# The Effect of Non-Nitric and Non-Cyanide Pretreatment On the Corrosion Resistance of Electroless Nickel on Aluminum Alloys

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#### Abstract:

Currently, the most common pretreatment processes for aluminum alloys utilize nitric acid and cyanide-based chemistries to produce a zincate surface compatible with electroplating. There has always been some concern over the risk associated with improper use of nitric acid or cyanide in these processes. This has lead to the recent development of pretreatment cycles based on less hazardous chemicals. This paper discusses these new processes and compares them to the more accepted cycles. The discussion will include a comparison of operating parameters of the cycles, resultant zincate morphology, and a direct comparison of resultant properties after EN deposition. In addition the corrosion resistance of various electroless nickel deposits using the new pretreatment chemistries will be compared to such using conventional pretreatment cycles.

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## Introduction:

Plating aluminum has been around for many years and the processes used to make electroplated and electroless plated coating on aluminum are well know. Currently the process cycle to plate aluminum encompasses using hazardous and toxic chemicals like cyanide and nitric acid. While these processes work there is an inherent risk associated with using hazardous and toxic chemicals.

The same basic pretreatment steps are needed to process aluminum in the less hazardous chemicals as in the hazardous cycle. This pretreatment consists of a soak cleaner, acid or alkaline etch, desmut, zincate, zincate strip, zincate and electroless nickel strip.

The soak cleaner is used to remove an assortment of contamination that would affect subsequent processing steps. These contaminants could be, but not limited to, cutting fluids, stamping fluids, other oils, greases buffing compounds and general shop dirt.

Having an effective soak cleaner makes the next processing step, typically etching, more uniform. A contaminated surface would produce a non-uniform etch that would effect the subsequent cycles and ultimately the plated deposit.

There are two types of etch, acid and alkaline, and both work the same. That is to remove the natural aluminum oxide, Al<sub>2</sub>O<sub>3</sub>, on the surface of the part. The removal of Al<sub>2</sub>O<sub>3</sub> is critical for proper zincating and ultimately good adhesion of the electro or electroless plate. Figure 1 shows a Pourbaix diagram of aluminum and water. This diagram shows the regions where aluminum is active, corroding, and passive, not corroding. From this region there is a wide operating window on the types of chemistries that will attack aluminum. Typical chemistries are either very acid, pH less than 1, or very alkaline, pH greater than 12. Figure 2 shows the open circuit potential of the acid etch versus the alkaline etch. From this graph the open circuit potential (OCP) of the alkaline etch is approximately twice as high as the acid etch. The high potential of the alkaline etch indicates a higher dissolution rate of aluminum and measuring the corrosion current of the alkaline and acid etch ones does see a higher etch rate with the alkaline etch. The corrosion current for the alkaline and acid etch was measured using linear polarization technique. In linear polarization a controlled-potential scan, typically  $\pm 20$  vs. the corrosion potential or E <sub>corr</sub>. The resulting current is linearly plotted versus the potential. The slope of this potential-current function at E corr is referred to as the polarization resistance (Rp) and is used with the Tafel constants to determine the corrosion current (I corr). For the alkaline etch the corrosion current was measured at 3.7 mA/cm<sup>2</sup> and for the acid etch the corrosion current is 0.73 mA/cm<sup>2</sup>. This work shows that the alkaline etch rate is five time more than the acid etch.

The etching solution leaves the surface covered with "smut" and since the alkaline etch is more aggressive than the acid etch the "smut" is greater using the alkaline etch. This smut has to be removed so the zincating step will form a uniform zincate on the surface. Typical desmutting solutions are based on nitric acid to dissolve the smut left from etching the substrate. This smut is typically made-up of alloying metals in the aluminum left after etching the aluminum. The typical smut composition is copper, magnesium, iron and silicon from cast alloys. The most common formula for desmutting aluminum is shown in Table 1. This formula is used because

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many job shops do not know what alloy they use and the above formula is universal in desmutting the most common wrought and cast alloys. Figure 3 shows the OCP of two new desmutting solutions as they compare to the solution in Table 1. The OCP measures the oxidizing power of the solution and from this graph the nitric acid and desmutter 1 have about the same oxidizing power. Desmutter 2 based on US patent 6,407,047 has some oxidizing power but not as much as desmutter 1 or nitric acid. The higher the oxidizing potential, the greater the potential to dissolve the undissovled material left on the surface of the aluminum.

The next step in processing the aluminum is the zincating. The zincating or immersion plate onto aluminum has been around for many years. <sup>1,2,3</sup> The basis of this process is the dissolution of aluminum in a alkaline zincate solution with the deposition of zinc onto the aluminum surface.

In this work four (4) zincates were evaluated. One zincate is a four metal zincate based on cyanide and the other zincates were two metal, three metal and four metal non-cyanide zincates. Since all the zincates in this experiment are based on caustic there is a slight attack of the aluminum by the zincate. Figure 5 shows the OCP of the various zincates. From this information the cyanide and the two (2) metal zincate has the highest potential and the three and four metal zincate has a slightly lower potential than the other zincate. This is probably due the difference in caustic and complexor concentration.

With three different variables an experimental design was set up to evaluate the affect of the different pretreatment steps on the corrosion resistance of the electroless nickel. Table 2 shows the design matrix. Since we are comparing different processes the design matrix is set up as a categorical design. The design matrix is set up as a 2x4x2 design. That is two factors for the etch, acid and alkaline. Also four factors for the zincate, two (2) metal, three (3) metal, four (4) metal non-cyanide and four (4) metal cyanide. The final design factor is the desmut, which are two factors, nitric and non-nitric. From this matrix a total of 16 experiments were run and five (5) panels were plated and tested by neutral salt spray according to ASTM B-117. Table 3 shows the percent contribution of the various factors and the percent contribution of the various interaction. From this one can glean that the main contribution is from the interaction of the etch, zincate and desmut. The next largest contributor is the interaction between etch and zincate. The only factor that had a significant contribution is the zincate. Figure 5 and 6 show the hours of salt spray of the various zincates with the alkaline and acid etch respectively. With the alkaline etch the corrosion of the panels with the non-nitric desmut is less than using the nitric desmut except for the cyanide containing zincate. Whereas the opposite is true with the cyanide zincate and nitric desmut this had a lower corrosion resistance than one would expect but the other panels processed in the nitric desmut had better corrosion resistance than the ones processed in the nonnitric desmut. Figure 6 shows the corrosion resistances of the panels processed with the acid etch. This cycle shows a higher corrosion resistance than using the alkaline etches cycle. From this, depending on the zincate, the corrosion resistance of the deposit using either the 4 metal cyanide zincate or the 4 metal non-cyanide zincate the corrosion resistance is equivalent in this test. In addition the two metal zincate performed well with either desmut with the acid etch.

The probable reason why the acid etch has higher average corrosion resistance with all the zincates than the alkaline etch is the type of etch. The alkaline etch is more aggressive than the

acid etch. Figure 7 and 8 show SEM images of the surface of the aluminum after etching from an alkaline and acid etches respectively. From this the surface of the alkaline etch shows a deeper etch on the surface as compared to the acid etch. This deeper etch opens up more pores and also attacks the grain boundary more. With this excess etch the plating needs to be thicker to protect the surface from corrosion. The acid etch on the other hand does not attack the aluminum surface as much as the alkaline etch therefore the electro/electroless coating does not have significant voids on the surface to plate over. This smoother surface therefore has a more pore free electroless nickel deposit and as a result better corrosion resistance.

Looking at the initiation on the surface with one (1) minute of electroless nickel a trend appears that shows that the electroless nickel initiates faster on the surface of the aluminum processed in the acid etch and non-nitric desmut, figure 9 shows the results.

## Conclusion

Environmentally safe material should not mean sacrificing quality or cost. Environmentally safe should mean using the best available technology to produce the best product with minimal waste and minimal use of hazardous material. When using the proper pretreatment cycle without cyanide or nitric acid corrosion resistance of the electroless nickel deposit is similar to those processed in the nitric acid and cyanide chemistry. This shows that using environmentally safe alternatives to nitric acid desmuts and cyanide zincates comparable corrosion resistance can be obtained while using non-hazardous and non-toxic material.

### **Bibliography**

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Figure 1. Potential-pH equilibrium diagram for aluminum-water at 25°C



Figure 2. Open circuit potential of various etches.

Material	Amount
Nitric Acid 70%	50% by volume
Sulfuric Acid 98%	25% by volume
Water	12.5% by volume
Hydrofluoric Acid 48%	12.5 % by volume

Table 1. Composition of desmutting solution.



Figure 3. Open circuit potential of various desmuts.



Figure 4. Open circuit potential of various zincates

Etch	Zincate	Desmut
alkaline	2 metal	nitric
alkaline	4 metal CN	nf
acid	4 metal CN	nf
alkaline	4 metal NC	nitric
acid	2 metal	nitric
acid	2 metal	nf
alkaline	4 metal NC	nf
acid	4 metal NC	nf
acid	3 metal	nf
acid	4 metal NC	nitric
alkaline	2 metal	nf
alkaline	3 metal	nitric
acid	3 metal	nitric
acid	4 metal CN	nitric
alkaline	3 metal	nf
alkaline	4 metal CN	nitric

Table 2. Experimental design matrix

Term	DOF	SumSqr	% Contribtn
Α	1	576	2.439
В	3	5184	21.951
С	1	1296	5.488
AB	3	7488	31.707
AC	1	144	0.610
BC	3	432	1.829
ABC	3	8496	35.976

Table 3. %Contribution of terms to the model.



Figure 5. Interaction graph of desmut and zincate versus hours of salt spray alkaline etch.



Figure 6. Interaction graph of desmut and zincate versus hours of salt spray acid etch.



Figure 7. Surface photograph of alkaline etched surface 10,000X.



Figure 8. Surface photograph of acid etched surface.



Figure 9. Initiation of electroless nickel on aluminum with various desmuts.