

Reduced Ion Electroless Nickel to Meet a Sustainable Future

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Background

Legislative directives have long been one of the primary drivers for innovation in many industries and, as environmental considerations have come to the forefront of discourse, demands from law-making authorities continue to push researchers to meet new regulations. Surface finishing is a prime example of an industry that is constantly evolving to meet the new demands that these regulatory bodies impose. Over the years, there have been numerous actions taken to reduce or eliminate harmful chemical substances from chemistries or processes used in the metal finishing industry, from the Clean Air and Clean Water Act of the early 1970s to the ELV, RoHS and WEEE, and REACH initiatives of the 2000s. Examples of banned or limited substances include, but are not limited to, the restriction of cyanide containing chemistries, solvent based cleaning, initiatives to reduce chromium emissions, phasing out cadmium plating and more recently the limitation on PFOS or PFAS compounds. The implementation of these types of requirements continue, and suppliers and applicators alike must react quickly to the ever-changing landscape of permissible technologies and processes to continue to meet application demands.

Nickel continues to be a substance of interest to health officials around the world as nickel compounds are classified as human carcinogens.⁽¹⁾⁽²⁾⁽³⁾⁽⁴⁾ In the 1990s, metallic nickel and four of its salts (nickel sulfate, nickel chloride, nickel nitrate, nickel carbonate) were prioritized and selected for extensive hazard and risk review by the European Union under the now repealed EU Existing Substances Regulation ((EEC) 793/93).⁽⁵⁾ These studies eventually were published, and while no immediate actions were taken, further work has been done to understand the effects of inhalation of nickel ions and the adsorption of soluble nickel into the body on human health. In fact, the Occupational Safety and Health Administration (OSHA) has established workplace exposure limits for those who work with nickel and its compounds for the associated health concerns.

These limits are imposed onto those who participate in any nickel plating and are especially important for consideration when deciding to work with electroless nickel chemistries. Electroless nickel chemistries are typically operated at elevated temperatures and generate emissions at a higher rate than ambient temperature processes. For these reasons, reduced ion electroless nickel technology (RI EN), or electroless nickel that operates at significantly lower metal concentrations than conventional chemistries, has an important role in the future evolution of sustainable, ecologically minded EN processes. This challenge was approached with total formula optimization to offer a seamless transition from traditional electroless nickel processes this the new class of reduced ion electroless nickel chemistries. Throughout the

development and subsequent qualification of this type of chemistry, some fundamental performance advantages were discovered and characterized and are the primary focus of this paper. For the purposes of this paper the three main advantages of reduced ion electroless nickel chemistries, henceforth referred to as RI EN, as compared to conventional or standard EN processes will be discussed. They are:

- RI EN provides improved tolerance for orthophosphite by-product
- RI EN provides a coating that has an intrinsic stress that is more compressive
- RI EN operating solutions have a lower amount of total dissolved solids

Brief Description

Electroless nickel (EN) deposits are a class of coatings, defined as functional, which are used primarily to enhance the surface performance properties of a variety of conductive and non-conductive substrates. The majority of applications require that the coating provide maximum protection against corrosion and abrasive wear resulting in an extension in the useful life of the component.⁽⁹⁾ Electroless nickel coatings function as barrier coatings with the aim of fully encapsulating the part or portion of the part that requires property modification. This type of coating is fundamentally different than those coatings that are used as sacrificial coatings, such as electroplated zinc, which offer protection by dissolving preferentially to the substrate, due to the coating's lower electrode potential as compared to the substrate it is applied on. EN has a high passivity, especially in the case of "high-phosphorus" deposits (*i.e.*, those deposits with phosphorus contents $\geq 10.5\%$ wt%). For this reason, if there are any defects in the coating, or if the intrinsic stress of the deposit causes microstructural non-uniformities, there can be a high potential for enhanced corrosion of the substrate due to acceleration by a galvanic mechanism. Accordingly, optimum performance of the mechanical and physical properties of the EN films will result by minimizing the defects in the coating. The absence of pores, nodules and pits, as well as optimized intrinsic stress, will improve the performance of the EN deposit. Defects in the EN deposit can be directly correlated to the deposition mechanism itself and EN film growth during the plating process. RI EN has demonstrated an effect on several of these fundamental mechanisms which serve to improve the overall performance of the operation of the plating solution and the performance of the EN film itself.

Orthophosphite Tolerance

In simplified terms, conventional electroless nickel-phosphorus deposition occurs as the result of a continuous catalytic reaction, where a phosphorus containing reducing agent (typically sodium hypophosphite) is oxidized at a catalyst. As a result of this oxidation, electrons are liberated and these electrons are then used to reduce nickel and phosphorus ions at the catalyst to form the coating itself. In the case of electroless nickel, the nickel in the film is the catalyst, so the deposition reaction is characterized as autocatalytic in nature. The formation of by-products, specifically orthophosphite (oxidation product of hypophosphite), during the plating process, prevents the EN plating bath from being used for extended periods of time. In practice, the useful life of an EN plating process is described in terms of Metal Turnovers (MTOs), where one MTO is equivalent to the replenishment of the initial nickel concentration.

In other words, if the original concentration of nickel ions in solution is 6.0 grams per liter (g/L) and subsequently 6.0 g/L of nickel has been deposited out of that solution, the bath is defined as “at 1.0 MTO,” and so on, in direct proportion to the amount of nickel ions deposited and replenished. In most conventional EN systems, the average orthophosphite generation for each MTO achieved is approximately 23 g/L of EN bath, and consequently the plating solution becomes highly concentrated with orthophosphite anions as the EN solution is used. As previously stated, this ultimately leads to the finite life of an EN solution, due to eventual solubility and performance related effects. At sufficient concentrations and conditions, free nickel ions can combine with the orthophosphite anion to form an insoluble precipitate as shown below.



The formation of this precipitate is increased by increasing the pH of the solution and decreasing the temperature of the solution.

These insoluble species can interfere with the formation of the EN layer, cause heterogeneities in the EN layer, and lead to increases in tensile stress and higher corrosion of the deposit in certain environments. To prevent this detrimental condition from occurring, a chelator is added to EN solutions. Chelates in EN formulations are usually organic molecules that have moieties that can donate electron density to the electropositive nickel ions and thus form complexes. The relative strength of these complexes and the concentration of the chelator(s) must be enough to prevent the formation of nickel orthophosphite to be considered effective.

Examples of common chelators in electroless nickel formulations are carboxylic acids such as citric acid and malic acids. Theoretical calculations can be made, based on the number of donor groups of the chelator, the molar mass and the concentration of the chelator and the concentration of Ni ions in solution, which determine how much of the Ni ions are theoretically complexed. This can be qualified as the percentage of Ni ions that are sufficiently complexed in the EN bath. Thus, at 100% chelation, theoretically 100% of the Ni ions are sufficiently complexed. This of course is an oversimplification of what is physically occurring in an EN solution, as many other considerations must be taken to actually characterize the state of complexation in the bath. Nonetheless, it is used for the purposes of this paper as a comparative tool for illustration of the effect of the RI EN. Figure 2 demonstrates the effect of solubility of the Ni ions in a RI EN bath at 3.0 g/L Ni ions and a conventional EN solution at 6.0 g/L Ni ions in the presence of a constant concentration of orthophosphite (60 g/L) and two Ni ion chelation % values at typical working temperature of bath (*i.e.*, 190°F). To demonstrate this effect, an alkaline (*i.e.*, dilute NH_4OH) was titrated into the solution until an observable nickel orthophosphite precipitate was formed. The chelation systems in each bath were identical in composition and ratio of concentration of each complexor to the concentration of Ni ions, but varied in absolute chelator concentration to effectively yield the stated chelation %. Figure 2 represents the formulations utilized for all testing in this paper. Note that succinic acid functions as a buffer in this formulation, due to steric hindrances that result because of the

length of the carbon chain of the dicarboxylic acid. As a consequence, no chelate ring can form with a Ni ion thus it cannot act as a chelator.

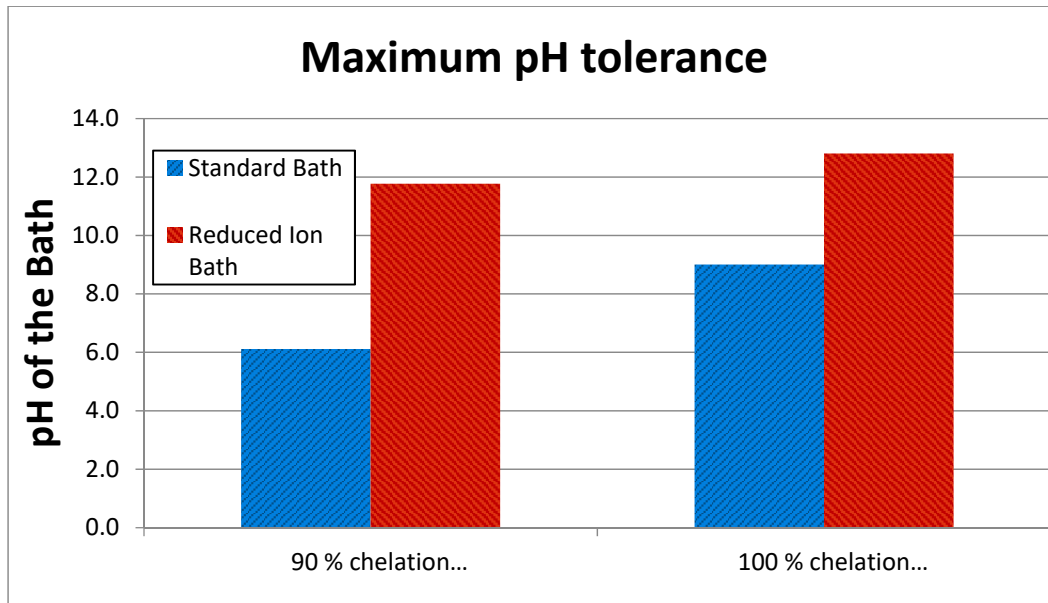


Figure 1. Nickel orthophosphite formation in RI EN and conventional EN at 90% and 100% effective Ni ion chelation at T = 190°F.

	Reduced Ion EN (g/L)	Standard EN (g/L)
Nickel Metal	3 (2-4)	6 (5-7)
Malic Acid	10	20
Lactic Acid	9	18
Succinic acid	4.5	4.5
Ammonium Hydroxide	to adjust pH	to adjust pH
Sodium Hypophosphite	30 (24-40)	30 (24-40)
Lead Acetate	0.00055	0.00055
pH	4.50 -4.55	4.50 -4.55
Temp (°F)	188 – 194	188 - 194F
Deposition Rate (µin/min)	3.6 – 4.0	3.6 - 4.0

Figure 1. EN formulations.

Figure 3 essentially shows the same effect. This test was conducted at two different orthophosphite concentrations (*i.e.*, 60 and 90 g/L) and the two baths were at only 55% theoretical Ni ion chelation. The pH of the solution was adjusted with alkali (*i.e.*, dilute NH_4OH) to the stated values in the figure and held constant. The temperature of the EN bath was then increased at a rate of $2^\circ\text{F}/\text{min}$ and the temperature at which a precipitate formed was recorded and plotted in the figure below.

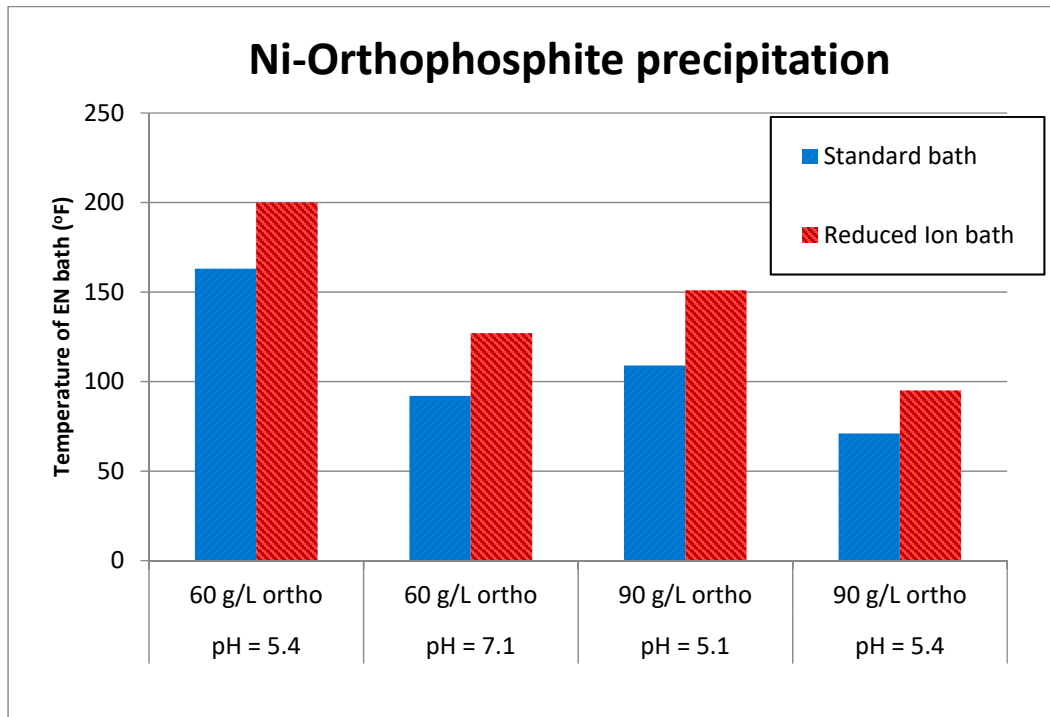


Figure 3. Effect of orthophosphite concentration and pH on the temperature at which nickel orthophosphite forms in RI EN and conventional EN.

According to Figs. 2 and 3, the RI EN bath shows insolubility of the Ni ions at higher pH values as compared to the standard bath. This shows that the RI EN has higher tolerance for orthophosphite which, based on previously stated findings, improves the performance of the coating by preventing the formation of the insoluble particles at the plating surface, which reduces the potential for both co-deposition of these particles or their potential for interference with the growth of the EN film.

Intrinsic Stress

Electroless nickel deposits contain internal stresses that are the result of two individual components, extrinsic and intrinsic stress. Extrinsic stress is caused by the thermal expansion coefficient differences that exist between the coating and the substrate.⁽⁶⁾ Intrinsic stress results from crystal and lattice growth defects introduced into the coating during deposition.⁽⁷⁾ Generally, higher tensile stress values lead to microstructural mismatches in the deposit, which

can result in heterogeneities in the deposited layer, which in turn can lead to reduced corrosion resistance of the deposit. It has been demonstrated that deposits with compressive stress exhibit enhanced resistance to chemical attack.⁽⁷⁾ In general, EN deposits that have lower (or more compressive) intrinsic stress are more desirable.

Intrinsic stress was measured by the bent strip method, where a very thin test strip is plated in the solution of interest. The strip is split into two legs, with opposing sides coated with a lacquer to prevent plating, so that when the EN layer is deposited onto the non-lacquered or plateable side of the strip to a sufficient thickness, the intrinsic stress of the deposit causes the strip to deform either as a concave or convex arc. The shape of the deformation is determined by the relative stress type (*i.e.*, compressive or tensile), the degree of stress in the deposit and the thickness of the deposited layer. The strip is then mounted on a measurement device and, based on the degree of deformation, the strips separate from one another, and the value is derived from the measurement scale. This value is then used as part of a calculation, and the intrinsic stress of the deposit is determined in pounds per square inch (psi). This methodology was developed by Specialty Testing and Development Co., Seven Valleys, PA, and is widely used in several metal finishing chemistries to determine deposit stress.

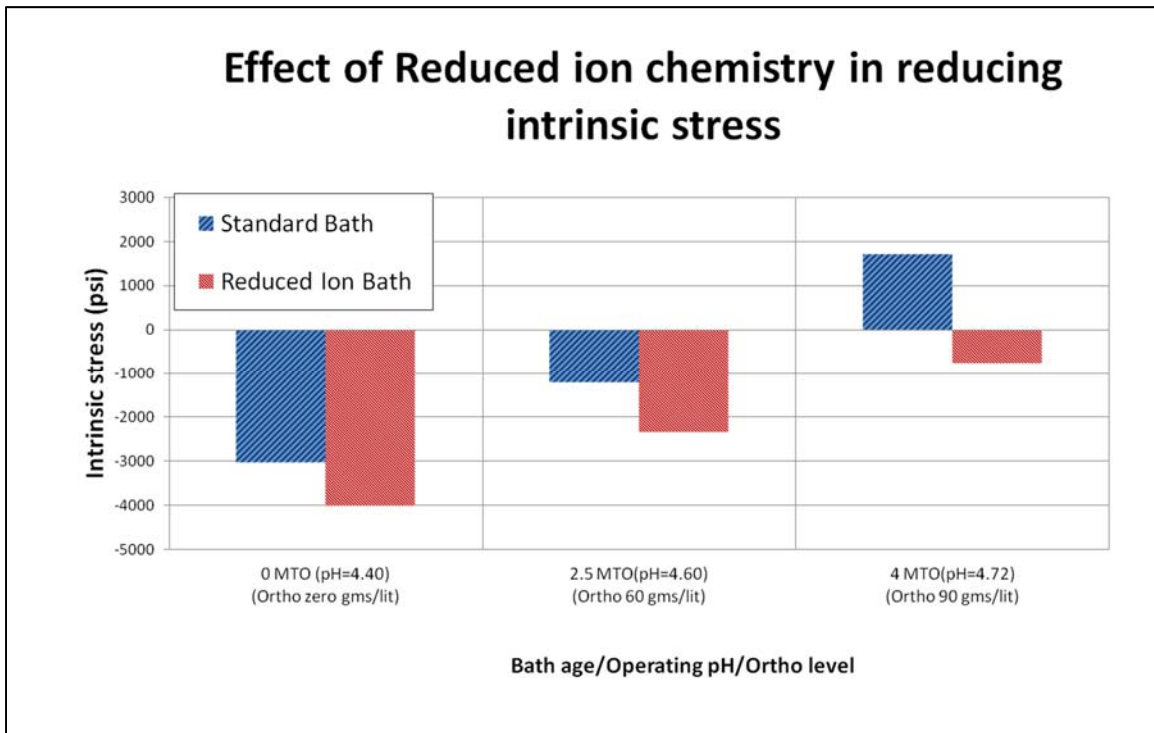


Figure 4. Relative stress of RI EN and conventional EN deposits at varying conditions.

Figure 4 illustrates the finding that the deposit generated from the RI EN bath demonstrates lower (or more compressive) stress values when tested at varying conditions. The baths contained chelation systems which were identical in composition and ratio of concentration of each complexor to the concentration of Ni ions, but varied in absolute chelator concentration to effectively yield the equivalent chelation %. Note that at the 4 MTO point, the standard or

conventional EN bath exhibits a deposit with tensile stress, whereas the RI EN deposit still retains compressive intrinsic stress. Figure 5 illustrates this effect again, by testing the stress of the deposits generated from the two aforementioned baths at 4 MTO at two different pH values. Again, the RI EN deposit yields a consistently lower compressive stress value as compared to the conventional EN bath. It should also be noted that the figure illustrates that at higher pH the stress increases in the tensile direction.

According to Figs. 4 and 5, the RI EN bath, when plated at comparable operating conditions, as compared to a conventional EN formulation of the same composition, generates deposits that exhibit lower intrinsic stress. This will lead to improved resistance to corrosive environments. This effect is demonstrated in Fig. 6, where the two aforementioned formulations from Fig. 1 were used to generate deposits of a thickness of approximately 400 μ -in. on aluminum substrates. The pretreatment process prior to EN consisted of a non-etch soak/acid etch and a “standard” double zincate process. This process has been shown to yield very good adhesion of the EN layer to the aluminum substrate. Once plated, the thickness of the EN deposit was verified via x-ray fluorescence. These specimens were then immersed into a solution 50 vol% deionized H₂O and 50 vol% 42° Baume nitric acid at a temperature of 72-74°F for 25 minutes. The weight loss was determined by taking the mass of the cleaned and dried specimen prior to and post immersion in the etch solution. The resultant weight loss was then used to derive an etch rate or corrosion rate by dividing this mass loss by the total area and the immersion time to yield a value represented by the unit (mg/cm²/min). The relative corrosion performance was characterized by comparing the data set to the highest value obtained in the experimental matrix and calculating the relative corrosion rate as a % of that value.

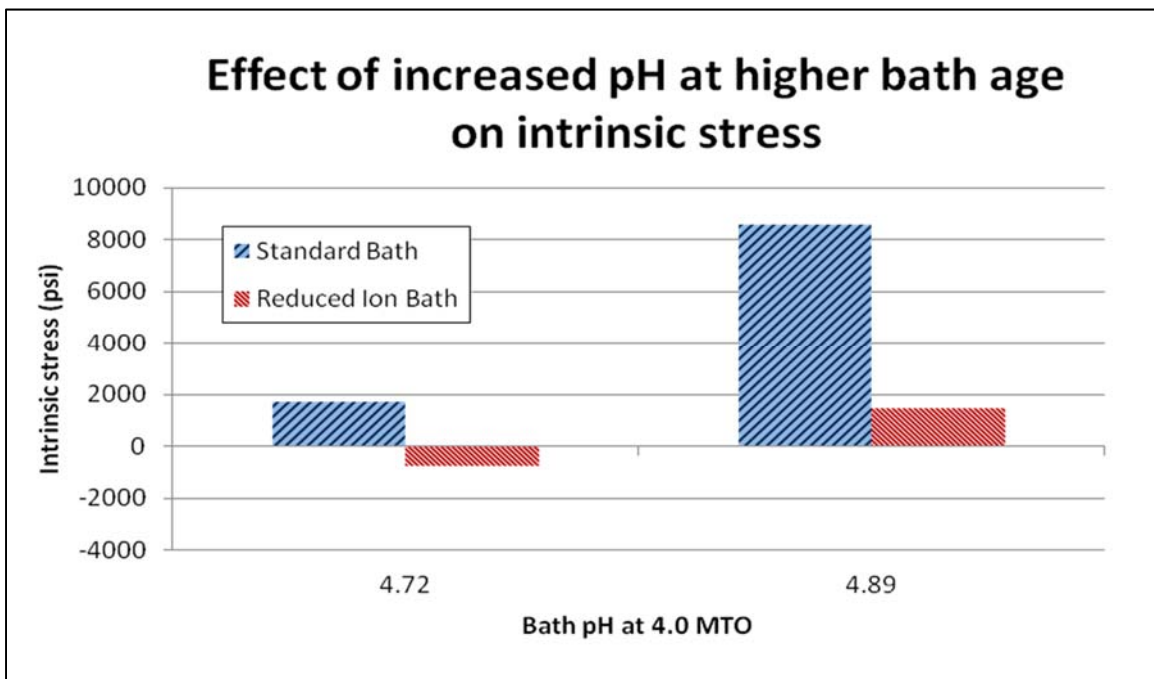


Figure 5. Effect of pH on Intrinsic stress of EN deposit at 4.0 MTO, T = 190°F.

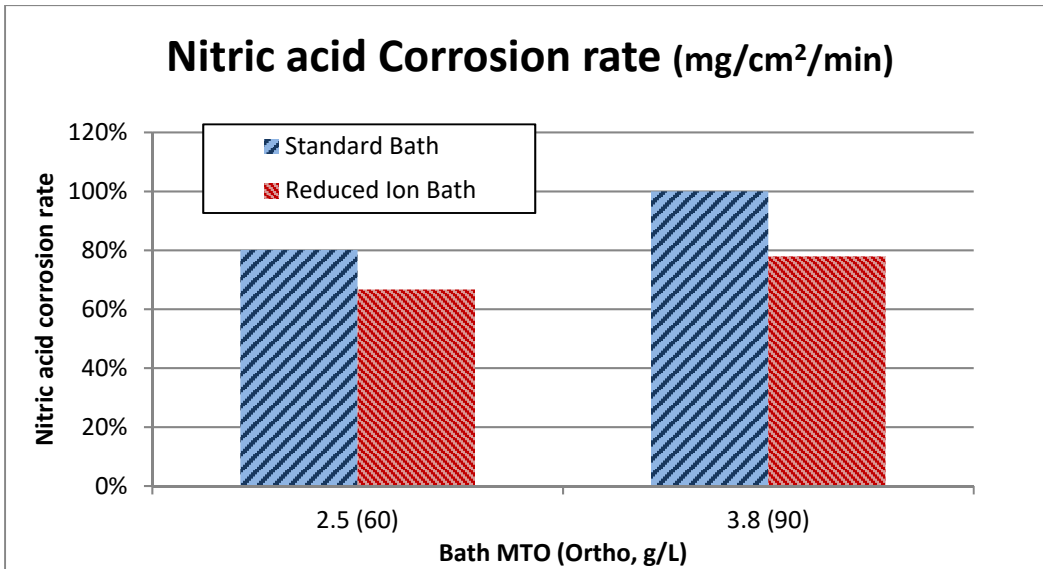


Figure 6. Corrosion comparison of deposits generated from RI EN and conventional EN in nitric acid.

Based on figure 6 it can be stated that the RI EN deposit exhibits higher corrosion resistance as compared to the deposit generated from the standard EN deposit.

Solution Density

Density is a measure of a substances mass per unit volume. Traditionally, solution densities have been characterized as grams per cubic centimeter (g/cm^3). The reduction of Ni ions in solution by 50% allows for the reduction of other species in the electroless nickel formulation without the sacrifice of performance and, as a consequence, the density of the solution at the same MTO is reduced. This condition may have an impact on the reduction of particle adsorption and the subsequent encapsulation of particles during the plating operation by reducing the number of dissolved ions both in the bulk of the solution and at the plating surface, thus allowing for improved migration of these particles away from the film. These undesirable particles may be generated in situ in the electroless nickel plating bath or can be introduced from the external environment. Figure 7 illustrates the reduction in the solution density as a function of the MTO of the bath.

Due to the previously stated mechanistic implications of operation of an EN solution at reduced solution density it can be theorized that the degree of co-deposition of undesirable particles will be reduced and thus a more homogenous EN film will result. This will ultimately improve the performance of the film and could be a contributing factor to the enhanced performance demonstrated by the corrosion test previously shared (figure 6).

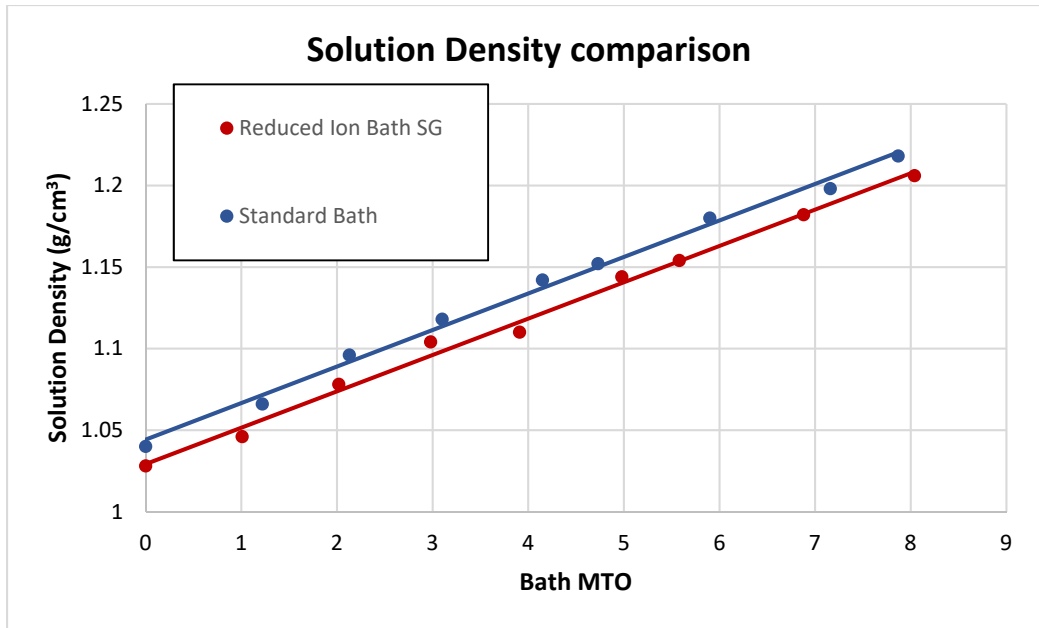


Figure 7. Solution density of RI EN bath and standard bath over the operating life.

Conclusion

Movement towards sustainability in the metal finishing industry, whether imposed by outside forces or as a result of internal motivation, can be viewed as an impediment to progress by some, but these challenges can also present opportunities for innovation and improvement to our industry and to the technologies that our industry employs. The creation of reduced ion electroless nickel technology is an example of this opportunity. This paper demonstrates the fundamental improvement of the reduced ion technology compared to current technologies. These motivations will continue to drive innovation and suppliers must continue to strive to keep pace to continually improve the environmental impact of the metal finishing industry.

References

- (1) International Agency for Research on Cancer, "Nickel and nickel compounds" in *IARC Monographs on the Evaluations of Carcinogenic Risks to Humans*, **100C**, 169–218 (2012).
- (2) Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on Classification, Labelling and Packaging of Substances and Mixtures, Amending and Repealing Directives 67/548/EEC and 1999/45/EC and amending Regulation (EC) No 1907/2006 [OJ L 353, 31.12.2008, p. 1]. [Annex VI](#).
- (3) Globally Harmonised System of Classification and Labelling of Chemicals (GHS), 5th ed., United Nations, New York and Geneva, 2013.
- (4) National Toxicology Program. (2016). "Report on Carcinogens", 14th ed., Research Triangle Park, NC: U.S. Department of Health and Human Services, Public Health Service
- (5) Nickel Risk Assessment, retrieved from <https://www.nickelinstitute.org/en/Sustainability/NickelRiskAssessment.aspx>

(6) Mallory, G.O. and Hajdu, J. B., *Electroless Plating: Fundamentals and Applications*, 1990; pp. 1-99.

(7) Mallory, G. O. and Altura, D., “The Effect of Stress on the Properties of Electroless Nickel—Phosphorus Deposits” *SAE Transactions* **92**, Section 3: 830693–831395 (1983); pp. 1-9.

(8) Ruffini, A. J., *et al.*, US2018209047 (A1) Washington, DC: U.S. Patent and Trademark Office (2018).

(9) LaPlante, J. “Building a platform for growth: Technology advances in electroless nickel provide practical benefits for platers” *Metal Finishing* **103** (12) 18-24 (2005).

About the author



Ambrose Schaffer is R&D Manager - Functional, at Coventya, Inc. His primary responsibilities involve the management of key R&D projects and personnel and drive strategic product development initiatives for both local and global functional technologies. He holds a B.S. in Chemistry from the University at Albany (2006) and a C.E.F. certification (2012). Mr. Schaffer started with Coventya as an R&D chemist in 2007 and has focused primarily on electroless nickel technologies for much of his career. He has written and presented multiple technical articles at industry conferences on the subject. He holds three patents on electroless nickel technology. He is married to wife Leah, and has two

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