

Electroless Nickel Formulation and Plating Concepts

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HISTORY & BACKGROUND

Electroless nickel (EN) technology has come a long way in the last few decades and then again, most of the science and techniques are still pretty much the same. I started working with EN in the late 1970's from a hands-on industrial chemistry-type approach. During that period, I personally formulated and scaled-up hundreds of EN baths from laboratory test solutions to heavy industrial systems up to 12,000 gallon in size (one of the largest in the southern US) which provided high phosphorus (P) contents, low P and everything in between. Much of this work was experimental followed by product/process scale-up on the production line. I was encouraged to do original research as well, and I developed one of the early low temperature EN systems before fully optimized versions were readily available on the market (other original innovations during that activity included electroless Cu, Ni/Cu, Ag, Ni/Ag, Sn, Ni/Sn, Co, Ni/Pd, Ni/ceramic, Ni/polymer and... electroless Cr, which has hit the market only recently; patents were not pursued for any of these products at the time (shame on me)).

As a Plating Chemist, my efforts were driven, in part, by the enthusiasm of Brenner and Riddle's work from 1946 (the recognized inventors of EN) and focused on discovering new and better reducing agents, coordination/complexing compounds, stabilizers, novel additives, process improvements and techniques for electrolessly depositing metals and alloys onto plastics, ceramics, fibers and bioorganic substrates (wood, polymers and cellular tissue surfaces). I optimized a standard hypophosphite/glycolate-based high temperature EN formulation essentially the same as many of the COTS formulations available today. Even on a small scale, these are some of the most trickiest plating systems to formulate, maintain and ensure consistent results on a daily basis without the bath decomposing and falling apart (you can imagine the challenges in constructing multiple 12,000 gallon full-time EN production baths... large enough to plate a small car body in without touching the sides of the tank).

Back in those days, the primary functions of EN coatings were corrosion protection and wearability. The early EN industry was essentially established on these two attributes. For the majority of industrial processes (particularly larger scale operations), the most common EN systems and services available were based on high P deposition platforms (~10% and greater), and for the most part, they still are (i.e... high phosphorous EN coatings are basically the norm, at least in the heavy manufacturing industries). In terms of raw corrosion protection, it is well established that high P deposits are superior to mid and low P coatings (EN deposits are degraded only by strongly oxidizing media such as hot nitric acid). There is plenty of historical salt fog data substantiating these facts. In the 1980's, the electronics industry became more interested in EN for plating component leads, connectors, circuit runners, solder pads, hybrid

circuits, and support structures, often in conjunction with electroless Cu. However, it was found that high P deposits, while providing exceptional corrosion properties, presented challenges when it came to high conductivity (low resistivity) requirements and the soldering of leads, pads and connectors plated with traditional EN. Thus, for electronic applications, a balance between corrosion protection and electrical performance was achieved by making slight adjustments in the formulation and procedural guidelines in order to reduce the as-deposited P content. It comes as no surprise that EN products and formulations geared for the electronics and electrical industries are notably different than those used in the steel factories and large scale metal fabrication industries. In other words, if you send your parts to a plater who normally processes electrical hardware, you will usually receive products with a lower P content than those acquired from an EN processor whose primary goal is corrosion protection or wearability properties.

FORMULATION & PROCESSING

Compared to electrolytic Ni plating (Watts Ni, Ni-sulfamate, etc...), EN, and electroless processes in general, are often more expensive overall, even though the cost has gone down over the years. There is also more sludge and waste generated from an EN bath during extended processing periods, as well as higher maintenance requirements. Production operations typically utilize a plating solution tank along with a much more elaborate plumbing system to accommodate continuous bath circulation, organic and inorganic filtration, and precision heat control (usually via an in-line heat exchanger). In most electroless operations, on a regular basis (at least once a week), the EN solution must be drained over to storage so the tank and plumbing can be stripped and passivated with hot concentrated nitric acid. Over a few days, hot EN will tend to plate out on just about any housing material, including SS, glass and many unactivated plastics (however, plate-out can be kept to a minimal on surfaces such as HDPE and PVC). For large operations, nitric acid cleaning/passivation is a nasty, hazardous process that no one wants to do. On the positive side, power supplies, rectifiers and traditional electroplating equipment are completely inapplicable to the electroless deposition process. In ordinary electrolytic plating solutions, the metal ions are coordinated with water molecules (as it is with all soluble metals) and then electrochemical oxidation takes place along the surface of the anodic electrode while the cathodic substrate attracts and reduces the hydrated metal ions along its surface.

In electroless plating solutions, specific organic acids (or their salts) are incorporated into the formulation which become the principal coordination agents for dissolved metal ions. When chosen appropriately, chelated metal ligands are responsible for regulating the electroless deposition process, and they do it much better than water (or ammonia). The selection and concentration of chelating agents in a given formulation are critical to the success of any electroless formulation. These complexed species act as anodes that are attracted to and deposit onto the activated substrate which acts as the cathode. In electrolytic baths, the reduction and oxidation (redox) reactions occur throughout the system, but in electroless systems, *all* the redox reactions take place within thousands of micro-galvanic cells along the surface of the substrate. The chemical reducing agent developed for a given electroless system (hypophosphite $\text{H}_2\text{PO}_2^{1-}$ in Ni-P baths and borohydride in Ni-B systems) provides the electrons which reduce the metal ions onto the substrate. The electroless process, which is characterized by surface-catalyzed chemical redox reactions, is based on bath chemistry and surface activation rather than applied current or current density. When effective pre-treatment steps are applied (degreasing,

pickling and activation), EN plating rates and coating thicknesses tend to become uniform across even the most complex-shaped articles and geometries providing capabilities and finishes that have always been untouchable using traditional solution-based electrolytic methodologies.

Most plating operations acquire their EN capabilities by procuring pre-formulated solution concentrates produced by outside vendors in ready-to-use two-part kits. Part A generally contains the complexed Ni salt in solution... NiSO₄ crystals dissolved in water followed by incorporation of the correct amount of complexing agents and buffer compounds (hydrated and organic chelated Ni²⁺ solutions are green while ammoniated Ni²⁺ solutions tend to be blue). My experience has taught that not one, but two or three specially selected chelating compounds are required to achieve the proper balance between deposition rate, bath performance, stability and compositional properties. Part A may be slightly acidic and the primary buffer action of the final bath is usually accomplished from a phthalate-ammonium hydroxide combination. Flakes of phthalic anhydride are formulated into the Part A pre-mix solution and then as the user makes up the plating bath and throughout the operational lifetime, ammonium hydroxide is added to keep the pH on right side of 4.0. Part B will contain the reducing agent... sodium hypophosphite, NaH₂PO₂ powder dissolved in water, along with one or more stabilizer compounds and possibly one or more of the required complexing agents.

Chelating agents incorporated in Part B solutions are intended to remain free in solution until later when they are compelled to undergo exchange coordination interactions with complexed Ni²⁺ ions introduced from Part A. I pre-formulated two-part kits for a while to see how they worked on a full-scale production line but found it more effective to incrementally formulate the solution from scratch in the actual line plating tank since I was specifying all the components anyway (that way, each component in the recipe could be incorporated into the bath in the proper manner and at the proper time before pH adjustments were made). Most platers generally mix Parts A and B into their tank and follow the directions provided by the EN product supplier. Many operators have minimal knowledge of the chemistry and the effects of all the components in the formulation (most of these are proprietary anyway). Consequently, it can become more difficult to troubleshoot defects and process problems or control the composition of the deposit. These types of operators rely heavily on the guidance, consultation and tailored product (formulation) modifications provided by the vendor to meet their needs. There have been many EN product providers over the years, MacDermid, Enthone, Elnic, Technic, etc... MacDermid is still among us and is certainly one of the more prominent EN vendors around.

In a nutshell, the primary factors that control P content in a Ni-P coating deposit are the combination of plating bath pH and solution temperature during the deposition process. It could be said that solution temperature has a more obvious effect on plating rate (in accordance with Arrhenius and parabolic growth kinetics), while ***the pH of the plating bath during electroless deposition exhibits the greatest influence over the actual level of P incorporated into the EN microstructure***. Most traditional large-scale EN systems run somewhere between 190°-200°F bath temperature with a pH in the range 4.0-5.0. In short, increasing solution temperature and/or increasing the pH will speed up the plating rate, while lowering the pH will increase the P content but will decrease the rate. This is not always economically feasible for high volume production operations. So for reduced pH systems (higher P in the deposit), the bath operating temperature is usually raised a few degrees to provide an acceptable plating rate, which means

that higher P deposits may require more energy for systems that are schedule-driven. However, if the bath becomes overheated at elevated pH, it will fall apart very quickly. Also, it should be realized that *as a given EN plating cycle progresses, the solution pH gradually drops over time* (even though buffers are included in the formulation), leading to a reduction in plating rate and an increase in the level of P incorporated into the deposit (...for a typical EN bath running at 190°-195°, the pH might drop a couple tenths of a point per hour and then some ammonium hydroxide must be added to bring it back up). In conjunction, the level of phosphite and white phosphorous (P₄) in solution increases as the process continues ($\text{H}_2\text{PO}_2^{1-} \longrightarrow \text{H}_2\text{PO}_3^{1-}$) which decreases the age of the bath (the phosphite does not go away and must be filtered out at some point). I have seen very used EN-P baths glow in the dark due to microparticles of phosphorescent phosphorus suspended in the bath.

Thus, a base must be added to bring the pH (and the rate) back up to the required production levels. As expected, these in-process variations also lead to variations in the cross-sectional P content (through the thickness). The use of ammonium hydroxide and sulfuric acid for daily pH adjustments are quite prevalent in NaH₂PO₂/NiSO₄-based systems throughout the world. Many modern operations now have tightly controlled plating baths which include continuous automatic monitoring, in-line titrations and precisely metered chemical additions to maintain very close limits on pH, bath temperature, metal ion concentration and reducing agent levels. However, there are a number of old fashioned laboratory tests that are still required during EN production for parameters and variables that do not yet lend themselves fully to automation methods. In some respects, controlling the level of specific complexing agents is more of an art than a science since there is not always an easy way to quantitatively determine constituents such as these.

For an EN formulation with the proper type and level of complexing agents, stabilizers, inhibitors and activators, a skilled plater can operate his bath on a daily basis at 4.5-4.6 pH and ~194-198° with a deposition rate of 1-2 mil/hr (the higher rates are for advanced platers) yielding a moderate-to-high P content. However, if the bath accidentally drifts to > ~202°F and pH > ~4.8, it will begin to fall apart and then it will go quickly. The decomposition process is spontaneous and self-fueling. Once one of these baths starts to decompose and precipitates begin to form, there is no going back. The operator must try to cool the system down as fast as possible and salvage as much of the solution as possible. The cooled solution can sometimes be filtered and recycled back into a new bath make-up. Dissolved phosphite (H₂PO₃) is one of the primary side products generated during the process. Once the phosphite level reaches saturation, Ni phosphite will begin to form providing high surface area particles for plating to occur and within a few minutes, the bath is flowing over the sides as rapid, violent decomposition commences.

In addition, P₄ is only slightly soluble in hot in water and so micro-particles of these side products must be continuously filtered during bath operation and phosphite/phosphorus analyses become primary control parameters for maintaining EN plating baths (usually determined via titration). A skilled plater can run one of these babies at pH 3.5-4.0, 205-210° pushing 14-16% P in the deposit (maybe even higher for advanced platers). These are all 'acid' EN baths. On the opposite end of the control spectrum are the high pH, low temperature EN formulations. One of the room temperature systems I developed deposited Ni at > ½ mil/hr at a pH >10 yielding 2-4%

P coatings. I could tweak this system to deposit P ranges from about 1 to 8 or 9%. By now, the industry offers an infinite number of formulations and process variations between these two extremes to suit almost any customer need. Classical electrolytic processes still have their place within the various industries, and electroless Ni-B, with relatively low boron levels, offers certain electronics companies an alternative to P-doped deposits, sometimes allowing for improved solderability and conductivity properties. For EN-P systems, it should be recognized that the P content is not the only property to take into account. There are trade-offs to be realized any which way you go.

EN & Ni-P MATERIALS SCIENCE

Pure Ni assumes a face-centered cubic (FCC) structure. Both low sulfur electrolytic Ni platings and low P electroless coatings (<1-2%) will try to crystallize into the SCC allotrope, generally with an abundance of the SCC structure dispersed throughout the medium. As the P (or rather P₄) content increases, the coating density decreases, the sizes of the Ni crystallites decrease and the microstructure starts to become amorphous. At about 10% P and above, the structure is completely amorphous. It seems that the presence of P₄ tends to prevent crystallization by inhibiting crystal formation and imposing higher compressive stresses on the Ni microstructure. This can be understood by visualizing the tetrahedral P₄ structures as becoming 'trapped' between Ni atoms in the lattice, preventing contact and hence crystallization of the Ni atoms. Thus, the P₄ content determines the microstructure which could be crystalline, amorphous or a combination of both. Overall, low phosphorus Ni-P deposits are classified as being crystalline, hard, brittle, electrically conductive and magnetic, having superior wear resistance, while high phosphorus (P) coatings are amorphous, high resistivity coatings, having superior corrosion resistance.

It is interesting to realize that the amorphousness of high P coatings virtually eliminates the intergranular regions in the structure – along with the propensity for stress corrosion cracking. These alloy coatings are superior to electrolytic Ni and ultra-low P EN in terms of corrosion inhibition, not only because of the P content, but because they are essentially *nonporous* (when applied properly). The lower the P content in EN coatings, the greater the microporosity. *Low to no porosity in high P nickel coatings is the key to being able to plate Ni onto Al alloy substrates.* Considering how cathodic a Ni coating is to an Al substrate, even a few tiny porosity interconnections to the substrate could have undesirable results. Also, thick Ni coatings on thin Al substrates are more risky than thin coatings on thick substrates (large cathode-small anode effects). Because of the low porosity (which is a direct result of the P content), the success of Ni-coated Al seems to defy traditional electrochemical logic. However, one should be very aware of any pores or pinholes that may exist after plating, or any cracks, chips and scratches subsequently imparted to Ni-coated Al articles as these kind of small defects can lead to some devastating results.

Many fabricators apply heat treat cycles to freshly plated EN articles in attempts to improve the final properties of the deposit. However, the effects of post-plate heat treatment are not always straightforward. Lower temperature treatments (<~600°F) will tend to increase hardness but also lowers the corrosion resistance. Higher temperature treatments will often decrease the hardness while increasing the corrosion resistance. It could be surmised that this 'flip-flopping'

of properties might be due to a combination of crystallization/re-crystallization effects and the formation, evolution and migration of intermetallic compounds. Lower temperature Ni phosphide compounds might include Ni-rich intermetallics with stoichiometries such as Ni₃P and Ni₅P₂ which tend to increase hardness and conductivity while higher temperature treatments facilitate the formation of P-rich compounds (NiP₂, NiP₃) which lead to improved corrosion and wear resistance. A number of Ni-P intermetallic compounds have been established over the years and NiP₃ has been well publicized for decades. Intermetallic compounds do not form during plating but only during heat treatment and throughout the lifetime (aging) of the coating. It is no surprise that high P coatings usually contain an abundance NiP₃ regardless of the post-plate heat treatment applied ($4 \text{ Ni} + 3 \text{ P}_4 \longrightarrow 4 \text{ NiP}_3$). When a given heat cycle progresses, rapid aging occurs leading to the precipitation of these 'intermetallic' compounds within the coating microstructure. As the compounds agglomerate, they grow or 'precipitate' into the intergranular boundary regions where they become more mobile and begin to migrate toward the surface (however, as indicated above, this movement may be insignificant or nonexistent in high P coatings).

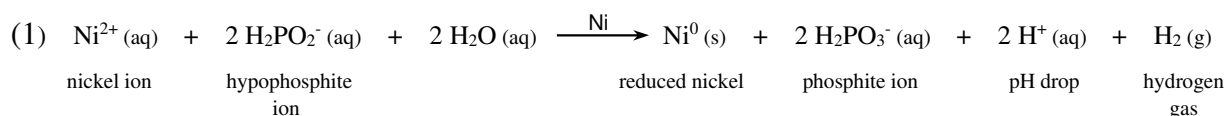
Increased levels of NiP₃ deposited to the surface during soldering (a rapid aging process) may be the primary contributor to poor solderability characteristics. The higher the overall P content is in the plating, the higher the surface tension (contact angle) and the lower its wettability. Freshly plated substrates are substantially more solderable than surfaces which have aged or been subjected to post-treatments. It could be suggested that the improved corrosion resistance observed at higher temps in certain circumstances are due to re-dissolution of the intermetallic compounds back into the microstructure leading to increased amorphousness and interstitial P. Note that compounds such as NiP₃ are not coordination complexes (such as Ni cyanide Ni carbonyl), but are stable, covalently bonded stoichiometries. It was recognized back in the early days by certain electronics industries that ultra-high P coatings almost exhibit the properties of high-band semiconductors. Low P coatings are not only hard and conductive, but are comparable to chrome which has led to the use of low-P EN in place of hexavalent chromium plating in many applications.

On the other hand, ultra high P coatings, while providing the best overall corrosion properties, are not always the most feasible for connectors and electrical hardware requiring high levels of conductivity or thermal protection. It should be realized that while high P coatings are the best for corrosion protection, the greater the P level, the lower the melting point of the deposit. Thus, high P coatings are substandard to pure or electrolytic Ni in terms of thermal oxidation, even though the thermal expansion (CTE) decreases with P content. An electrical connection with very high P content may fail to meet the conductivity requirements from the onset while one with ultra low P might run a greater risk of current-induced galvanic effects in aggressive environments.

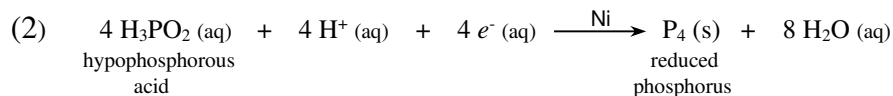
There have been a number of reaction mechanisms proposed over the years which have done a fairly good job of describing the chemistry behind the EN process, but no single mechanism has ever been able to account for all the measured properties or variations and dependencies observed concurrently. None of those specific scenarios will be utilized here. Following from the spirit of Brenner, Riddel, Randin and Hintermann, I have also conducted a great deal of work in this area in attempts to characterize the electroless deposition process from a chemical

perspective, particularly EN (...yet another EN reaction scenario). A couple factors that were pursued included the incorporation of a believable explanation for the deposition of phosphorous in the coating *and* the catalytic effects that freshly reduced Ni can play in this process.

Only a portion of the model will be illustrated here in order to demonstrate that the most important observables, all occurring pseudo-simultaneously, can be effectively represented by just a couple of relevant reactions: (a) the oxidation of hypophosphite to phosphite ($\text{H}_2\text{PO}_2^{1-} \longrightarrow \text{H}_2\text{PO}_3^{1-}$), (b) the reduction of Ni^{2+} ions to deposited Ni^0 , (c) the production of hydrogen gas H_2 which can clearly be seen effervescing from the plating surface throughout all electroless processes, (d) the generation of H^+ ions (with accompanying pH drop), (e) the fact that more sodium hypophosphite (NaH_2PO_2) is generally needed in the formulation than NiSO_4 , (f) the observation that the primary deposition reaction appears to follow first order SN1-type kinetics relative to the $\text{H}_2\text{PO}_2^{1-}$ level, and (g) the production of elemental phosphorus (P_4) in low pH plating solutions which ends up in the deposit and/or is filtered out..



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. . . where the growing Ni lattice structure acts as a catalyst for both the reduction of Ni^{2+} and the reduction of the P(I) hypophosphite compound into elemental P^0 . Note that conditions (a), (b), (c), (d), (e) and (f) are all accounted for in reaction (1) while condition (g) is illustrated in Reaction (2). Reaction (1) depicts the simultaneous reduction (and deposition) of Ni(II) to Ni^0 and oxidation of P(I) hypophosphite to P(III) phosphite) with the production of hydrogen ions (which lowers the pH) along with effervescing hydrogen gas. Reaction (1) may be essentially kinetic-controlled... to a certain point. Reaction (2) is the half reaction counterpart to reaction (1) which shows the reductive decomposition of hypophosphite (or its acid form) into deposited elemental phosphorus occurring in adjacent regions of falling pH. When an excess of H^+ ions locally accumulates, hypophosphite is converted into its acid form and then decomposition of the acid commences as the pH continues to drop leading to the production of elemental P. Regionally, the reactants in reaction (2) may be in relatively low concentration (that is, locally starved), so reaction (2) would be kinetic-driven but is both dependent on and in competition with reaction (1) (the corresponding half reaction would be the oxidation of hypophosphite to phosphite, $\text{P(I)} \longrightarrow \text{P(III)}$). Catalysis effects from the finely growing crystallites of Ni help to drive this reaction (...analogous to those of Raney Ni catalysts).

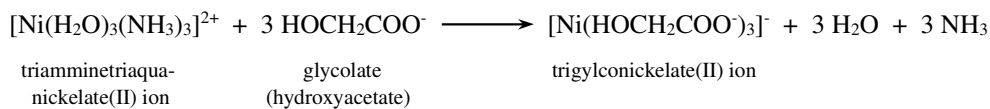
The chemical properties of metal ions in solution are altered when they are combined with complexing agents (ligands), including color, solubility, chemical activity and *reduction*

potential. When a soluble metal salt is first dissolved into water, molecules of water form coordinated hydrates with the metal. For instance, an atom of Ni²⁺ generally exhibits six coordination sites, making its complexes octahedral in orientation. That is, each Ni²⁺ ion will interact (coordinate) with six water molecules. Depending on the solution pH, stronger (Lewis) bases will displace the weaker ligands, as ammonia does with water...

$[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + 6 \text{NH}_3 \longrightarrow [\text{Ni}(\text{NH}_3)_6] + 6 \text{H}_2\text{O}$. Much of my research involved experimental characterization of the various complexing/chelating compounds for EN formulations which was expanded into the discovery of agents for electroless deposition of other metals, alloys and ‘composite’ coatings.

There are literally hundreds of potential organic (and a few inorganic) compounds which will coordinatively interact with a host of the *d*-block transition metals. Such complexes are most prominent in aqueous solutions but only specific compounds will effectively enhance a given electroless formulation. The challenge is to find the most effective agents for the particular system under discovery (once a stable solution of metal-ligand complex has been achieved, you are half way home to developing an electroless deposition process for that specific metal). For low pH, high temperature EN systems, a few of the agents with the longest track record of success include acetate, hydroxacetate (=glycolate), lactate, tartrate, succinate and many others with the most common being glycolate (in practice, the acid forms may be added to the solution and the pH adjusted accordingly). The most common complexing agents for high pH / low temperature systems include citrate, malate, maleate, fumaric (and others). Some of these same compounds are also used in electroless Cu formulations (and other formulations as well). There are some proprietary concepts in this area which have demonstrated extraordinary effects in terms of plating rate and deposit composition that most companies seem to have never exploited, but these ideas will not be covered here.

When one of these agents is mixed into solution containing Ni²⁺ ions already coordinated with H₂O or NH₃ ligands, interchanges at some or all of the possible six available coordination sites will occur. The plating reaction, and indeed the plating rate, are dependent on the fraction of *free* Ni²⁺ ions in solution. Regulation of that process via mixed ligand formation can have profound effects. Glycolate is perhaps the most prominent EN complexing agent around, it is difunctional (two reactive oxygen groups... the carbonyl and the hydroxyl), permitting the possibility for full saturation of Ni²⁺ ions with three glycolate ligands per ion...



This complex is known to substantially reduce the Gibbs free energy during the deposition of free Ni²⁺ ions onto almost any activated substrate (metallic or nonmetallic) when used in formulations operating in the 3-7pH range at elevated temperatures. When one of the hydroxyacetate ligands on a Ni²⁺ atom is replaced by a special compound (let’s call it complexing agent #2), the exchange-release process time is cut in half, resulting in almost double the rate of metal deposition onto the substrate. When the right components and additives are selected and properly incorporated into the formulation, continuous operation EN plating baths in the > 1 mil/hr range at almost any P content to 15% are easy to formulate and run. There are

other agents that can influence the incorporation (doping) of P₄ into the deposit over a much wider pH range, partially relinquishing the dependency of P content on pH to other factors or techniques under user control.

During the deposition process, complexed metal ions introduce a steric factor which can influence the reaction kinetics as large bulky ligands and ions which are saturated with ligands tend to hinder access of the metal to the substrate (but that's not necessarily a bad thing). Large multi-dentate coordinating compounds such as citrate and tartrate or metal-center complex ions which are hexa-coordinated with larger mono-dentate ligands such as propionate would fall in this category. Strictly hydrated Ni²⁺ ions produce poor coating deposits (unless electrolytically-driven) along with poor bath performance (confirmed by experience). However, the behavior of metal ions fully and partially saturated with organic coordinating agents is vastly different.

For ions complexed with glycolate (hydroxyacetate), the reaction is probably dominated by kinetic parameters, but when other chelating agents are incorporated and allowed to exchange with the complex (particularly multi-protic compounds such as citrate), steric and diffusional factors begin to play a role in the deposition process as well as variations in local pH. Such effects can augment the deposition process leading to deviations in activation energy, Ni²⁺ concentration and the relative predominance between reactions (1) and (2). At some point when reaction (1) just become diffusion-controlled, the region of maximum plating rates is realized. To a degree, complexing agents are 'recycled' as the process continues. However, most of the agents contain acid (ROOH) groups, and phosphites will react with ROOH to give alcohols and phosphates (more precisely, small phosphate esters in our case). The alcohols will readily volatilize out of the plating bath but the phosphate esters will build up in solution and must be filtered out. As it is with phosphite build-up, at some point, anionic phosphates will also combine with Ni²⁺ ions reducing their concentration, starving the plating process and leading to potential microscopic seeds for plating fall-out to occur.

ALLOY & COMPOSITE EN COATINGS

One of the easiest metals to alloy in with EN during the formulation/deposition process is copper (Cu) in which the Ni and Cu levels and distribution can be controlled with good precision. It is also fairly easy to co-deposit controlled amounts of Ag, Au, Co, Pd, Pt, Sn and even Cr. From another perspective, it is fascinating to realize the growing number of *nonmetallic* constituents that can be co-deposited along with EN and EN-P to produce 'composite' coatings. In general, EN coatings are already considered to be low friction, high corrosion-resistant coatings. When particles of Teflon are co-deposited along with the Ni, even lower coefficient of friction coatings are achieved. Ni/PTFE composite coatings incorporate microscopic particles of Teflon during the deposition process which can be controlled up to > 30% polymer. Like most plastics, Teflon is an electrical insulator and Ni/Teflon coatings exhibit their greatest attributes as ultra-low friction coatings used mainly on soft-loading, self-lubricating bearings, mold tooling and mandrell surfaces for plastics and composite fabrication (these are very good at sliding wear but poor for high-load, abrasive and erosion wear). Ni/PTFE (Teflon) coatings have excellent corrosion resistance and are acceptable for *high* resistivity plug-in connectors requiring a balance of tribological and corrosion properties. If hypophosphite is used

to apply the EN, then these become ternary Ni/PTFE/P composite coatings (...with even higher resistivity). The tribology guys and corrosion folks would love this option, however, the Teflon particles are expected to impart greater resistance effects than P, and it becomes difficult to fully understand how Ni/PTFE/P coatings could be considered for electrical interfaces requiring $< 2.5 \mu\Omega$ resistance.

Additionally, such coatings are only good to about 500°- 600°F when the PTFE begins to soften, eventually leaving the Ni layer porous, and completely destroying the corrosion protection. Without a doubt, Ni/PTFE has some extraordinary properties, but electrical conductivity and elevated temperatures are not on that list. In some applications, the answer to these disadvantages is to augment the EN process with microscopic boron nitride particles (instead of PTFE) which provide for high hardness, lubricity and corrosion protection in a single coating. For more advanced applications, one could co-deposit micro-particles of a carbide ceramic, such as SiC, which provide exceptional performance for high-load abrasive wearing, erosion and fretting, as well as hardness properties comparable to hard chrome, very high thermal stability and oxidation protection, low CTE, and unbeatable corrosion resistance. Ni/SiC/P electroless coatings can be tailored for a variety of field conditions from high tech to low tech, but they are not necessarily economical (yet).

There was a concern about the presence of Zn compounds in the protective layers of some of the connectors, namely, Zn-Ni platings. It should be realized, many EN processes which are used for plating Al substrates apply an alkaline Zn dip solution (so called zincating) prior to the EN step because the Ni will not bond well to the native oxide on Al surfaces (aluminum oxide, Al_2O_3). The strong base in zincaid formulations dissolves the surface oxide on contact and forms an intermediary layer that is rich in Zn in which the Ni more readily interacts with. There are other ways to activate Al substrates but ***if a zincaid pre-treatment is being applied to Al substrates prior to EN plating, elemental Zn is already present in the finished article.*** In addition to electroplating processes that can deposit Zn-dominated alloys of Zn-Ni onto Al (which precipitates intermetallic compounds such as $Zn_{11}Ni_2$ and $Zn_{22}Ni_3$), it is also possible to electrolessly co-deposit Zn along with EN-P under certain conditions (and with special formulations). However, coatings containing Zn are often meant to be sacrificial in some respect or another and it has been shown (as expected) that the higher the Ni fraction in Zn-Ni deposits, the higher the corrosion resistance. In lieu of vapor deposition-type methods (CVD, PVD, sputtering, etc...), metals such as Zn, Al and Ti are generally too active to deposit from aqueous solution (electrolytically or electrolessly) since water will reduce the metal ions before they can plate out on the substrate. One day however, electroless techniques may offer the most feasible means to deposit these types of metals in practical water-based formulations.