Corrosion Resistance of ELV-compliant Mid- and Low/Mid-Phosphorus Electroless Nickel

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Mid- and low/mid- phosphorus electroless nickel (EN) deposits exhibit good resistance to corrosive media. Due to regulations in recent years (i.e., ELV, WEE, RoHS), many new mid- and low/mid- phosphorus EN processes have been introduced using alternative stabilizers in order to comply. Electrochemical testing is used to compare conventional and ELV-compliant mid- and low/mid-phosphorus deposits in acidic and neutral solutions. Results are compared to the corrosion resistance of high phosphorus EN. Differences in corrosion resistance due to bath age and deposit thickness are also investigated.

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1

Introduction

High phosphorus EN deposits have "excellent" corrosion resistance while mid- and low/mid-phosphorus electroless nickel (EN) deposits have "good" corrosion resistance. Less attention is paid to electroless nickel corrosion resistance for deposits having less than 10%P, since high phosphorus (10-12% P) EN is known to have excellent corrosion resistance properties for a diverse set of media.[1,2] But how do EN deposits with 5-7%P and 8-9%P compare? What dictates "excellent" and "good" corrosion resistances?

With increasing restrictions on several elements (i.e. cadmium and lead) conventionally used in electroless nickel plating baths, many new low/mid- and mid- phosphorous processes have been introduced. How do the corrosion resistances of these new ELV-complaint systems compare to conventional systems? It has been reported that the corrosion resistance of EN decreases with increasing bath age.[3] Therefore in this work, the corrosion rates of 5-7%P and 8-9%P electroless nickel deposits are evaluated over the bath life from 0 to 6 MTO.

Two techniques are used to evaluate and compare the corrosion properties of low/mid- and mid- phosphorus electroless nickel processes over the bath life. Traditional salt spray testing and electrochemical testing are performed. The results from both techniques are presented and discussed. The effect thickness has on corrosion resistance for a mid-phosphorus system is explored. Also, the low/mid- and mid-phosphorus corrosion resistances are compared to high phosphorus corrosion results, both ELV and conventional.

Electrochemical Testing

Electrochemical techniques can be useful for the rapid evaluation of the corrosion behavior of a metal or alloy. These methods have been widely used to study the corrosion of iron, low alloy steels, stainless steels, nickel alloys, and various other high strength or corrosion resistant alloys. The technique is designed to systemically accelerate the oxidation and reduction reactions associated with the corrosion process while measuring the response.[4] Specimens can be rapidly evaluated once certain constants are obtained and a variety of test solutions can be selected.

When a specimen is in contact with a specific electrolyte, it assumes a certain potential (relative to the reference electrode) referred to as the corrosion potential, E_{corr}. At E_{corr}, the sample has both anodic and cathodic currents that are equal in magnitude, so the net current is zero ($i_{ox} = i_{red}$). At this potential, the rate of oxidation equals the rate of reduction.

Polarization characteristics are experimentally measured by plotting the applied potential versus the current response. Using a potentiostat, the potential is adjusted step-wise in either a negative or positive direction from E_{corr} and the current is recorded after each adjustment. The potential (voltage) displacement from E_{corr} is called the polarization or overpotential. By polarizing in a systematic manner and measuring the resulting total currents, it is possible to extrapolate the

2

values of i_{ox} and i_{red} at E_{corr}.[4] The extrapolated current is referred to as the "corrosion current" (i_{corr}).

Two techniques are used to determine the corrosion rate of the mid and low/mid-phosphorus deposits in this work. The Tafel technique is a controlled-potential scan applied to a specimen, starting at E_{corr} and going either in the anodic (+) or cathodic (-) directions for a few hundred millivolts. Tafel plots provide data that are inputted in a subsequent linear polarization plot. Linear polarization (polarization resistance) is a quick electrochemical technique that is used to calculate the corrosion rate. A controlled-potential scan is applied over a small range surrounding E_{corr}. Using constant values obtained from the Tafel plots and running a linear polarization plot gives i_{corr} (the corrosion current density). The corrosion rate can be calculated in mils per year (mpy) or milli-inches per year using equation 1.

(1) Corrosion Rate (mpy)= $((0.13*i_{corr}*E.W.)/ d)$

I_{corr} is the corrosion current density in $\mu A/cm^2$. E.W. is the equivalent weight of the corroding species, g. And d is the density of the corroding species in g/cm^3. Further information and a more detailed description of electrochemical testing can be found in references 4 and 5.

Experimental
Mid-Phosphorus and Low/Mid-Phosphorus EN Deposits

The corrosion resistances of four EN systems are presented. Two conventional (which contain lead and cadmium) and two EN processes specifically designed to comply with ELV requirements are compared. The EN processes evaluated are outlined in Table 1.

Two of the processes are in the 5-7%P range, while the other two contain a slightly higher %P (8-9%P). Most of the systems have a similar plating rate when compared within their respective %P groups. The processes labeled "conventional" contain lead and cadmium as their main stabilizer and brightener. Systems labeled "ELV" were designed to exclude lead or cadmium and depend on a new stabilizer and organic brighteners. The organically stabilized (OS) process does not rely on metallic stabilizers or brighteners, the only metals contained in the deposit are nickel and phosphorus.

Panels were plated for each system at 0, 2, 4 and 6 MTO. Each process was run according to optimal parameters outlined in their technical data sheets. Temperature, pH, and agitation were kept constant throughout the bath life. Each specimen was checked for %P (by SEM analysis) prior to testing to ensure the content fell within the specified phosphorus range.

3

Table 1: Basic Characteristics of Mid- and Low/Mid-Phosphorus Electroless Nickel Systems

Process	ELV Compliant	Plating Rate mil/hr (um/hr)	Ni (g/L)	Hypo (g/L)	Process Details
5-7% P	Yes	0.8-1.0 (20-25)	6.0	30.0	ELV/ OS
5-7% P	No	0.6-0.8 (15-20)	6.0	30.0	Conventional
8-9% P	Yes	0.5-0.7 (13-18)	6.0	30.0	ELV
8-9% P	No	0.5-0.7 (13-18)	6.0	30.0	Conventional

OS= organically stabilized

Test Methods

Figure 1 shows the corrosion test set-up. The instrumentation consisted of an EG&G/ PARC Instruments Model 263A Potentiostat/Galvanostat, an EG&G/PARC flat corrosion cell, and Model 352 Corrosion Analysis Software version 2.60 (Princeton Applied Research Co., Oak Ridge, TN). The working electrode (WE), the reference electrode (RE)- a saturated calomel electrode, and the counter electrode (CE)- a platinum foil, are connected to the potentiostat, which in turn is controlled by the corrosion analysis software. The potentiostat applies the potential and measures the resulting current. The corrosion analysis software creates graphs and calculates i_{corr}.

Two different steel panels were used for the electrochemical and NSS testing. Better corrosion resistance is achieved on smoother surfaces [2]. Therefore, a 2.75" x 3.88" 267-mL size zinc-coated Hull cell panel (Larry King Corp., Rosedale, N.Y.) was plated for each electrochemical sample to a thickness of 1 mil (25 μm). Steel panels were prepared by the following cleaning cycle: 50% HCl, rinse, anodic soak and cleaning, rinse, acid activation, rinse, and plate. The pretreatment cycle was chosen based on the experimental results by Beer.[6] Plating bath loading was 0.28 ft^2/gal (0.69 dm^2/L). All EN plating solutions were neutralized using ammonium hydroxide. The pH was kept constant throughout the bath life, so that deposits variations were kept to a minimum. Plated panels were wet polished with 400 grit SiC paper, rinsed, and soaked in acetone and then alcohol prior to testing, to remove any oxidation. Panels were placed in the flat cell for 30 minutes prior to testing to allow the E_{corr} value to stabilize. The corrosion cell is depicted in Figure 2.
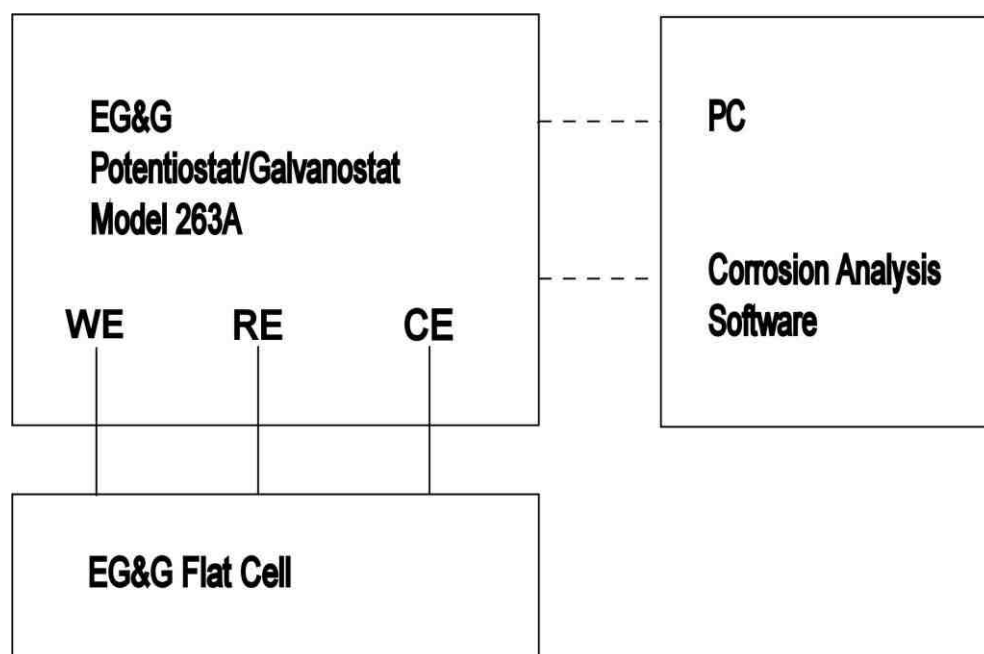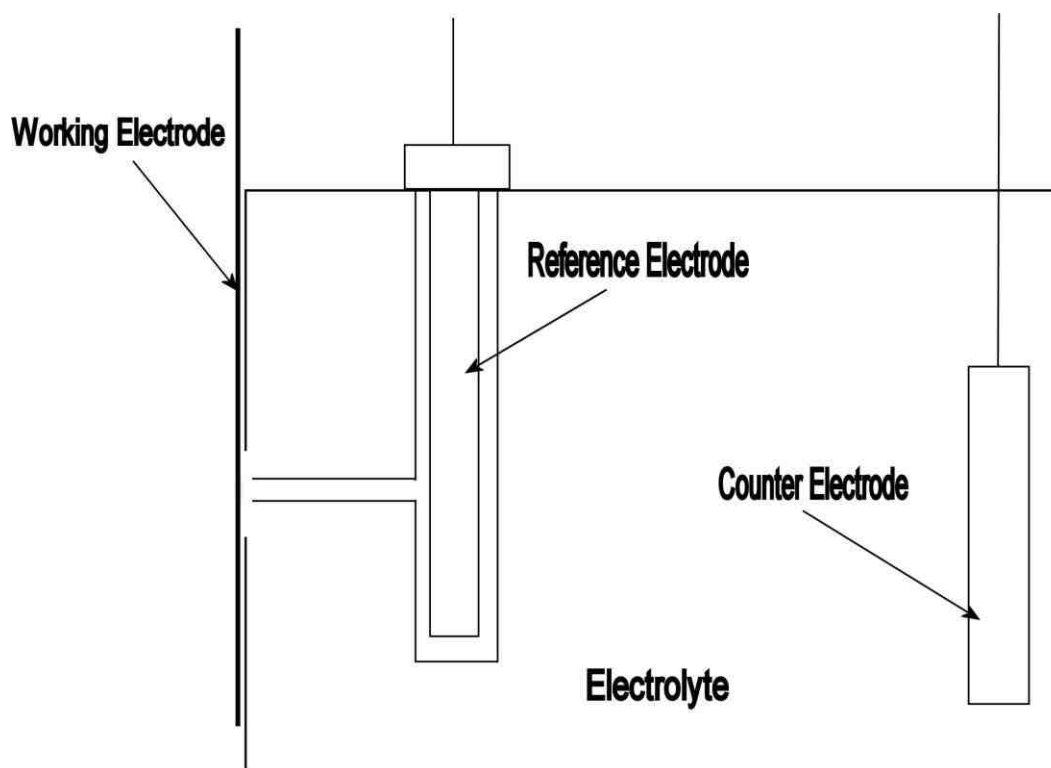
4

Figure 1. Instrumentation Set-Up for Corrosion Testing

Figure 2. Diagram of the EG&G Flat Cell Used for Corrosion Testing

5

A 1 cm^2 area of the sample (or working electrode) was exposed to the electrolyte in the flat cell (volume to area ratio: 300 ml/cm^3). The electrolyte tested was a 1.0 N sulfuric acid (H_2SO_4) solution (pH of 0.3). The sulfuric acid solution was chosen because of its low pH which as been shown to increase corrosion [1]. All testing was completed at ambient temperature and pressure and in the presence of oxygen. The electrolyte was not deaerated with nitrogen. Duncan found that deaeration of acid solutions reduced the corrosion by about one-half [1].

It should be noted that most corrosion testing is completed in the absence of oxygen. Test cells usually have inert nitrogen or hydrogen pumped through before testing commences. It is known that cathodic currents can occur during anodic polarization due to oxygen effects. Negative loops can happen when the total cathodic current is higher than the total anodic current. No such currents occurred during the testing described in this work. The work completed can only be compared to other samples tested in the presence of oxygen and cannot be compared to testing completed under inert conditions. Actually, testing in the presence of oxygen should mimic more "real" world corrosion behavior. Rarely will a sample be corroding in the absence of oxygen.

Two electrochemical techniques were used to determine the corrosion behavior of the mid- and low/mid-phosphorus systems mentioned in Table 1. Three plots were created for each sample- a linear polarization, a cathodic and anodic Tafel plot. Although an estimate of the corrosion current can be obtained by assuming values for the Tafel constants, the most accurate results are obtained when the constants are determined experimentally for the metal/solution system of interest [4]. Therefore, Tafel plots in the cathodic and anodic directions were ran to obtain the anodic and cathodic constants for each sample. These constants are used with the linear polarization plot to obtain an i_{corr} value, which is inputted in equation 1 to calculate the corrosion rate. The average reproducibility for the i_{corr} value of a specimen (same panel but different 1 cm^2 area) was calculated to be 5.1%. Since the same spot cannot be used over again, no repeatability results are given. The electrochemical testing parameters are provided in Table 2.

Table 2: Electrochemical Testing Parameters

Plot	Initial Potential (V) (relative to Ecorr)	Final Potential (V) (relative to SCE)	Rate (mV/s)
Linear Polarization	-0.020	0.020	0.166
Cathodic Tafel	0.020	-0.250	1.0
Anodic Tafel	-0.025	1.0	1.0

6

The influence that thickness and bath age have on corrosion resistance was evaluated. The 8-9%P ELV system was used to compare the corrosion rates at 0 and 6 MTOs and at several thicknesses. Corrosion resistance trends concerning these test parameters are discussed.

The corrosion rates of high, mid- and low/mid- phosphorus electroless nickel are compared. Table 3 contains the basic characteristics for the high phosphorus processes that will be compared to those presented in Table 1. All panels were run using electrochemical testing in the 1.0 N sulfuric acid solution.

Table 3: Basic Characteristics of High Phosphorus Electroless Nickel Systems

Process	ELV Compliant	Plating Rate mil/hr (μm/hr)	Ni g/L	Hypo g/L	Process Details
11-13% P	Yes	0.3 (8)	7.8	37.5	Conventional
10-12% P	Yes	0.4-0.5 (10-13)	6.0	30.0	Conventional
10-12% P	Yes	0.5 (13)	6.0	30.0	ELV
10-12% P	Yes	0.4-0.5 (10-13)	3.0	20.0	ELV LMO

LMO= Low Metal Operation

In addition to electrochemical testing, neutral salt spray (NSS) testing was also completed for the processes listed in Table 1. Two 3" x 6" unpolished cold rolled steel (CRS) panels (ACT, Inc., Hillsdale, MI) were plated at 0, 2, 4, and 6 MTO, with a thickness of 1.0 (±0.05) mil for each process. The rougher panels were used for NSS testing, so that any deposit porosity would be easily identified. The same pretreatment was used as for the electrochemical samples. The plating bath loading was 0.47 ft^2/gal (1.16 dm^2/L). Plated panel edges were covered with stop-off material prior to being placed in the salt spray chamber. Panels were checked daily for red rust and black spots. The total survival time of the panels without red rust appearing in the middle region was recorded for each panel.

All panels were run in accordance with ASTM B117 [7]. This is probably the most widely specified corrosion test. The test features a 5 % chloride electrolyte, elevated temperatures and utilizes a fine-fog mist. Salt spray results provide an evaluation of corrosion protection for each deposit (i.e. the ability to protect the substrate). Therefore, corrosion resistance and protection studies offer an overall look into a deposit's corrosion properties.

7

Results

Electrochemical Testing

The corrosion rates determined for the mid- and low/mid-phosphorus deposits with a 1 mil thickness in the 1.0 N H_2SO_4 solutions are presented in Table 4.

Table 4: 1.0 N Sulfuric Acid Solution Corrosion Results for Mid- and Low/Mid- Phosphorus Electroless Nickel Processes

EN Processes	0 MTO (mpy)	2 MTO (mpy)	4 MTO (mpy)	6 MTO (mpy)
5-7%P-ELV/OS	17.47	33.23	34.71	34.85
5-7%P-Conventional	19.96	30.77	22.58	27.00
8-9%P- ELV	7.04	19.21	22.94	19.48
8-9%P-Conventional	16.65	21.07	21.26	21.69
Steel	389.26			

Overall, the corrosion resistance of a deposit decreases with bath age. This is expected, since orthophosphite and various salts (i.e. sulfate left over from the reduction of nickel), organic acids, and either sodium or ammonium hydroxides or potassium carbonate to neutralize the hydrogen ions formed during deposition build-up in the bath. Duncan confirms that the change in corrosion resistance with age is caused by the changing chemistry of the plating solution and especially its salt content [3].

The ELV and conventional systems exhibit similar corrosion resistance in the 1.0N sulfuric acid solution. The ELV low/mid- and mid- phosphorus processes have a better corrosion resistance and than their "conventional" counterparts at 0 MTO. The 8-9%P ELV corrosion rate at 0 MTO is roughly half that of the 8-9%P conventional system. After 0 MTO, the 8-9% ELV system starts to exhibit corrosion rates similar to those seen for the 8-9% conventional process. Both 8-9%P systems exhibit very consistent corrosion rates, especially with increasing bath age. The data reveals that the corrosion resistance of the deposits is not significantly affected by the build-up of salts in the bath.

Overall, the 5-7%P systems have a slightly higher corrosion rate than the 8-9%P processes. This is expected; since the deposits have a lower %P. The greatest difference in corrosion resistance between the two %P groups is seen at 6 MTO. The 8-9%P systems have corrosion rates of approximately 20 mpy, while the 5-7%P conventional and ELV/OS have corrosion rates of 27 and 34.85 mpy, respectively.

8

The 5-7%P data reveals some slight corrosion resistance differences. In general, the ELV/OS system possesses higher corrosion rates than the conventional process. Both systems show very consistent corrosion rates with increasing bath age. The 5-7%P ELV/OS system has a corrosion rate that steadily increases from 2 to 6 MTO. At 6 MTO, the corrosion rate of the two 5-7%P systems only differs by 7.85 mpy (which represents a 23-30% difference in corrosion resistance). Whether or not a slight increase or decrease in %P during bath age plays a significant role in these differences will be investigated in the future.

Thickness

Deposit thickness can play a significant role in determining corrosion rates. In general, the thinner the deposit the more likely it will be porous and have a higher corrosion rate [8]. Several panels were plated in the 8-9% ELV bath at 0 and 6 MTO and with thicknesses ranging from 0.4 to 1 mil. The electrochemical results in the 1.0 N sulfuric acid solution are shown in Figure 3.
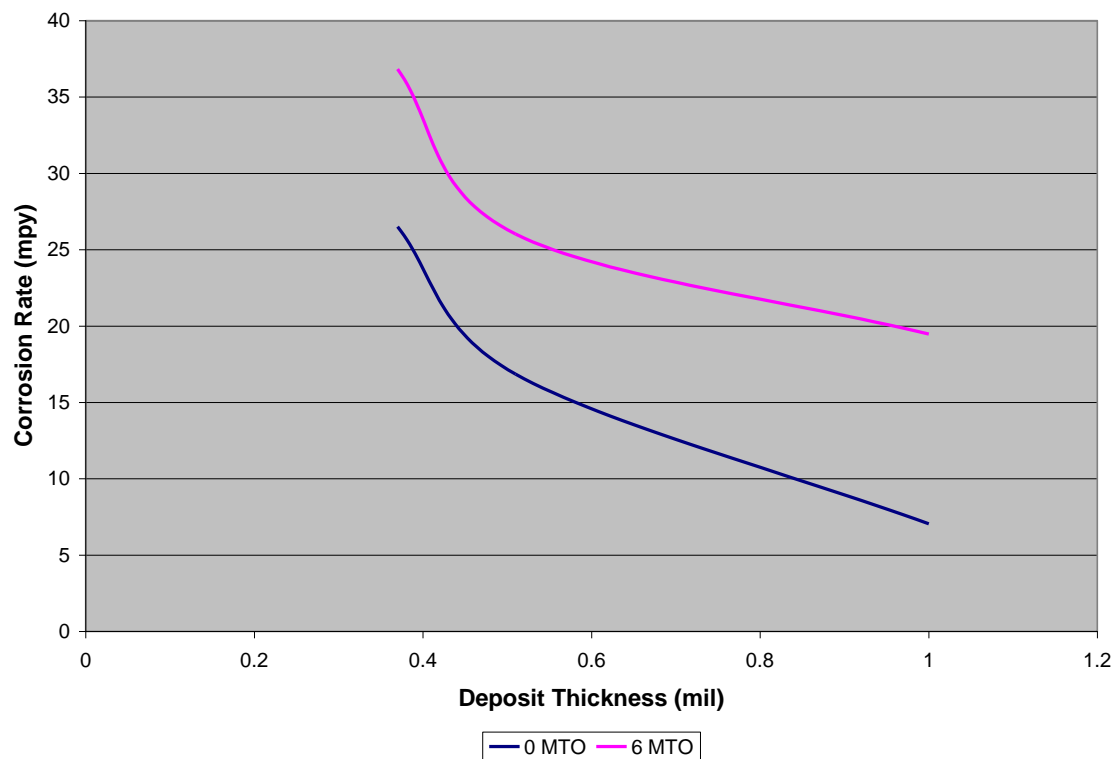
Figure 3. Corrosion Rate of 8-9%P ELV Process at Various Thickness and Bath Ages in the 1.0 N Sulfuric Acid Solution

9

As expected, the 0 MTO panels exhibit lower corrosion rates than the 6 MTO deposits. A 1 mil thick deposit at 6 MTO has the same corrosion resistance as a 0.4 mil deposit plated at 0 MTO. Both the 0 MTO and 6 MTO trend lines in Figure 3 show a dramatic increase in corrosion rates when there is less than 0.4 mils of deposit. Overall, thicker deposits are needed as the age increases if the desired corrosion resistance is to remain constant.

High Phosphorus vs. Mid- and Low/mid- Phosphorus Corrosion Rates

The corrosion rates of high-, mid- and low/mid- phosphorus processes differ greatly. Table 5 combines the 0 to 4 MTO results from Table 3 and corrosion rate results for several high-phosphorus ELV and conventional systems in 1.0 N sulfuric acid taken from reference 5. The high phosphorus systems exhibit a similar reduction in corrosion resistance with bath age as the mid- and low/mid-phosphorus processes did. At 0 MTO, the 8-9% ELV process has a lower corrosion rate than any of the high phosphorus systems listed. At 2 and 4 MTO, the 8-9%P systems exhibit corrosion rates only slightly higher than the 10-12%P conventional high phosphorus process. At 4 MTO, all the high phosphorus processes have a lower corrosion rate than the mid- and low/mid-phosphorus baths. Overall, the 5-7%P processes have corrosion rates roughly 2x and 1.5x higher at 4 MTO than the high-phosphorus and mid-phosphorus baths, respectively.

Table 5: Corrosion Rates of High-, Mid- and Low/Mid- Phosphorus Electroless Nickel Processes in 1.0 N Sulfuric Acid Solution

EN Processes	0 MTO (mpy)	2 MTO (mpy)	4 MTO (mpy)
5-7%P- ELV/OS	17.47	33.32	34.71
5-7%P- Conventional	19.96	30.77	22.58
8-9%P- ELV	7.04	19.21	22.94
8-9%P- Conventional	16.65	21.07	21.26
11-13%P- Conventional	10.76	12.74	
10-12%P- Conventional	14.53	17.80	20.05
10-12%P- ELV	13.12	10.93	14.59
10-12%P- ELV LMO	8.50	10.26	13.90
Steel	389.26		

LMO= Low Metal Operation

From 2 to 4 MTO, the 8-9%P systems have corrosion rates only slightly higher than those exhibited by the 10-12%P conventional system. While the corrosion rates only differ slightly, keep in mind that the deposits themselves will have very different properties. First, the high phosphorus system will have compressive stress until it becomes tensile after 4 MTO. The high phosphorus system seems to have a similar corrosion resistance to mid-phosphorus systems with an increase in bath age, but it will have much higher corrosion protection. Corrosion protection is evaluated by neutral salt spray results and shows the pitting tendencies associated with a specific deposit. High phosphorus EN will survive 1000 hours in NSS without red rust, while mid- and low/mid- phosphorus EN should survive 96 hours.

Neutral Salt Spray

The NSS test results for the mid- and low/mid- phosphorus systems are in Table 6. The number of hours that each panel survived without any red rust developing on the panel (not including the area coated with stop-off material) is shown. Deposit thickness is 1 mil for all panels.

Table 6. Neutral Salt Spray Results for Mid- and Low/Mid- Phosphorus EN Deposits at 0, 2, 4 and 6 MTO

EN Process	0 MTO	2 MTO	4 MTO	6 MTO
5-7%P- ELV/OS	144	96	24	24
5-7%P- Conventional	96	48	24	24
8-9%P- ELV	192	72	72	24
8-9%P- Conventional	96	72	72	24

All the electroless nickel deposits at 0 MTO, as shown in Table 6, reach 96 hours before red rust occurs in the middle section of the test panel. However, as observed with the electrochemical testing previously, the deposit changes with bath age and the corrosion properties are affected. The corrosion protection decreases with increasing bath age. At 6 MTO, regardless of 5-7%P or 8-9%P, panels only survive 24 hours in the salt spray chamber before red rust is observed. Please refer to reference 5 to compare these results to those obtained for the high phosphorus systems provided in Table 5.

Conclusion

The combination of electrochemical testing and neutral salt spray testing offers a powerful evaluation tool for corrosion resistance and protection. Overall,

11

the results confirm that the corrosion behavior of the conventional and ELV low/mid- and mid-phosphorus EN systems differ only slightly.

In addition, the results clearly indicate that while some mid-phosphorus systems can achieve better or equal corrosion resistances at early bath age when compared to high phosphorus systems. It does provide the same corrosion protection (NSS results) that high phosphorus processes possess. The ratings of "excellent" and "good" for corrosion resistance are ambiguous. In most cases, the ratings are simply based on NSS data. However, as shown, the NSS data can vary greatly between and within certain %P groups and especially with bath age.

Deposit thickness and composition has a direct impact on corrosion resistance and protection. This work confirms, as previously reported, the thicker the deposit, the higher the corrosion resistance. Thicker deposits are needed with bath age in order to keep a certain corrosion resistance level.

Accelerated corrosion testing can quickly evaluate new deposits and changes in treatments. Both electrochemical and neutral salt spray testing are considered accelerated tests. Of the two tests, the electrochemical one offers faster results. Individual electrochemical results for a deposit in this work took approximately 1.5 hours to run, while the NSS testing still required upward of 192 hours (approximately 8 days). In most cases, the corrosion resistance and corrosion protection results correlated, when corrosion resistance decreased, the number of hours to red rust increased and vice versa.

Running both tests appeared to provide a good overall evaluation of a deposit's corrosion properties (chemical resistance and chemical protection), but keep in mind that both tests correspond to an artificial method for corroding a sample. These procedures can aid in predicting how a sample might behave over the long term but they cannot replace long term studies where other mechanisms may occur.

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