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Electroless Nickel Duplex Coatings Using RoHS-Compliant Systems

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ABSTRACT

Duplex coatings can offer corrosion and wear resistance that exceed those of conventional electroless nickel (EN) deposits for specialty applications. Duplex coatings consisting of a high-phosphorus EN or a new ternary alloy underlayer and an upper layer of low-, low/mid- or mid-phosphorus electroless nickel were investigated. Wear, adhesion and corrosion resistance properties for numerous combinations of EN duplex coatings are presented here, both as-plated and after heat-treatment. Duplex coating results are compared with single layer EN deposits.

Keywords: Electroless nickel, duplex electroless nickel, ROHS-compliant coatings

Introduction

Double-layer (or duplex) systems use two coatings in conjunction in order to create superior properties for the combined finish. Duplex coatings offer an advantage over a single layer for certain applications when an individual deposit does not provide the necessary physical / mechanical properties. There are numerous examples of duplex coatings already used in the surface finishing industry, including: high-phosphorus electroless nickel (EN) with an EN/PTFE co-deposit layer for lower coefficient of friction[1] and high-phosphorus EN with a low-phosphorus upper layer that is oxidized to create a black EN deposit for appearance purposes.[2] It is also common in decorative plating for two, three or four layers to be used to obtain both a good corrosion-resistant coating as well as an attractive finish.

This paper will evaluate duplex coatings consisting of electroless nickel as both the upper and lower finish. Usually, a high-phosphorus electroless nickel is the lower layer to provide corrosion resistance while the upper layer endows a particular property needed for a specific application. Duplex EN coatings can improve properties such as surface wear, hardness, corrosion resistance and appearance. Different combinations of electroless nickel systems result in specific properties which might offer alternatives to existing surface finishing applications. In this study, the lower layer provides corrosion resistance (in the form of a high-phosphorus EN or ternary alloy) and the upper layer consists of a low-, low/mid-, or mid-phosphorus electroless nickel.

Electroless Nickel Systems

A total of five electroless nickel systems were tested. Table 1 provides a list of the processes, along with plating rates and percent phosphorus (%P) for each system/deposit. All systems are RoHS/ELV/WEEE-compliant systems and have no intentionally added lead or cadmium. There are two systems used as the lower layer to provide corrosion resistance. A high-phosphorus (HP) system with 10-12% P and a ternary alloy[3] (TA) with 9-10% P and 1-3% Sn that provides superior corrosion resistance. The upper layers are either low-phosphorus, low/mid-phosphorus or mid-phosphorus electroless nickel. All EN systems tested are metallically-stabilized processes, except the low/mid-phosphorus system, which is organically-stabilized.[4,5]

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Table 1 - Electroless nickel systems.

Process	Rate, mil/hr	Composition	RoHS/ELV/WEEE compliant	Layer
High-P (HP)	0.4 - 0.5	10 - 12 wt% P	Yes	Lower
Ternary alloy (TA)	0.25 - 0.35	9 - 10 wt% P 1 - 3 wt% Sn	Yes	Lower
Low-P (LP)	0.5 - 0.6	1 - 4 wt% P	Yes	Upper
Low/Mid-P (LMP)	0.7 - 0.9	4 - 7 wt% P	Yes	Upper
Mid-P (MP)	0.6 - 0.8	8 - 9 wt% P	Yes	Upper

All duplex panels consisted of 15 µm (0.6 mil) of high-phosphorus or ternary alloy as the lower layer and 10 µm (0.4 mil) of an upper layer (either LP, LMP or MP) for a final combined thickness of 25 µm (1.0 mil). Figure 1 is a SEM photo of an EN duplex coating. This particular panel has a lower layer and upper layer of ternary alloy and low/mid-phosphorus EN, respectively, after heat-treatment at 320°C (608°F). The duplex panel results are compared to panels having a single deposit. Single layers of each system listed in Table 1 were also plated to a thickness of 25 µm (1.0 mil).

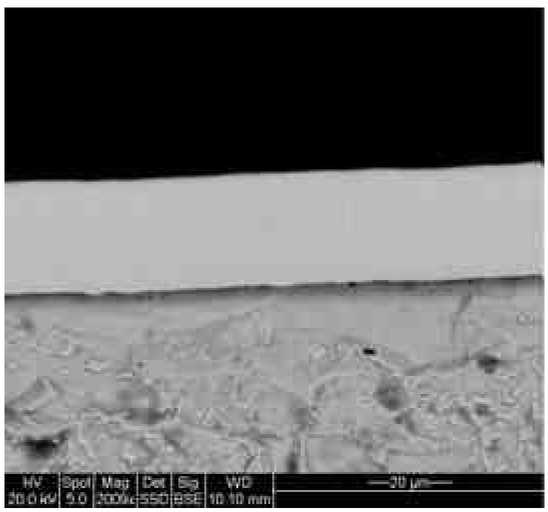

Figure 1 - SEM photo of an electroless nickel duplex coating.

Test parameters

All panels were processed in 15-gal tanks, with 0.3 ft²/gal loading. All systems were run according to their technical data sheets, keeping the nickel concentration within 10% of optimum and the pH to within 0.1 units. Rate panels were plated along with the duplex panels to calculate the plating time required and the rate panels were used to verify wt% P content of the deposits. Corrosion and gloss panels were unpolished cold rolled steel (CRS) panels (ACT, Hillsdale, MI), wear panels were S-16 steel test specimens (Taber Industries, North Towanda, NY) and hardness panels were steel hull cell panels (Larry King Corp, Rosedale, NY). All panels were soaked (5 min), anodically electrocleaned (30 sec) and activated in a mixed acid solution (30 sec). Panels requiring two layers were rinsed briefly with room temperature de-ionized (DI) water during bath transfer. Transfer times from the upper layer plating tank to the lower layer bath were less than 1 min.

Plated panels were tested for corrosion resistance, wear, hardness and gloss. Corrosion resistance was determined by neutral salt spray (NSS) according to ASTM B117.[6] The panel edges were stopped off with wax and placed in the salt spray cabinet until red rust appeared and the number of hours were recorded. Wear resistance was tested using a Taber Abraser (model 5130) with a 1000-g load and CS-10 wheels. Weight loss after 1000 cycles was recorded and the Taber wear index (TWI) was calculated after ten 1,000 cycles. Hardness samples were plated on steel panels to a thickness of 63.5 µm (2.5 mil). A Micromet 5104-V/K (Buehler, Chicago, IL) with a load of 100 g and using a Knoop indenter was used for hardness testing. Five indents were made in mounted cross-sections from each single layer sample and an average reported. Gloss panels were plated to 12.7

µm (0.5 mil) deposit thickness for the single layer panels. The gloss was checked at a 20° angle with an Elcometer 406 statistical glossmeter (Elcometer, Rochester, MI). Ten gloss readings were taken per panel and the average reported.

Each set (there are 11 sets in total) of NSS panels consist of six plated specimens. Three panels were left as-plated and three panels were heat-treated. The number of hours to red rust provided in this paper is an average of the three panels. For panels plated with the ternary alloy (TA) or the low-phosphorus (LP) systems, the heat treatment was 320°C (608°F) for 1 hr. For all other panels the heat treatment was 1 hr at 350°C (662°F) to achieve maximum hardness. Panels after heat treatment were removed and allowed to cool in air, rather than allowing the panels to cool in the oven.

Results

Wear

The wear resistance of the low-phosphorus system as an upper layer is compared to the wear resistance of the lower layers as single deposits both as-plated and heat-treated (HT) in Fig. 2. The low-phosphorus system as a single layer has a Taber wear index (TWI) of 8.03 and 7.2 mg loss/1000 cycles, as-plated and after heat-treatment, respectively. Reducing the amount of LP to 10 µm (0.4 mil) and having 15 µm (0.6 mil) of either high phosphorus or ternary alloy under it did not seem to change the TWI of the upper layer.

The TWI values are still in the 7 - 8 mg loss/1000 cycles range for as-plated and in the 6 - 7 mg loss/1000 cycles range after heat-treatment. The low-phosphorus system has a much lower TWI when compared to the HP and TA systems. They produce 23 - 26 mg loss/1000 cycles and 12 - 15 mg loss/1000 cycles for the as-plated and heat-treated deposits, respectively. Overall, the low-phosphorus system has wear results that are one-third that of the HP and TA systems as-plated and half that of the heat-treat results.

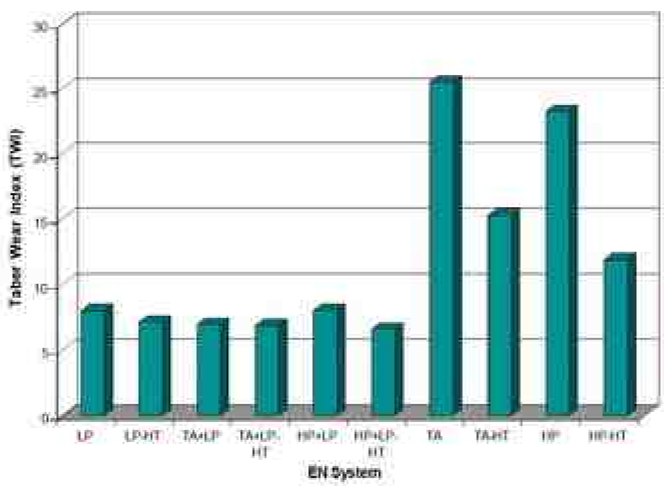

Figure 2 - Taber Wear Index for low-phosphorus system duplex panels compared to high-phosphorus and ternary alloy single layer panels.

Figure 3 compares the TWI of duplex panels with low/mid-phosphorus upper layers and single layer deposits of the HP and TA systems. The low/mid-phosphorus process has a TWI of 12.91 and 12.01 mg loss/1000 cycles for as-plated and heat-treated deposits, respectively. The duplex panels with high-phosphorus and ternary alloy lower layers and the LMP system as the upper layer, produce similar wear results. Most TWI values are in the 12 - 13 mg loss/1000 cycles. Overall, the Taber wear index of the low/mid-phosphorus system is approximately half that of the HP and TA systems as-plated, but fairly close to the same values after heat-treatment. For the low/mid-phosphorus system, the heat-treatment did not offer much more wear resistance.

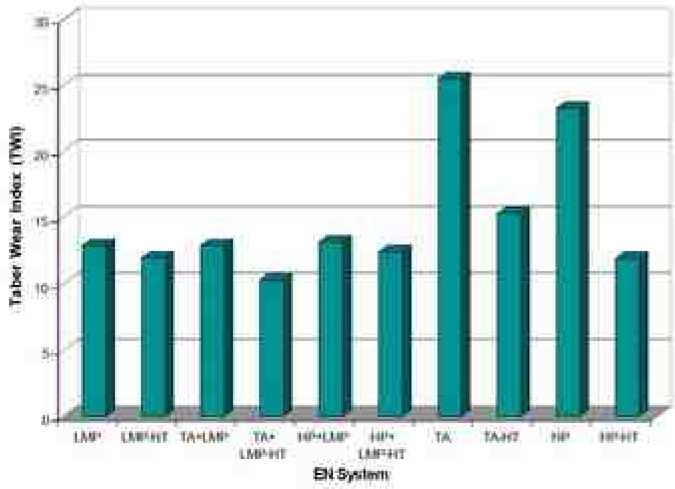

Figure 3 - Taber Wear Index for low/mid-phosphorus system duplex panels compared to high-phosphorus and ternary alloy single layer panels.

The Taber wear indexes for the mid-phosphorus system both as-plated and heat-treated are compared to HP and TA results and duplex panel values in Fig. 4. The mid-phosphorus system has a TWI value of 23.47 and 12.28 mg loss/1000 cycles, as-plated and heat-treated, respectively. The duplex panels with the MP as the upper layer have very similar Taber wear index numbers. The high-phosphorus and ternary alloy also have comparable TWI results to the mid-phosphorus system. The HP and TA systems only have as-plated and heat-treated values that are 2 - 3 mg loss/1000 cycles more than the mid-phosphorus process.

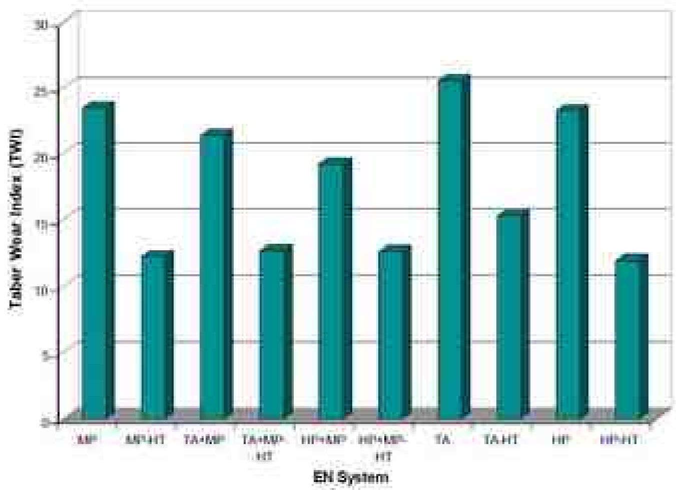

Figure 4 - Taber Wear Index for mid-phosphorus system duplex panels compared to high-phosphorus and ternary alloy single layer panels.

Hardness

The hardness of electroless nickel systems, both as-plated and after heat-treatment, as a single layer is shown in Fig. 5. The hardness of the high-phosphorus and ternary alloy are very comparable, 480 HK_{100} as-plated and 790 HK_{100} after their respective heat-treatments. The low-phosphorus system is the hardest of all the systems tested. It has an as-plated hardness of 755 HK_{100} and a heat-treated value of 899 HK_{100}. The low/mid-phosphorus process has an as-plated hardness of 729 HK_{100}. Though this value is fairly close to that of the low-phosphorus system, the low/mid-phosphorus process doesn't gain as much hardness with heat treatment (similar effect was shown with the wear results). The LMP system produced a deposit hardness of 819 HK_{100}

after 1 hr at 350°C (662°F). The mid-phosphorus deposit has a hardness as-plated and heat-treated that is comparable to the high-phosphorus and ternary alloy values.

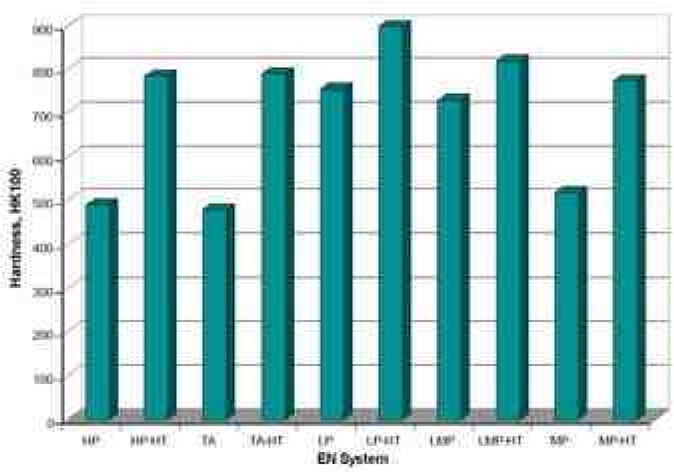

Figure 5 - Hardness of the single layer deposits both as-plated and heat-treated.

Corrosion resistance

Neutral salt spray results are provided for all combinations of duplex layers both as-plated and heat-treated. The number of hours to red rust gives an evaluation/estimation of the corrosion protection for each deposit (*i.e.*, the ability to protect the substrate). The results give an indication of the porosity of the finish. In general, the lower the amount of porosity, the lower the number of potential corrosion sites, which results in a longer amount of time in a salt spray cabinet without red rust occurring. Table 2 contains the results of the as-plated duplex coating neutral salt spray results.

Table 2 - As-plated neutral salt spray results of duplex panels and single layer deposits.

Duplex panels	Hours to red rust
High-P + Low-P	893
High-P + Low/Mid-P	1382
High-P + Mid-P	1462
Ternary Alloy + Low-P	933
Ternary Alloy + Low/Mid-P	1590
Ternary Alloy + Mid-P	1718
Single-layer panels	
High-P (HP)	1818
Ternary Alloy (TA)	2598
Low-P (LP)	36
Low/Mid-P (LMP)	168
Mid-P (MP)	192

The single layer panel results for the LP, LMP and MP systems have the lowest number of hours to red rust. These systems traditionally have higher porosity when compared to the high-phosphorus processes, so the results are as expected. Low-phosphorus systems last about 24 hr. They are normally used for their hardness and excellent corrosion resistance in alkaline environments. But with a high-phosphorus or ternary alloy lower layer, the low-phosphorus system can withstand approximately 900 hr in NSS. The LMP system passed 168 hr in salt spray as a single layer, but with a HP or TA lower layer, the results increase to 1382 hr with HP and over 1500 hr with TA. The mid-phosphorus system completed nearly 200 hr in NSS before the appearance of red rust. However with 15 μm (0.6 mil) of a high-phosphorus or ternary alloy system underneath, the results improved to nearly 1500 hr and above.

Electroless nickel (especially high-phosphorus) shrinks when exposed to temperatures over 220-260°C (428-500°F). If the coating shrinks enough during heat treatment, cracking can occur, which exposes the substrate to attack during NSS testing. The panels in this study were allowed to cool in air after heat treatment which allowed for even wider cracks than if the part had been allowed to cool in the oven. In addition, with high temperature baking, the internal structure goes from amorphous to crystalline. Nickel phosphide crystals form, causing shrinkage and cracking of the deposit. High-phosphorus systems shrink more than low-phosphorus, low/mid phosphorus and mid-phosphorus with high heat treatment, which makes it more susceptible to cracking.

The neutral salt spray results for the heat-treated panels are very different than those featured in Table 2. The ternary alloy and low-phosphorus processes were heat-treated for 1 hr at 320°C (608°F) to obtain optimum hardness and wear. All other panels were baked at 350°C (662°F) for 1 hr. Even though heat treating to attain optimum hardness is needed for some applications, it is not advantageous for the corrosion resistance. Heat treatment will severely reduce the corrosion resistance, as seen in Table 3.

Table 3 - Neutral salt spray results for heat-treated duplex and single layer electroless nickel coatings.

Duplex panels	Hours to red rust
High-P + Low-P	257
High-P + Low/Mid-P	184
High-P + Mid-P	160
Ternary Alloy + Low-P	321
Ternary Alloy + Low/Mid-P	499
Ternary Alloy + Mid-P	249
Single-layer panels	
High-P (HP)	72
Ternary Alloy (TA)	72
Low-P (LP)	36
Low/Mid-P (LMP)	48
Mid-P (MP)	48

Nearly all the NSS results were affected by the heat-treatment. The single layer panels with high-phosphorus and ternary alloy systems had the most drastic reduction in corrosion resistance (from 1800+ hr to 72 hr). Overall, the duplex panels and the single layer panels with low/mid-phosphorus and mid-phosphorus had a corrosion resistance reduction of approximately 75%. The one exception is the low-phosphorus system, which survived 36 hr in NSS both as-plated and after heat-treatment. The corrosion resistance seems to be slightly better for the duplex panels with the ternary alloy underlayer. Perhaps, the lower temperature heat treatment (320 vs. 350°C) for the TA and LP systems lead to slightly less shrinkage and fewer cracks in the lower layer (*i.e.*, fewer potential corrosion sites). The best result among the high phosphorus duplex panels is with the low-phosphorus upper layer. This panel set was also subjected to the lower heat treatment, which might account for its elevated corrosion resistance.

Figure 6 is a SEM photo of a cross-section of a duplex panel (TA + LMP) after heat-treatment at 320°C (608°F) for 1 hr and 340 hr in NSS. There are cracks visible through both layers of the duplex coating. The cracks made attack on the underlying steel very straightforward. However, the duplex coating shown in Fig. 6 did not fail until after 340 hr in NSS. A magnified surface photo of a corroded area on the same panel is shown in Fig. 7. The low/mid-phosphorus upper layer has corroded areas that are clearly visible. However no cracking is seen on the surface of the LMP layer. Inside the corroded areas, cracking is clearly evident. The cracking caused by high heat treatment may not have gone through both layers. It is possible that the lower layers cracked and, when placed in salt spray, the upper layer provided the corrosion resistance until the susceptible areas (with cracking underneath) started to corrode.

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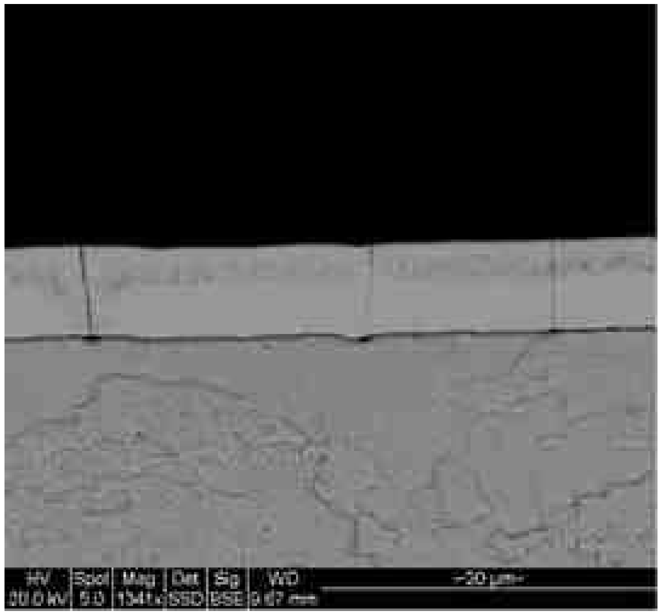

Figure 6 - Cross-section of duplex coating after 320°C heat treatment and 340 hr in neutral salt spray.

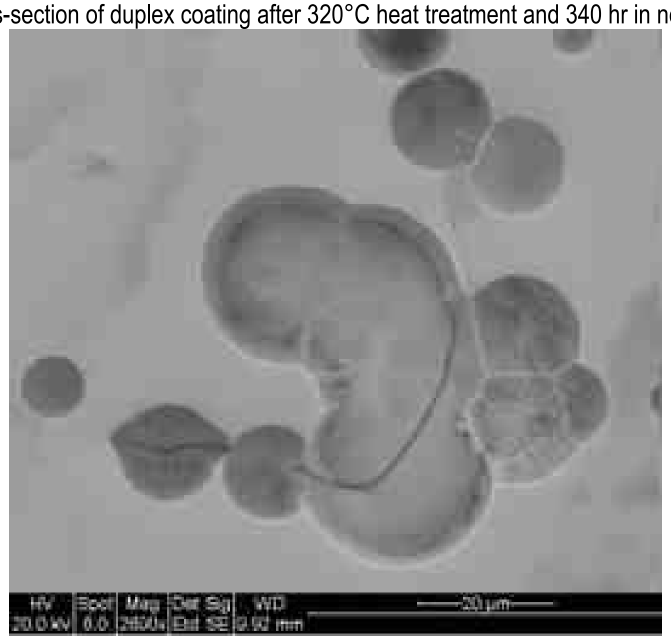

Figure 7 - Surface photo of duplex coating after 320°C heat treatment and 340 hr in neutral salt spray.

Appearance

The gloss of the single layer deposits are compared in Fig. 8. The appearance of the deposit brightness was measured and compared by gloss readings.[7] The gloss of the high-phosphorus and ternary alloy systems are in the 90-110 GU range. The low/mid-phosphorus and mid-phosphorus processes have gloss averages between 85-95 GU. The low-phosphorus system has the lowest gloss reading with 28 GU. The LP deposit is not considered “bright,” but semi-bright/matte. There are mid-phosphorus systems that are RoHS, ELV, WEEE-compliant that are considered ultra-bright (UBMP). These deposits have brightness readings near 160 GU, which is comparable to conventional mid-phosphorus systems that contain cadmium as the brightener. A difference of 10 GU in brightness is easily detectable with the human eye. The upper layer can supply a finish that ranges from very low gloss to ultra-bright, regardless of the lower layer gloss.

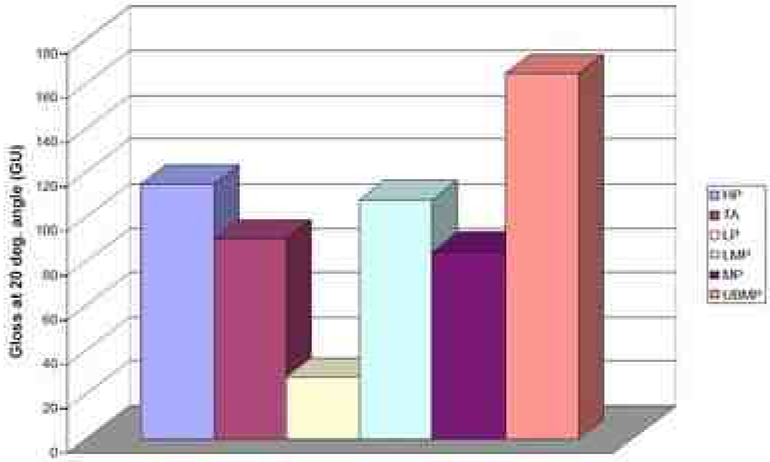

Figure 8 - Gloss of electroless nickel systems.

Delamination

Neutral salt spray testing is a fairly straightforward evaluation of the porosity of a deposit. In most instances, the deposit (of a single layer) will produce red rust spots that are quite easy to detect and count. The neutral salt spray testing for this project was run according to ASTM B117. Panels were left in the salt spray cabinet until red rust appeared. There was however a phenomenon that occurred before red rust appeared on the low-phosphorus systems and on some of the low/mid-phosphorus panels. The individual LP and LMP systems were not intended to survive nearly 900 hr in neutral salt spray. However the high-phosphorus and ternary alloy underneath the upper layer was designed to last a great deal longer in NSS. After just 96 hr in NSS, the low-phosphorus system started to create black spots on the panel. The low-phosphorus system proceeded to create larger black areas, but did not produce any red rust, indicating that the high-phosphorus layer was maintaining integrity. After approximately 900 hr, the panel finally had one red rust spot. By then, the low-phosphorus layer had corroded, had created a lot of black areas and had noticeable areas of upper layer material missing. Figure 9 is a photo of a duplex panel (LP+TA) as-plated, after 894 hr in neutral salt spray.

Figure 9 - Duplex panel of low-phosphorus upper layer and ternary alloy lower layer - as-plated after 894 hr in neutral salt spray.

Conclusion / Summary

Electroless nickel duplex layers offer a wide range of properties that can fit certain applications. The high-phosphorus EN and the ternary alloy both provide excellent corrosion resistance (*i.e.*, low porosity coating) as a lower layer. The upper layer gives a versatility to obtain a specific combination of desirable properties. A low-phosphorus coating can be used when high hardness and wear resistance are necessary. Even without heat treatment, the low-phosphorus coating has the highest hardness and wear resistance available when compared to heat-treated HP, TA, LMP and MP. The wear results show that having a high-phosphorus lower layer under the low-phosphorus system did not change the wear results. The low/mid-phosphorus electroless nickel can give better hardness and wear than a single high-phosphorus layer. The mid-phosphorus electroless nickel upper layer and HP or TA lower layer provided excellent corrosion resistance. The mid-phosphorus system, especially ultra-bright processes, can offer a very bright deposit, so that the duplex layer would have a combination of excellent corrosion resistance and a bright finish.

Heat-treating to obtain maximum hardness and wear can destroy the corrosion resistance of any coating (not just duplex coatings) due to shrinkage. Heat-treating at a lower temperature for a longer period of time can still provide a hard deposit (perhaps not optimum). The most important factor is to maintain the corrosion protection of the high-phosphorus layer. Further work would have to be done to each system to determine the exact heat treatment necessary to gain additional hardness and wear without sacrificing corrosion resistance. Also, allowing heat treated panels to cool in the oven with varying temperatures and times would have to be explored.

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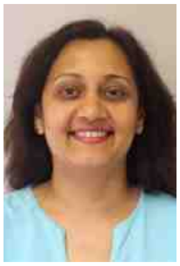

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