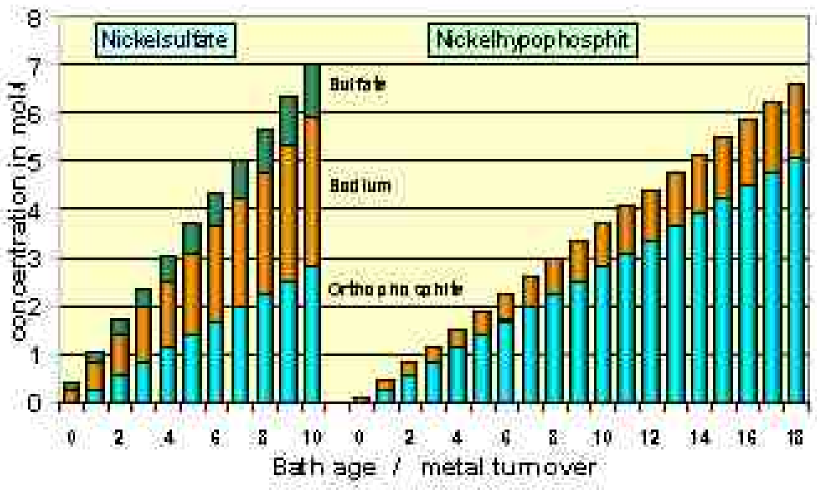


Fig. 2:
Comparison of the theoretical total salt concentrations of a conventional EN-bath (sodium hypophosphite and nickel sulphate basis) versus a nickel hypophosphite based process.

The selective chemical precipitation technique is mainly based upon differences in solubility of the calcium-, magnesium- and sodium salts of hypophosphite and orthophosphite under pH-controlled conditions [7,8,10]. Such methods have the disadvantage of relatively high losses of hypophosphite, introduction of Ca and Mg ions into the bath and high labour. According to the authors' knowledge only a few industrial applications have been realised.

Ion exchange of sodium orthophosphite and sodium sulphate against sodium hypophosphite has also been described in literature. Again high losses of hypophosphite and nickel ions due to insufficient specific ion exchange resins prohibit application of this technique.

Direct cathodic reduction of orthophosphite to hypophosphite in a separated electrolytic cell has been claimed. Low efficiency and limitation to sulphate free solutions has prevented any technical exploitation of this method.

The concept of "Bleed and Feed" is used under production conditions. By the permanent removal of part of the bath and replacing with new make up, the process can be operated on quasi steady state conditions. Whilst the objectives of constant plating rate and deposit parameters can be achieved by this method, the loss of valuable chemicals is very high, due to both by-products and essential products are removed without any selectivity. Additional waste material is generated and costs are therefore high.

A review of these technologies has been compiled by Bolger and Szlag [13]

Electrodialysis for solution regeneration

Separation of ions at semi permeable membranes by electrodialysis is an established technology for many chemical, pharmaceutical and food applications. It allows treatment of process solutions without any additional chemicals being introduced into the process and can easily be up scaled and automatically controlled. The application for EN solution regeneration has been described by various authors in the literature [11, 12] and has also been used in very few cases under industrial production environments. Despite positive results and reports of bath-lives achieved of more than 100 metal turn over, this method has not been introduced into the industry on a broader scale.

The reason for this is, that both methods (precipitation, standard electrodialysis) do not reach the required selectivity between the desirable and by-products of the Electroless process and are always used in batch mode. As a consequence, the plating bath has to be taken out of production for the regeneration process. In addition, the objective of consistent operating parameters is only achieved to a limited extent, as the bath age follows a "jig-saw" curve from 0-1 MTO up to 6 – 8 MTO before it is regenerated and restarted at approximately 1 MTO.

The main reason for application of the electrodialysis technology for regeneration of Electroless nickel process solutions only in batch mode is the insufficient selectivity of standard electrodialysis membrane types and their arrangement.

Continuous Electro-Dialysis for regeneration of EN process solutions

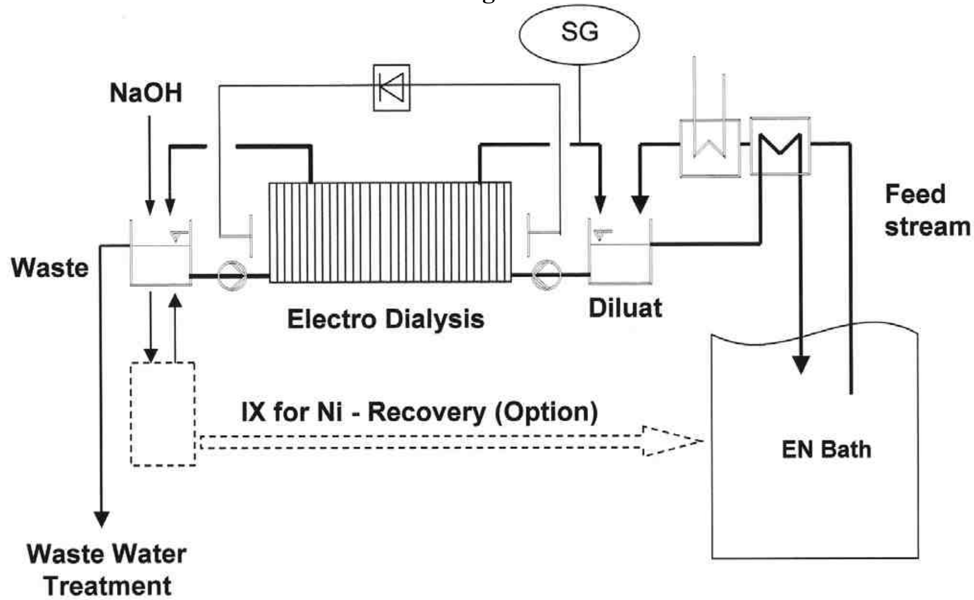
Only by development of special membrane types and the design of membrane stacks tailored specially for Electroless nickel solutions permits the application in a continuous mode without significant losses. Furthermore, the replenishment solutions have to be designed for operation with electrodialysis regeneration.

By selection of special membrane types involving monopermselective ion exchange membranes and a modified arrangement of anionic and cationic ion exchange membranes for the Electro-Dialysis of Electroless Nickel (EDEN) the difference between transport rates of hypophosphite and orthophosphite, i.e. the selectivity, can be improved considerably. Use of such techniques led to the development of the EDEN system which was granted European patent No.1123424 and United States patent No. US 6,379,517B1 both awarded in April 2002.

Continuous Electro-Dialysis for regeneration of EN process solutions

A flow-chart of the continuous regeneration of Electroless nickel solutions by a specialised electrodialysis arrangement is shown in fig. 3.

Fig. 3



The electrodialysis stack is supplied with high volume pumps from 2 reservoir tanks for the diluate and the concentrate, respectively. The diluate tank is continuously supplied with a low volume flow (appr. 30 – 50 l/h) from the Electroless nickel-plating tank cooled by a counter flow heat exchanger to limit the solution temperature in the stack to maximum 40°C. The current density supplied to the electrodialysis stack is controlled by a specific gravity sensor in the diluate reservoir and therefore adjusts the stack performance to the actual plating bath loading or operating time. The second solution circuit of the concentrate comprises an automatic pH-control and automatic water dosing to keep the concentrations of sodium, sulphate and orthophosphite in the optimum range. The typical bleed stream is app. 10 – 20 l/h.

The regeneration unit also contains an automatic controller for the Nickel content in the plating bath (photometric analysis of Ni) and the pH-value to allow for fully automated addition of the replenishment chemicals to the Electroless plating bath.

Regeneration of Electroless Nickel process solutions under production conditions.

<u>Case study 1:</u>

Job shop processor
Automotive Industry
Substrate Cast Aluminium (Manufacturing costs lowered)

Requirements
Hard wear and corrosion resistant coating
Surface hardness as plated 650 – 750 VHN
EDEN low P system (4 – 6% P)
Ammonium, Cadmium and Mercury free system

Operation
500 litre plating tank
ED4500 unit
Temperature 85 - 91°C
pH 4.7 – 5.0
Bath loading 0.65 – 1.7 dm.sq. /l.
Plating rate 20µ/hr

Result
Consistent plating rate, appearance, as plated surface hardness and deposit properties
Has now reached the equivalent of >2150 MTO

<u>Case study 2:</u>

In-house manufacturer
Office/Business Machine manufacturer
Low carbon free cutting mild steel

Requirements
Very high quality demands
Very smooth surface finish 0.1 Rp (noise reduction – normally required post polishing)

Wear and corrosion resistant coating
Fully automated processing
EDEN medium P system (8-10%P)
Ammonium and Mercury free system

Operation
3000 litre plating tank
ED1000 unit
Temperature 86 - 90°C
pH 4.4 – 4.7
Bath loading 0.2 – 2.0 dm.sq. /l
Plating rate14 - 18μ/hr

Result
90% of production without polishing
Improved productivity (Operates one shift instead of two, with the same through-put)
Energy and Labour cost reductions
Consistent plating rate, appearance and quality
Less down time – greater solution stability
Less plate outs
Fully automated production
In house waste treatment – significant savings

Case Study 3:

Job shop processor
General Engineering
Steel 65%, Aluminium 25%, Brass & Copper 10%

Requirements
Fully automated system
Consistent appearance and quality
Improved image with clients (Environmental)
ISO certificated

EDEN high P system (9 – 11% P)

Operation
Three shifts per day, five days per week
Twin Stainless steel plating tanks 3800 litres
No additional agitation (Only return flow from Filter pump)
Deposit thickness range 3 - 75µ
Bath loading 0.2 – 1 dm.sq. /l
PH 4.8 Temperature 90°C
Plating rate 11µ /hr

Result
P content 10 – 11%
Passes RCA Nitric acid test
Consistent appearance and quality
Deposit compressively stressed (After > 120MTO)
In house waste treatment
Higher solution stability, less plate outs

Conclusion

The EDEN system for continuous regeneration of Electroless nickel solutions comprising of modified electrodialysis equipment and adapted Electroless nickel bath compositions has been described. Compared to presently used technologies under production environments, this technology has a higher selectivity for separation of those by - products responsible for the limited bath-life under conventional operation of EN solutions, namely sodium, sulphate and orthophosphite. The advantages of this technology are:

- Theoretical unlimited bath-life extension, proven under production conditions for at least 2150 MTO
- Higher productivity due to consistent higher than average plating rate, higher bath loading (up to 70% more), higher yield, less rework, less down time (less tank stripping, infrequent make ups
- Consistent high quality, uniform coating properties and appearance
- Easy automation, no adjustment of temperature, pH etc.
- Higher stability
- Lower maintenance, automated replenishment
- Higher yield of EN chemistry, less losses, recycling of rinse water possible

- Environmental demands easier to fulfil, no ammonia, easier waste treatment, reduction in waste volume and concentration
- Less overall energy consumption
- Easier production

In combination these advantages can lead to lower process costs.

References:

1 A. Brenner, G. E. Riddell US Patent, US2532283 (1950)

2 A. Brenner, G. E. Riddell, Plat. and Surf. Finish. 85 [8], 54–56 (1988)

3 J. Bates, Plat. and Surf. Finish. 85 [5], 14-16 (1998)

4 J. Haydu, Proceedings of the 1999 Electroless Nickel Conference, Gardner Publications, Cincinnati, Ohio: pp 4-1 to 4-5

5 Y. Zeng, S. Zhou, Electrochemistry Communications 1, 217-222 (1999)

6 G. O. Mallory in: Mallory GO, Hajdu JB (eds) Electroless plating: fundamentals and applications, AESF, Orlando, Florida: pp 1-56 (1990)

7 K. Parker, Plat. and Surf. Finish. 67 [3], 48-52 (1980)

8 G. O. Mallory, K. Parker, Plat. and Surf. Finish. 81 [12], 55-58 (1994)

9 R. Duncan, Plat. and Surf. Finish. 83 [10], 64-68 (1996)

10 C.V. Bishop, G.W. Loar, M. J. Thomay , US Patent, US5221328 (1993)

11 D. J. Vaughan, US Patent, US5419821 (1993)

12 D. E. Crotty, Proceedings of the 1999 Electroless Nickel Conference, Gardner Publications, Cincinnati, Ohio: pp 22-1 to 22-12 (1999)

13 P.T.Bolger, D.C.Szlag, (USA EPA, National Risk Management Research Laboratory) private communication

