Electroless Nickel as a Preplate for Aluminum Alloy Wheels

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In this paper, we investigated the use of electroless nickel (EN) as a preplate on cast aluminum alloy wheels for subsequent electroplating. The structure and properties of the EN layers have been determined. The results show that, compared to electrodeposited nickel, the EN preplate exhibits better adhesion and corrosion resistance. Small-scale production tests on aluminum alloy wheels with 12- and 28-cm (4.7- and 11.0-in.) window depths indicate that the subsequent coatings on EN layers are more uniform and compact and impart improved corrosion resistance to the aluminum wheels.

With increased demand for automobiles having enhanced features such as light weight, safety, economy and multi-functions, aluminum alloys have become one of the best basis materials for the production of car wheels because of their low density, high strength, good thermal conductivity, workability and corrosion resistance. Ever since its introduction to the automobile industry in the late 1970s, aluminum alloy wheels have shown their advantages and taken considerable market share around the world. Recently, steel wheel hubs have been completely dominated by aluminum alloys.

The most common surface treatment method for aluminum wheels is spray painting. However, electroplated aluminum wheels have shown great popularity today because of their better decorative appearance and corrosion resistance. The demand for electroplated aluminum wheels has grown each year around world. In the United States, for example, only 400 to 500 thousand electroplated aluminum wheels were sold in 1992, but sales increased to more than four million in 1997, and to six million in 1999.

The primary plating processes used for aluminum wheel manufacturing around the world include several steps: (1) preplating with an electrodeposited nickel as a strike layer, (2) electroplating with copper, (3) then with tri-layered nickel and finally, (4) a nickel seal and chromium plate. Due to the complex shape of the wheel hub, and the resulting non-uniform current distribution encountered with the electroplating process, the thickness distribution of the nickel strike layer is not uniform and further treatments like polishing are usually required for the final product. Furthermore, the corrosion resistance and quality with a plated nickel strike are unsatisfactory. Therefore, further research and improvements are needed.[2] Because electroless nickel has been extensively studied and applied in industry for its uniform thickness and good corrosion resistance,[3-8] we investigated the use of electroless nickel as a strike layer for subsequent electroplating on aluminum wheels.

Experimental

Aluminum alloy composition

The alloys used were high-silicon aluminum alloys. Their composition and performance are shown in Table 1.

Pretreatment of aluminum alloy wheels

The main processes for pretreating aluminum alloys include ultrasonic cleaning, chemical cleaning, etching, zincate treatment, acid etching, a second zincate and electroless nickel. Prior to cleaning, polishing was done with sandpaper. The pretreatment solution composition and operating conditions are shown in Table 2.

Nuts & Bolts: What This Paper Means to You

Aluminum alloy wheels are a major market in automotive plating. In this paper, electroless Ni was compared to electrolytic Ni as a preplate on cast aluminum alloy wheels. Tests were extended to production samples with 12- and 28-cm (4.7- and 11.0-in.) window (recess) depths. Generally, the electroless Ni showed better adhesion and corrosion resistance.

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Table 1
Composition and Performance of the Aluminum Alloy

Composition, wt%				Hardness, H_B	% Elongation	Tensile Strength, MPa (lb/in.^{2})
Si	Mg	Impurities	Al			
≤ 7.5	0.25-0.60	≤ 1.0	Balance	≥ 60	≥ 1.0	≥ 200 (≥ 29,000)

Surface morphology and microstructure

The structure of the EN layer was analyzed by x-ray diffraction (XRD)**. The surface morphology was observed with an atomic force microscope (AFM)*** in contact mode. The substrates of the AFM samples were polished with sandpaper and polishing equipment prior to chemical cleaning. The electroless nickel composition was measured using an electron probe (EPMA)†. The chemical valence of the surface atoms was analyzed with by x-ray photoelectron spectroscopy††.

The coating adhesion was measured by hot vibration and scratch tests. Finally, the deposit thickness was measured using an electrolytic thickness-tester.

Corrosion performance

Corrosion resistance was evaluated by the Tafel, aluminon and CASS (copper-accelerated acetic acid salt spray) test methods. The Tafel study was conducted in 5 wt% NaCl solution. Oxygen was removed by nitrogen bubbling. The aluminon corrosion test paste was prepared using about 15 to 20 g (0.53 to 0.70 oz) TiO_2 and 5 mL (0.17 fl.oz) H_2O_2 (Specific gravity = 1.14 to 1.15) for each 10 mL (0.34 fl.oz) of 2% aluminon solution. The paste was uniformly applied to the surface of the aluminum alloy wheel. After 10 min, the corrosion rating could be directly evaluated according to the number of the colored points in the paste.[9] The CASS test was carried out in a salt-spray chamber under the following conditions: 50 ± 5 g/L (6.7 ± 0.7 oz/gal) NaCl; 0.26 ± 0.02 g/L $CuCl_2 \cdot H_2O$; pH 3.0-3.2; temperature, 50 ± 2°C (122 ± 3.6°F) and spray volume, 1.0 to 2.0 mL/L. All solutions were prepared from analytical reagents and doubly distilled water.

Results and discussion

Preplating treatment

Cast aluminum alloy is very easily oxidized in air. The natural oxide layer on the surface will affect the adhesion between the plated layer and the aluminum alloy substrate. The removal of the natural oxide layer and the subsequent formation of new layers to passivate the active surface are the key steps in the preplating process for electroless nickel. When aluminum alloys are directly immersed in the electroless nickel solution, because of the large potential difference between aluminum ($\varphi_{Al^{+3}/Al}$ = –1.662 V) and nickel ($\varphi_{Ni^{+2}/Ni}$ = –0.250 V), the displacement reaction between Al and Ni^{+2} will have a very strong tendency to occur. This will result in poor adhesion of the nickel to the aluminum alloy. In general, zinc, whose standard potential ($\varphi_{Zn^{+2}/Zn}$ = –0.763 V) is closer to that of aluminum than that of nickel, is used to form an underlayer via a zincating process. In general, most commercial zincating solutions are based on cyanide chemistry, posing environmental pollution considerations. However, non-cyanide processes do exist, including the one used in this study (Table 2).

** *Hitachi Natural D/max-γB x-ray diffractometer, Hitachi, Tokyo, Japan.*
*** *Digital Instruments Dimension 3100 Scanning Probe Microscope, Veeco Instruments, Freeport, NY.*
† *JEOL JCXA733 electron microprobe, JEOL USA, Inc., Peabody, MA.*
†† *VG ESCALAB MkII, VG Scientific, Thermo Electron Corp., Waltham, MA.*

Table 2
Pretreatment Solution Composition and Operating Conditions

Process	Solution Composition		Operating Temperature
Chemical Cleaner	Na_2CO_3	15-20 g/L (2.0-2.7 oz/gal)	65-75°C (149-167°F)
	$Na_3PO_4 \cdot 12H_2O$	15-20 g/L (2.0-2.7 oz/gal)	
Etchant	HNO_3	500-750 mL/L (64-96 fl.oz/gal)	15-30°C (59-86°F)
	NH_4HF_2	100-150 g/L (13.4-20.0 oz/gal)	
Zincate #1	ZnO	20 g/L (2.7 oz/gal)	15-30°C (59-86°F)
	NaOH	100 g/L (13.4 oz/gal)	
	$KNaC_4H_4O_6 \cdot 4H_2O$	10-80 g/L (1.3-10.7 oz/gal)	
	$FeCl_3 \cdot 6H_2O$	2 g/L (0.27 oz/gal)	
	$NiCl_2 \cdot 6H_2O$	1 g/L (0.13 oz/gal)	
Acid etchant	HNO_3	500 mL/L (64 fl.oz/gal	15-30°C (59-86°F)
Zincate #2	Same as Zincate #1		

Table 3 shows that both the commercial zincating solution and the solution we developed can greatly improve the adhesion and brightness of the electroless nickel. It has been found that the zincate layer can be dissolved during the electroless nickel process.[3,6,8] Once the electroless nickel layer starts to form on the alloy surface, auto-catalytic electroless deposition occurs. Thus the electroless Ni-P alloy plates directly on the active aluminum alloy surface with no oxide or zinc, and that improves the adhesion between the electroless nickel layer and the aluminum alloy.[8]

Electroless nickel

The facts that aluminum is an active metal and is easily etched in electroless nickel solution, pose the potential for a decrease in coating adhesion, even as severe as blistering or peeling. Moreover, the existence and accumulation of SO_4^{-2} and Cl^- ions can deteriorate the EN solution and reduce the diffusion rate of Ni^{+2} and $H_2PO_2^-$ ions, and thus diminish the deposition rate. At the same time, the accumulation of Cl^- causes increased tensile stress in the deposit, and further decreases the corrosion resistance.[10] Therefore, sulfate and chloride ions must be avoided in the electroless nickel solution.

The optimum solution composition and operating conditions for the electroless nickel used in our work are listed in Table 4.

Surface structure of the deposit

AFM analysis of the electroless nickel strike layer. AFM images of the electroless and electrodeposited nickel layers on polished aluminum substrates are shown in Fig. 1. The results reveal that the electroless nickel layers were finer-grained and more uniform than those of electrodeposited nickel. Within a 1 μm × 1 μm test area, the surface roughness (R_a) of the electroless nickel layer was 0.935 nm, close to the R_a of the substrate (0.915 nm), while the R_a of electrodeposited nickel was around 5.04. In terms of evaluation as a good primer layer for subsequent electrodeposition on aluminum alloy, the EN strike layers were uniform and smooth.

XRD and XPS analysis. Figure 2 shows the x-ray diffraction (XRD) pattern of the electroless nickel on cast aluminum alloy. An amorphous structure was dominant. By EPMA analysis, the phosphorus content was found to be 9.5 wt%.

Table 3
Results of Different Preplating Treatments

Preplate treatment	Results
Etch	Poor adhesion and appearance
Etch + Double Zincate (Table 1)	Good adhesion and appearance
Etch + Double Zincate (Commercial)	Good adhesion and appearance

In order to study the surface composition of the electroless nickel, x-ray photoelectron spectroscopy (XPS) was used. The nickel in the EN layer was in the form of Ni^{+2} and atomic Ni, while phosphorus was in the form of the negative ion and PO_4^{-3} [Figs. 3(a) and (b)]. However, when the EN plating layer was sputter-etched with Ar^+ for 60 and 240 sec [Figs. 3(c) and (d), respectively], the nickel was primarily in the form of atomic Ni, and the phosphorus was in the form of the negative ion. The results revealed that P and Ni have different chemical states on the EN surface compared to that of the bulk deposit. Flis[11] found that corrosion resistance can be improved by the enrichment of $Ni_3(PO_4)_2 \cdot 8H_2O$ on the electroless nickel surface.

Table 4
Solution Composition and Operating Conditions for Electroless Nickel

Ni^{+2} (as Ni carbonate)	5.0-5.5 g/L (0.67-0.73 oz/gal)
$NaH_2PO_2 \cdot H_2O$	25-30 g/L (3.3-4.0 oz/gal)
$C_3H_6O_3$	25 mL/L (3.2 fl.oz/gal)
$NaC_3H_5O_2$	15 g/L (2.0 oz/gal)
Stabilizer	As required
Temperature	88 ± 2°C (190 ± 3.6°F)
pH	4.3-4.9

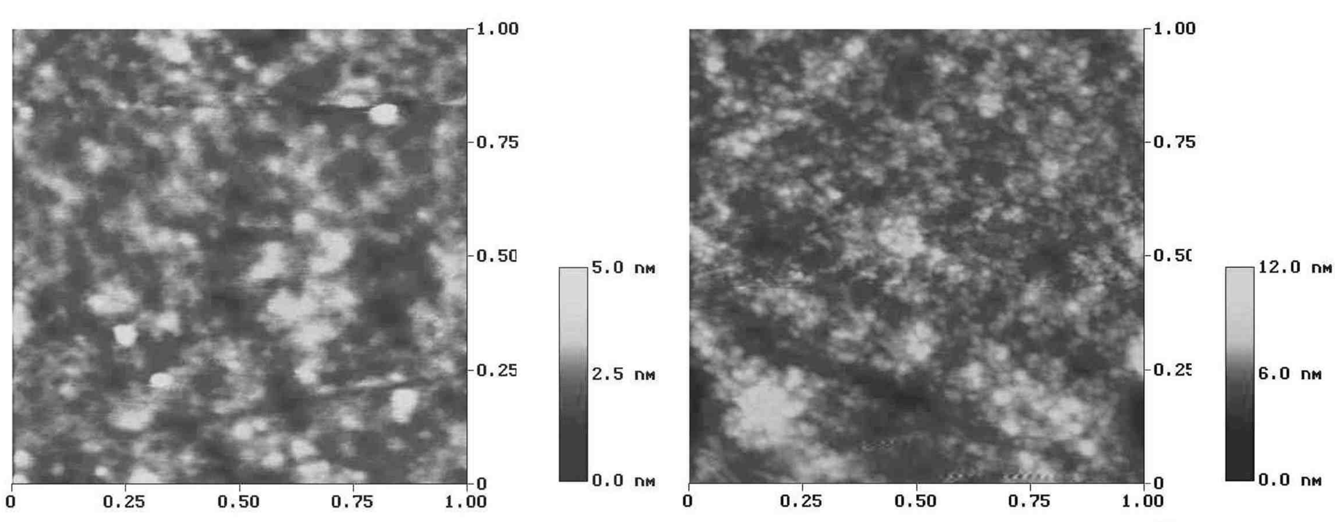

Figure 1—Atomic force microscope (AFM) image of the (left) electroless nickel layer and (right) electrolytic nickel layer on cast aluminum alloy.

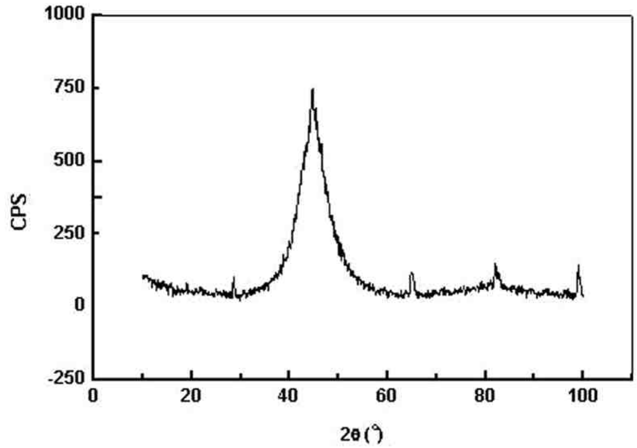

Figure 2—X-ray diffraction (XRD) pattern of the electroless nickel layer on cast aluminum alloy.

Corrosion resistance of the EN strike layer

Tafel curves. In 5 wt % NaCl solution, the corrosion potential, φ_{corr}, of the EN layer (20 μm; 0.8 mil) on the cast aluminum alloy was about 0.200V and its corrosion current was 1.85 μA/cm^2. The results show that the electroless nickel layer had good corrosion resistance in NaCl solution.

Aluminon corrosion test. Electroless nickel strike and electrodeposited nickel layers on cast aluminum alloy with varying thicknesses were prepared. Corrosive paste testing was then conducted on these samples. The results are listed in Table 5.

It was noted that the EN strike layers showed better corrosion resistance than the electrodeposited Ni layers at the same thickness. This might be related to the amorphous structure of EN layer, which had few defects and interfacial dislocations. Thus it was difficult to corrode. Another reason was that EN layer had a thin solid film of $Ni_3(PO_4)_2 \cdot 8H_2O$ on its surface.

Small-scale production

Uniformity of the preplating layers

The electroless nickel and electrodeposited nickel strike layers were each produced on 500 pieces of cast aluminum alloy wheel material with 12-cm (4.7-in.) window thickness. The window thickness is the inset, or depth of the recess in the wheel design, shown as *d* in Fig. 4. The same procedure was applied to wheels with a 28-cm (11.0-in.) window thickness. The results show that the surfaces of the cast aluminum alloy wheels with the 12-cm (4.7-in.) window thickness were fully covered by both the electroless and electroplated nickel deposits. However, the 3-μm (118 μ-in.) electroless nickel strike layer appeared bright, while the electrodeposit was dull in the low current density areas and further

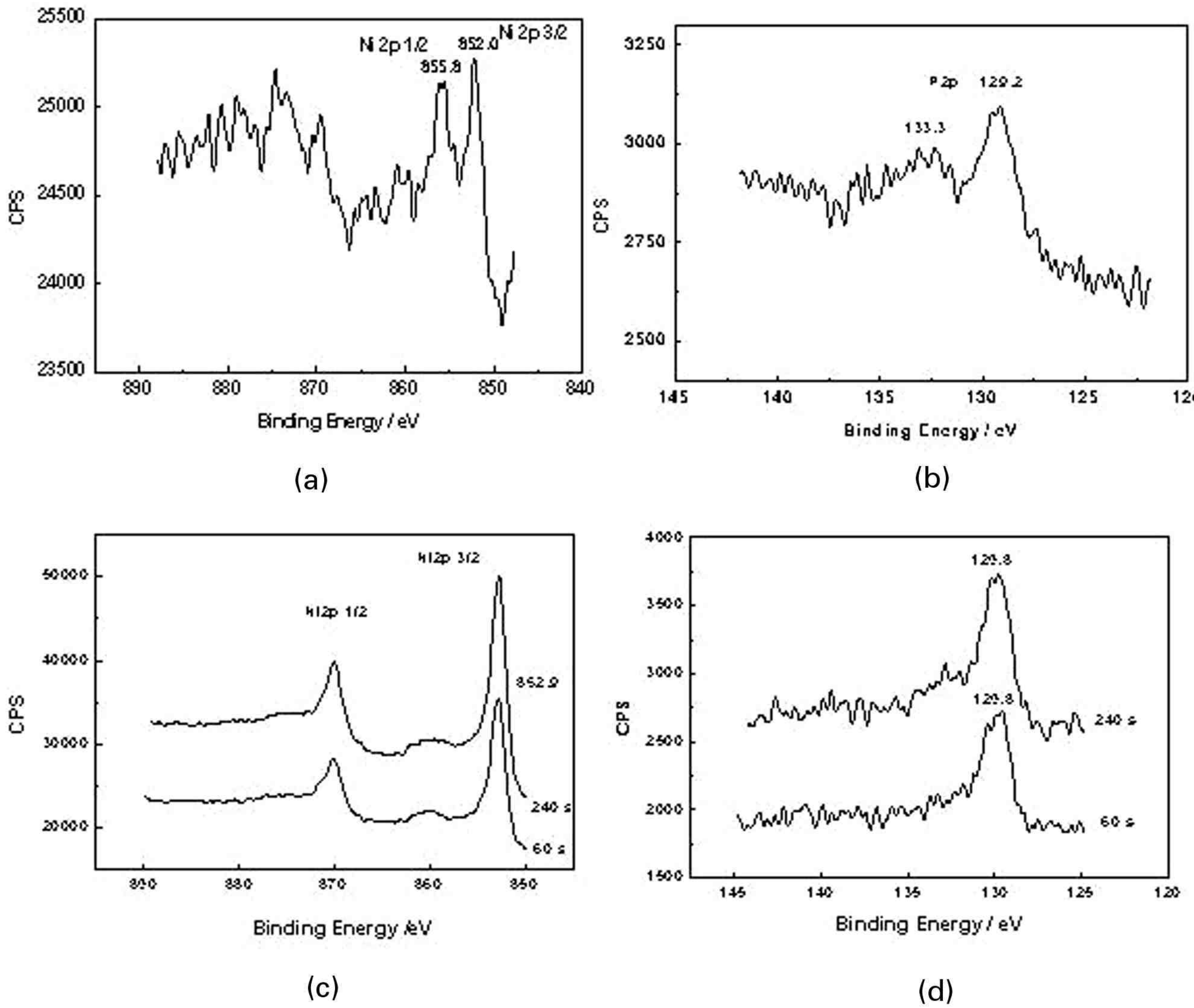

Figure 3—X-ray photoelectron spectroscopic (XPS) analysis of the electroless nickel layers: (a) Ni2p spectrum without etching; (b) P2p spectrum without etching; (c) Ni2p spectrum with different etching times and (d) P2p spectra with different etching times.

Table 5
Corrosion Rating of the Preplated Electroless Nickel Layers and Electrodeposited Nickel Strike Layer on Cast Aluminum Alloy Wheel Hubs

Preplate layer thickness	Corrosion Rating (0-10)	
	Electroless Ni Preplate	Electrolytic Ni Preplate
5.0-6.0 μm (197-236 μ-in.)	6 – 7	2 – 3
10.0-12.0 μm (394-472 μ-in.)	8 – 9	5

polishing was required. As for the cast aluminum alloy wheels with the 28-cm (11.0-in.) window thickness, the electroless nickel fully covered the surface, but the electroplated nickel did not do so.

Table 6 shows the thickness distribution of the cast aluminum alloy wheels with the 12-cm (4.7-in.) window thickness with different preplate technology and deposition times. The layer thickness on five different areas of the wheels were randomly tested and the results were averaged.

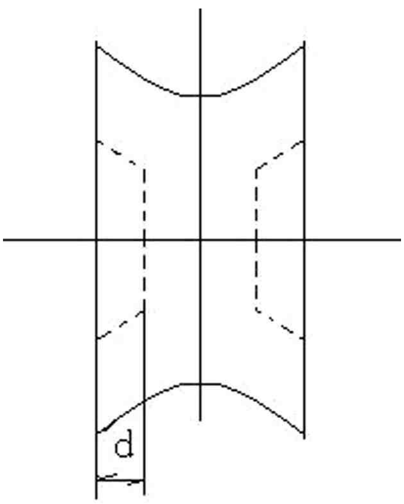

Figure 4—Schematic diagram of a wheel hub, showing the window thickness d.

The results indicate that the electroless nickel layer was more uniform than the electroplated nickel layer because the electroless nickel distribution was not influenced by the part geometry and resultant current distribution. However, the electrodeposited nickel layer had varying thickness in different areas because of the non-uniform current distribution. The difference between the maximum and minimum thickness was more than 20 μm (0.8 mil). Thus, the non-uniform thickness distribution with the electrodeposition nickel can explain the poor corrosion resistance.

Acceptable quality level and corrosion resistance of electroplated aluminum wheels

The aluminum alloy wheels preplated with electroless or electrodeposited nickel were subsequently plated with acid copper, tri-nickel, nickel-seal and bright chromium. The acceptable quality level and anti-corrosion performance of the plated articles are listed in Table 7. The EN layer clearly improved the acceptable quality level, and the finished workpiece passed the 44-hr CASS test. However, the finished workpiece given an electrodeposited nickel strike only passed the 22-hr CASS test.

Conclusions

1) When compared to an electrodeposited nickel strike, an electroless nickel preplate can remarkably improve the acceptable quality level and enhance the corrosion resistance of plated aluminum alloy wheels.

Table 6
Thickness Distribution on Cast Aluminum Alloy Wheel Hubs with 12 cm Window Thickness with Different Preplates and Coating Times

Preplate Layer	Coating Time (min)	Maximum Thickness	Minimum Thickness
Electroless Ni	20	6.5 μm (256 μ-in.)	6.3 μm (248 μ-in.)
Electrolytic Ni	40	26.3 μm (1040 μ-in.)	3.5 μm (138 μ-in.)

Table 7
Eligibility and Corrosion Resistance of Aluminum Alloy Wheel Hubs with Different Preplates

Window Thickness	Electroless Ni Preplate		Electrolytic Ni Preplate	
	Eligibility	CASS Results	Eligibility	CASS Results
12 cm (4.7 in.)	95%	> 44 hr	75%	22 hr
28 cm (11.0 in.)	93%	> 44 hr	0%	—

2) The electroless nickel preplate is a more suitable primer layer for aluminum alloy wheels with large window depths.
3) The CASS test results show that the electroplated aluminum alloy wheels preplated with an electroless nickel layer can pass the 44-hr CASS test.

The electroless nickel technology we describe here provides extended product life and quality. We also recognize that there is a cost premium associated with electroless nickel. However, the benefits may well be worth the added expense to the customer.

References

1. S.M. Zeng. *Chinese J. Nonferrous Metals*, **7** (1), 65 (1997).
2. S.J. Yu, G.J. Shao & J.K. Yu, *Electroplating & Finishing*, **17** (2), 52 (1998).
3. S. Armyanov. *Metal Finishing*, **79**, 36 (July 1992).
4. K. P. Thurlow. *Trans. IMF,* **67**, 82 (1989).
5. G. Qi , L.G.J. Fokkink & K.H. Chew., *Thin Solid Films*, **406**, 219 (2002).
6. S. Armyanov, O. Steenhaut & N. Krasteva, *J. Electrochem. Soc*., **143**, 3692 (1996).
7. E. Valova, S. Armyanov & J-L. Delplancke, *J. Electrochem. Soc*., **143**, 2804 (1996).
8. D. Baudrand, *Proc. Electroless Nickel '97 Conference*, Gardner Publications, Cincinnati, Oh, 1997; p. 14-1.
9. N Y Shen, *et al*., *Surface Treatment Technology Manual*, Shanghai Science and Technology Press, Shanghai, China, 1997; p. 410.
10. K. Parker. *Plating & Surface Finishing*, **74**, 60 (February 1987).
11. J. Flis & D.J. Duquette, *Corrosion*, **41**, 700 (1985).

Micro-roughening of Epoxy and Cyanate Ester Laminates as a Precursor to Electroless Plating

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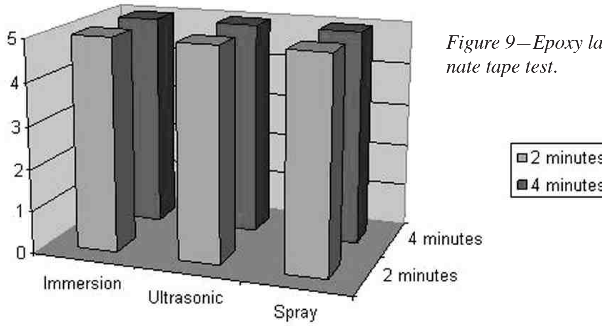

Figure 9—Epoxy laminate tape test.

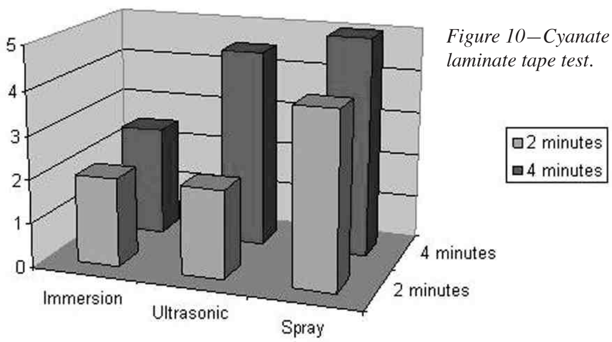

Figure 10—Cyanate laminate tape test.

The process for each system still needs to be optimized for metal film adhesion strength. The tape test indicates that plated film has adhesion strength of at least 1.4 MPa (200 lb/in.^{2}). A quantitative method to measure the exact adhesion strength of the film should be explored. In addition to optimizing the etching process, the laminate systems that were investigated could be improved to promote better micro-roughening conditions. A carbon fiber fabric, instead of a tape could be used to provide an initial surface that is more susceptible to micro-roughening. In addition, the resin content of the laminate could be increased to provide more bulk material to etch with out exposing fibers.

Acknowledgements

The author would like to thank Space Systems Loral for funding this research and fabricating the resin and laminate samples.

References

1. R. Parkinson, *Plating & Surface Finishing*, **81**, 32 (Sept. 1994).
2. N. Simpkins, *Electronic Manufacturing*, **35** (13), 32 (1989).
3. C.E. Thorn & M.K. Walsh, *Printed Circuit Fabrication*, **10**, 30 (1991).
4. C. Deckert, *Plating & Surface Finishing*, **82**, 48 (February 1995); **82**, 58 (March 1995).
5. A.S. Kao, H.G. Stenger, C. Georgakis, K. L. Covert, *J. Electrochem. Soc*., **139**, 2202 (1992).
6. H. Xu, Masters Thesis, San Jose State University, San Jose, CA, 1999.

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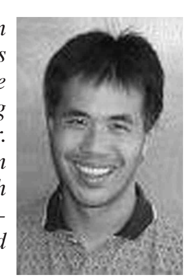

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