Extending the Operating Life of Electroless Nickel by Chemical Means

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The need to extend the operating life of electroless nickel solutions is as old as the technology itself. Over time, decomposition products and the remaining sulfate from the nickel, will reach a critical level, thereby limiting solution usefulness. Apart from the obvious costs involved in repeated solution make-up, replenishments and disposal, the main motivation for increasing the operating life is the desire to operate under constant working conditions and provide consistent deposit properties. Most known life-extending techniques are costly and/or involve production interruptions. This paper will discuss a new chemical answer to long life electroless nickel plating.

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The need to extend the operational life of electroless nickel (EN) solutions, or even to operate these endlessly, is probably as old as the technology itself. Decomposition products from the reducing agent, and the resulting sulphate from the nickel, will over time raise the density of the electrolyte to a critical level of 1.3 g/cm^3, thereby limiting the use of the solution. This operational time is normally expressed as "Metal Turn Overs" (MTO). This refers to how often the original nickel concentration in a given volume can be replenished, before the critical limit is reached, at which time the operating solution has to be disposed of. With conventional EN systems, and the usual nickel concentration of 5 to 7 g/l, a maximum amount of 60 g/l of nickel can be deposited from 1 litre of electroless nickel solution. This corresponds to a surface area of 30 dm^2 (approximately 3.2 ft^2) with a deposit thickness of 25µm (1 mil).

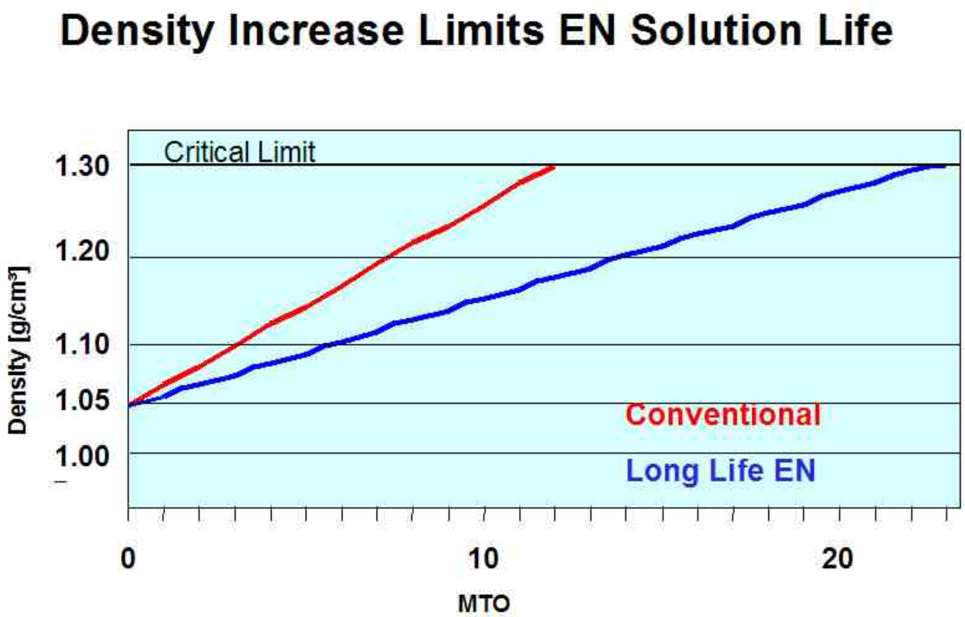
Apart from the obvious costs involved in repeated solution make-up, replenishments and disposal, the main motivation for extending the operational life is the desire to operate under constant working conditions, and of course provide consistent deposit properties. There have, until recently, been three possibilities each with their own disadvantages:

1. "Bleed and Feed" operation. Continuous disposal and replenishment of a portion of the operating solution in order to maintain a density of about 1.2 g/cm^3. Not technically complicated, but this method involves substantial solution loss and the associated costs and effort of disposal.

2. Another technique is the use of nickel hypophosphite as the combined metal carrier and reducing agent in order to prevent an increase of sulphate. The operational life can be extended to 16 MTO. However, the high raw material costs involved has prevented this technique from achieving noteworthy success. In addition, the solubility of nickel hypophosphite is so limited, that the evaporation losses are not sufficient to enable the replenishment components to be used with a workload, which is higher than 0.6dm^2/l (0.24ft^2/gal).

3. The use of two-stage electrodialysis equipment to remove orthophosphite (decomposition product from the reducing agent) and sulphate enable a continuous manner of operation at a consistent density and electrolyte quality. The high equipment investment and operational costs involved do not fully justify an economical use.

All of these techniques mentioned above involve regular recurring interruptions of the production process, due to the necessity to remove by stripping in nitric acid any plate-out which may have occurred, along with the need to re-passivate the plating tank and equipment.

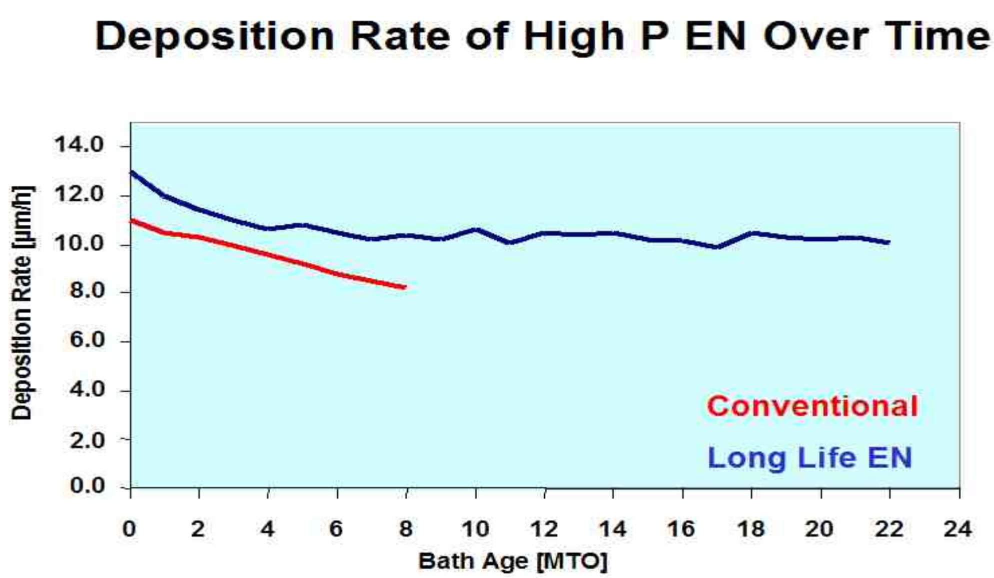


The primary theory in the development of a new kind of chemical solution to extend the working life of an EN solution was; that by avoiding the build-up of sulphates in the operating solution we will be able to eliminate their negative effect on solution performance and maintain consistent deposit characteristics over an extended operating life. Additional considerations included making the chemical nature of the electrolyte so robust, that stripping cycles, and nickel plate-out could largely be avoided and also that optional use of this chemistry at a high MTO level in electrodialysis equipment would provide an improved degree of operating efficiency making this a more viable economic operating method.

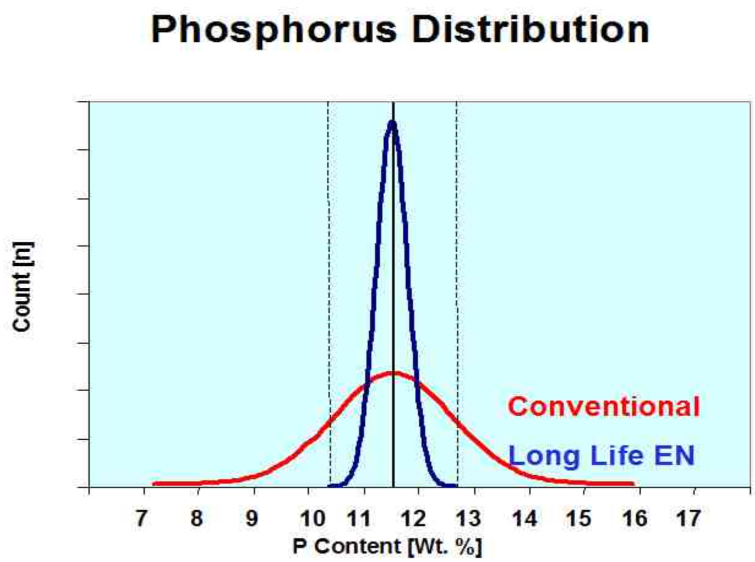
The first commercial process developed based on these thoughts, produces deposits containing a high percentage of phosphorus. With phosphorus concentrations above 11% one has deposit characteristics that provide good corrosion resistance, avoids tensile stress, and offers good ductility. Because of the absence of sulphate any increase of density is slowed down until the critical limit of 1.3 g/cm³ is reached at 22 MTOs compared with 11 MTOs with conventional EN sulphur containing systems.

Conventional high-phosphorus processes lose their desired stress characteristics, which contribute to the positive effect on corrosion resistance, after more than 5 MTOs. This effect can be slightly delayed by slowing down the deposition rate. But this is not an economical proposition. In addition, if the electrolyte is used after this figure has been reached, then the deposit quality will suffer. For this reason, both with "Bleed and Feed" and when electrodialysis equipment is used, a steady state of equilibrium of 3 MTOs is aimed for. This new extended life EN process maintains its compressive stress through 20 MTOs. This is mainly achieved by operating the process at a strongly acidic pH.

Of economical importance is the maintenance of the deposition rate at the highest possible level. While conventional EN processes under ideal conditions will slow down to 8µm/hr (0.3 mil/hr) after 8 MTOs, this new extended life process will consistently remain at 10µm (0.4 mil/hr) after being in use for 3 up to 22 MTOs. This has the resulting effect of reducing the plating time by at least 10%.

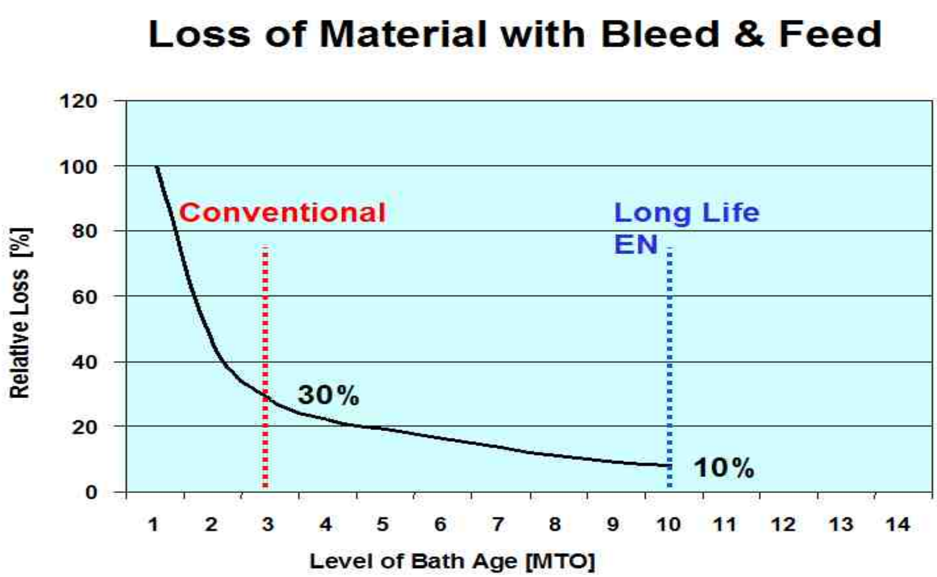


Although the prescribed phosphorus concentration of 11.5% is comparable to conventional EN processes, corrosion tests showed considerably better results. Tests on steel and aluminium with deposit thicknesses of 25µm (1mil) were discontinued after 1000hr neutral salt spray test and more than 10 rounds of the Kesternich-Test without any corrosion whatsoever. X-ray tests were able to explain this improved behaviour. The local distribution of phosphorus was examined. It was seen, that, although the same average concentration was present the distribution within the new extended life EN process was far more clearly defined. At no measuring point on the surface was the reading lower than 10.5 or higher than 13%, while with conventional EN processes a dispersion range of between 8.5 and 14.5% was noted. As is the case with conventional EN processes, it follows that there are no local areas with a low phosphorus concentration. Areas with low local phosphorus concentrations are said to be points, which are susceptible to attack by corrosive media.



Practical experience. The characteristics described were successfully implemented to their full extent in four beta site evaluations, with a volume of 4000 litres on the practical tests. This applied for operations both with and without ammonium, in stainless steel and PVDF plating tanks. The deposition rate of at least 10µm/hr (0.4 mil/hr) was maintained up to 22 MTOs. This was supported by a moderate increase in temperature initially at 88°C to 91°C after 20 MTOs. The self-regulating pH value never exceeded the critical value of pH 4.8 even after 20 MTOs. After this process had been installed exceptional stability was noted in all cases. This was to be seen either on the low potential of the anodic protection equipment on the stainless steel tanks, or by the only very delayed plate-out on the PVDF plating equipment. Today, it is considered, that compared to conventional EN processes in use, at least every second stripping cycle can be avoided, regardless of the type of plating equipment being used. In this manner the capacity of available plating equipment will be increased by between 5 and 30% alone because of the fact, that the need for nitric acid treatment is greatly reduced, and also by the fact that new make-ups are reduced by a factor of 2 to 4.

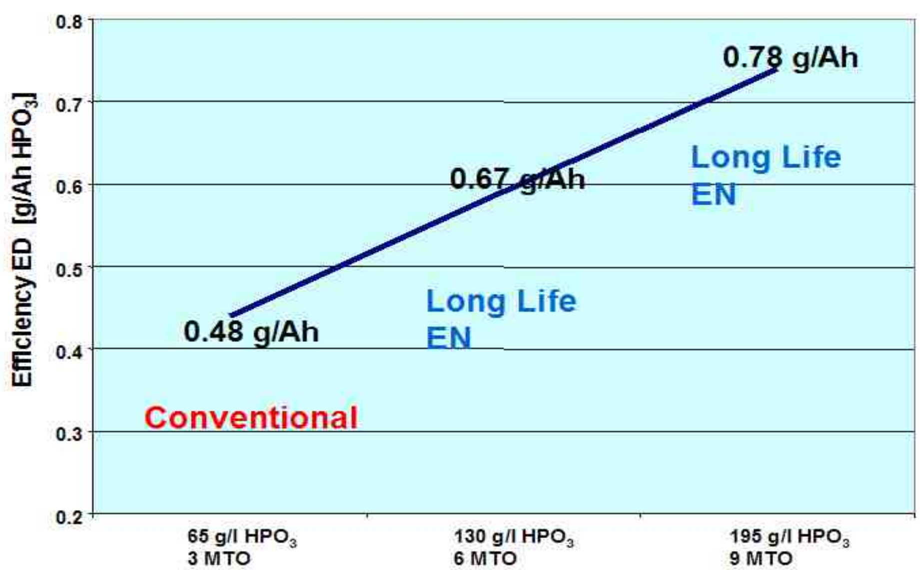
This new extended life EN has a considerably longer operational life while at the same time it constantly maintains the requisite deposit characteristics. In addition, the formation of tensile stress does not have to be counteracted by slowing down the deposition rate. Should the need arise, to operate the process without any new make-ups, or to operate the process at a constant pH level, then it becomes quite apparent, that the ability to work at a higher MTO level should be taken advantage of. If one uses the “Bleed and Feed” operating method at an equilibrium state of 10 MTOs for example, versus 3 MTOs, then the material value loss can be reduced from 30% to 10%. Conventional EN processes must be operated at a level of about 3 MTOs, to avoid tensile stress and the corresponding loss of quality, which accompanies it. This is no longer a necessity when operating with the new extended life EN system. Because it has the ability to operate at a higher equilibrium state of 10 MTOs, “Bleed and Feed” becomes a more economical method of operation.

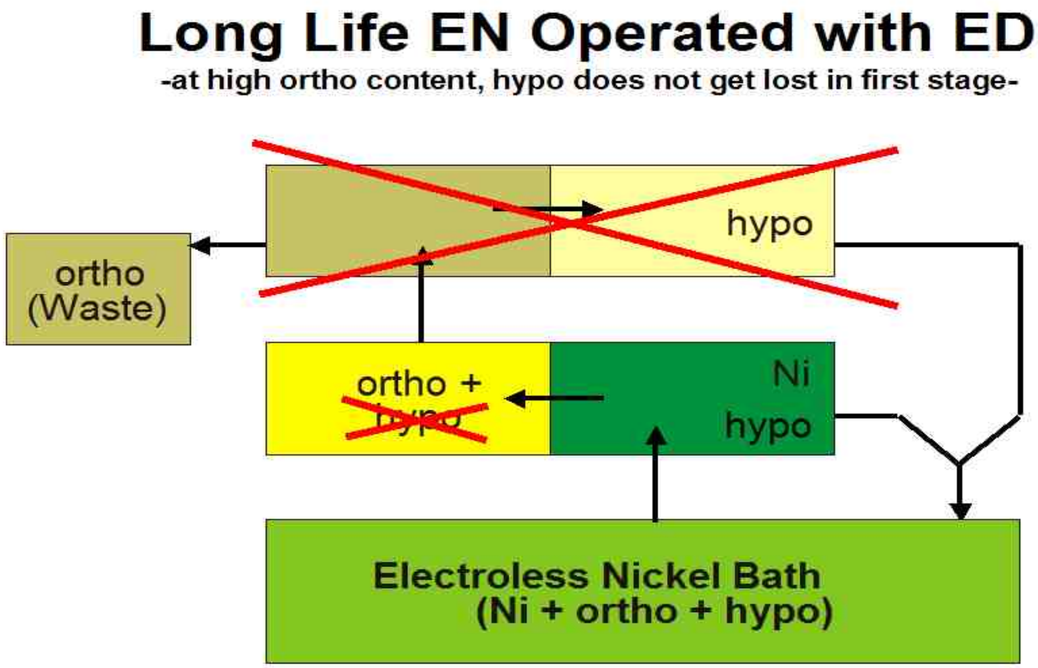


When used with electrodialysis equipment in continuous operation, advantages are also offered by the possibility of operating the process at a higher MTO level. When removing orthophosphite with current operating equipment, the yield has been 0.48 g/Ah with a concentration of 65 g/l orthophosphite. This corresponds to a level of 3 MTOs. With higher concentrations the efficiency will increase to 0.78 g/Ah (+60%) with a state of equilibrium of 9 MTOs and 195 g/l orthophosphite. The size of the required equipment will, therefore, be much smaller.

In addition it has been seen, that due to the presence of large quantities of orthophosphite, the resource hypophosphite remains in the first phase of the electrodialysis equipment. There is no longer any necessity of separating the reducing agent and its decomposition products in a separate phase. The advantage is simpler, less complex and more efficient electrodialysis equipment and a resulting reduction of at least 30% of investment costs.

Efficiency of ED Equipment Operated at Different MTO's





To summarize it is established, that with this new sulphur-free EN Process chemical laws applicable to electroless nickel processes are overcome. The quality of the deposits is no longer automatically dependent on the age of the electrolyte. The rate of deposition must no longer decrease in relation to the age of the operating solution. For the very first time a chemical formula has made it possible to produce compressively stressed deposits with a clearly defined phosphorus distribution during the entire operational life of 20 MTOs.

Whether a user will only make use of the advantage of the longer operation life of this chemical process, or whether, after consideration of the economical facts he will use this process continuously will always remain his own decision. With the possibility of continuously operating the electrolyte at a considerably higher MTO level the economical prerequisites have been clearly improved.

Use of second rectifier eliminated with Long Life EN