A new pretreatment cycle for Plating Magnesium Alloys.

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Abstract

There are two ways to process magnesium for electroplating, zincate and alkaline copper plate and fluoride activation and electroless nickel plate. This paper will discuss a new pretreatment that is hexavalent chromium free pretreatment and also an ELV compliant electroless nickel process.

The electroless nickel pretreatment cycle for magnesium was first developed in the late 1950's and early 1960's and is typically referred to as the Dow® process. The Dow® process characteristically consisted of hexavalent chromium/nitric acid etch and a hydrofluoric acid activation step before direct electroless nickel plating could commence. The new pretreatment cycle is hexavalent chromium and hydrofluoric acid free. This pretreatment cycle consists of an alkaline etch used in conjunction with an acid fluoride activation.

This paper is going to discuss the differences between the old chromic acid etch as compared to the new alkaline etch. In addition this paper will also discuss the differences between the non-ELV electroless nickel process as compared to the new ELV compliant electroless nickel. We will show that the non-chromic acid etch is a significant improvement over the standard chromic/nitric acid etch in both corrosion resistance and adhesion.

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Introduction

End of Life Vehicles (ELV) should not only mean the elimination or reduction of hazardous material, Cd, Hg, Pb and Cr (VI), in the final coating but in the use of these chemicals in the processing of the parts. The standard practice to process magnesium castings before electroless nickel plating was using hexavalent chromium etch to remove oxide off the surface and to roughen the surface for subsequent electroless nickel deposition. This etching does two things, cleans the surface of oxides plus micro roughens the surface for the electroless nickel to anchor onto the surface.

Recently there is more work being done on direct plating of magnesium alloys with electroless nickel [1,2]. The original work was done in the late 1950's to early 1960's. [3] From these works you will find the classical electroless nickel formula of nickel carbonate, citric acid and fluoride. What are missing from this formula are the stabilizer and accelerator that are formulated in today's electroless nickel chemistry. The new ELV electroless nickel described in this paper is only stabilized with organic compounds and does not use any metal stabilizers.

What is the most important process step, I feel, is the etch. Proper etching of the surface will ensure excellent adhesion of the electroless nickel. In addition, the etch provides an excellent surface for the activation to take place on. With the new alkaline etch you do not have to worry about the contamination of the activator or electroless nickel with hexavalent chromium. Also the etch rate of the alkaline etch is less than that of the standard chromic/nitric acid etch. This makes this process more adaptable for an automatic line. The typical time in the chromic/nitric acid etch was between 30-60 seconds whereas the alkaline etch is between 2-4 minutes.

The electroless nickel used in this process is designed more as a pretreatment step for further processing and not for extended corrosion protection. The operating parameters of the special electroless nickel for plating on magnesium limits the phosphorus content of the deposit and therefore limits the corrosion protection from the electroless nickel. The typical phosphorus content from this electroless nickel solution ranges from 3-7% by weight. With the proper design of other electroplated or electroless plated coatings one can obtain 100's of hours of salt spray on good quality castings.

Magnesium is the eighth most abundant element in the earth's crust and the third most abundant element in seawater. In addition, magnesium is the world's most readily available metal. The ocean is an enormous reservoir of magnesium, whereas other engineering metals face the eventual exhaustion of their most economical ore bodies or political instability where they are mined may limit their supply. Therefore, it may be expected that magnesium could become increasingly more important in the future as costs of production of other structural metals increases.

Processing Magnesium

The usual steps of cleaning, chemical treatment, anodizing, electroplating and painting, finish magnesium parts. As with other metals, cleaning is a very important step in the surface treatment of magnesium, since the effectiveness of subsequent coating processes depends to a marked extent upon removal of all surface contamination. Most magnesium alloys, unlike aluminum or zinc, are unaffected by strong alkaline cleaners. Most high alkaline steel cleaners will work on cleaning magnesium alloys whereas the low alkaline aluminum cleaners would not be recommended. Figure 1 shows the potential-pH plot of magnesium in water. This diagram shows that with a pH of less than 9 the protective hydroxide layer is unstable and the magnesium is attacked. With high pH the magnesium hydroxide film, Mg $(OH)_2$, on the surface prevents attack.

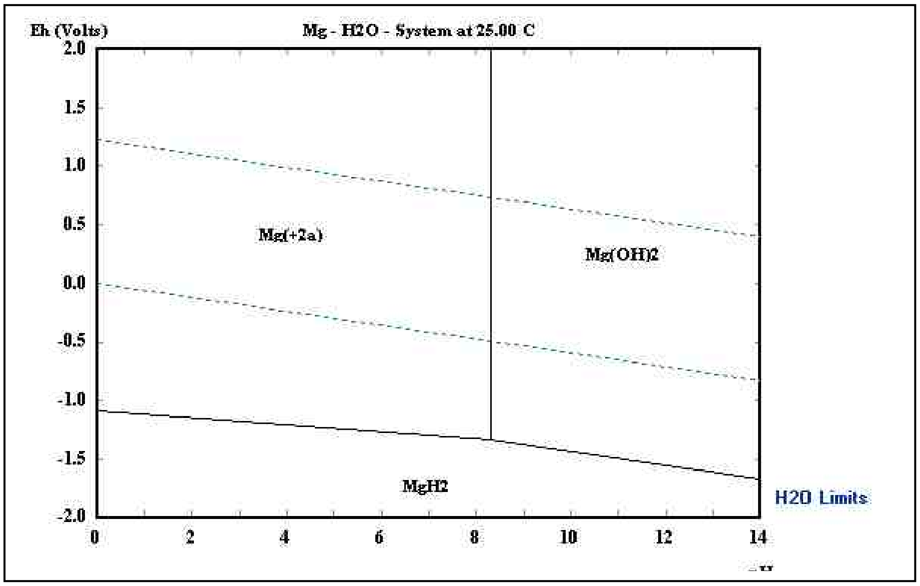

Figure 1- Potential-pH diagram of Mg in water

After cleaning, the parts are etched or pickled in a chromic/nitric acid solution to remove any oxide layer or certain chemical coatings not fully removed by alkaline cleaning. In this work we are going to compare the chromic/nitric acid etch to the new alkaline etch. The main difference between the two etches, besides pH, is the time needed to etch the surface. The chromic/nitric etch removes ≈10times more material than the alkaline etch. For the chrome etch a three level four factor design was used to evaluate the amount of material removed from a 2 in^2 magnesium coupon. Table 1 shows the design matrix. From this work the main factor that effects etch rate was time and nitric concentration. In addition there was one main interaction between time and nitric acid. Table 2 shows the ANOVA of the design. Figure 2 shows the effect of the main factors on etch rate in the chrome/nitric acid etch.

Evaluating the alkaline etch only a two level two factor design was used, Table 3, shows the design. From this work additive A had the largest effect on the etch rate. The time was held constant on this work and also the temperature. The standard time for the alkaline etch is three minutes and the temperature is in the range of 65-75°C (150-167°F). Figure 3 shows the results of the alkaline etch. This work shows that the chrome/nitric etch is more aggressive than the alkaline etch with about 10 times the removal rate. Measuring the rates by linear polarization the chrome/nitric etch is about four (4) times higher than the alkaline etch. Table 4 shows the results.

The main effect that we are looking for is what the surface looks like after etching. Figures 4 and 5 shows the surface of etched panels in the chrome/nitric and new alkaline etch respectively. This work shows that the alkaline etch produced an excellent micro roughed topography for further processing. The chrome/nitric etch also produces a micro roughed topography but also traps some solution that will get carried over to the activate solution and to the electroless nickel solution. The alkaline etch solution will also get carried over but will be neutralized in the activator solution plus this material in not as detrimental as hexavalent chromium to the electroless nickel solution.

Table 1. Chromium/Nitric Acid Etch matrix.

Factor	Name	Units	Low Actual	High Actual
A	Time	seconds	20	120
B	Temp	°F	68	77
C	CrO3	g/L	125	175
D	E	%Vol	8	12

Table 2. ANOVA for the Chromium/Nitric Etch

ANOVA for Response Surface Reduced 2FI Model
Analysis of variance table [Partial sum of squares - Type III]

	Sum of		**Mean**	**F**	**p-value**
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**
Model	0.024	8	3.02E-03	22.14	< 0.0001
A-Time	*0.017*	*1*	*0.017*	*121.26*	*< 0.0001*
B-Temp	*1.01E-03*	*1*	*1.01E-03*	*7.39*	*0.0159*
C-CrO3	*1.01E-03*	*1*	*1.01E-03*	*7.42*	*0.0157*
D-% D	*8.40E-03*	*1*	*8.40E-03*	*61.67*	*< 0.0001*
AB	*4.88E-04*	*1*	*4.88E-04*	*3.58*	*0.0779*
AC	*4.85E-04*	*1*	*4.85E-04*	*3.56*	*0.0788*
AD	*4.36E-03*	*1*	*4.36E-03*	*32*	*< 0.0001*
CD	*5.37E-04*	*1*	*5.37E-04*	*3.94*	*0.0657*
Residual	2.04E-03	15	1.36E-04		
Lack of Fit	*1.65E-03*	*11*	*1.50E-04*	*1.52*	*0.3673*
Pure Error	*3.95E-04*	*4*	*9.89E-05*		

Table 3. Alkaline etch design matrix.

Factor	Name	Units	Type	Low Coded	High Coded
A	Additive A	g/L	Numeric	-1	1
B	Additive B	g/L	Numeric	-1	1

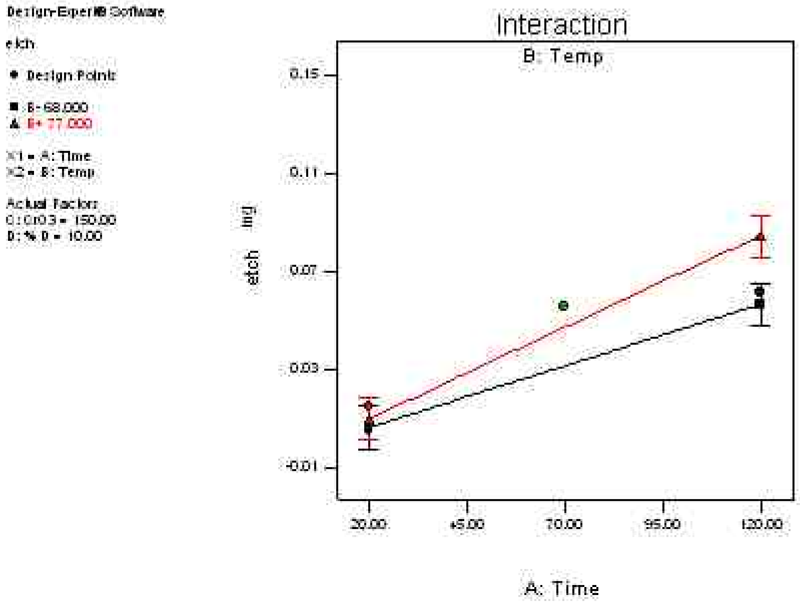

Figure 2. Chrome/nitric acid etch results.

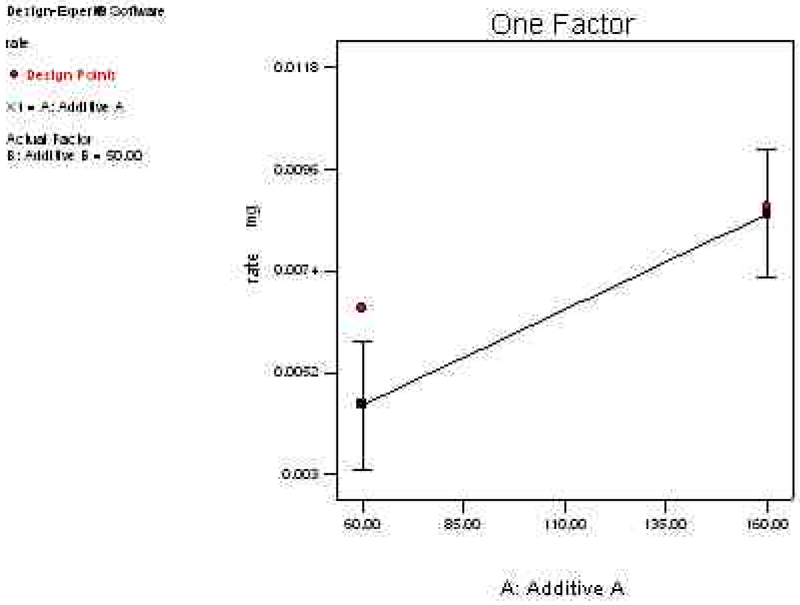

Figure 3. Alkaline etch results.

Table 4. Linear Polarization measurements of etch.

Etch	E(I=0) (mV):	Icorr (µA):	Co. Rate(mpy)
Chrome/nitric	-782.236	6.97E+03	5.98E+03
Alkaline	-1502.11	1.94E+03	1.58E+03

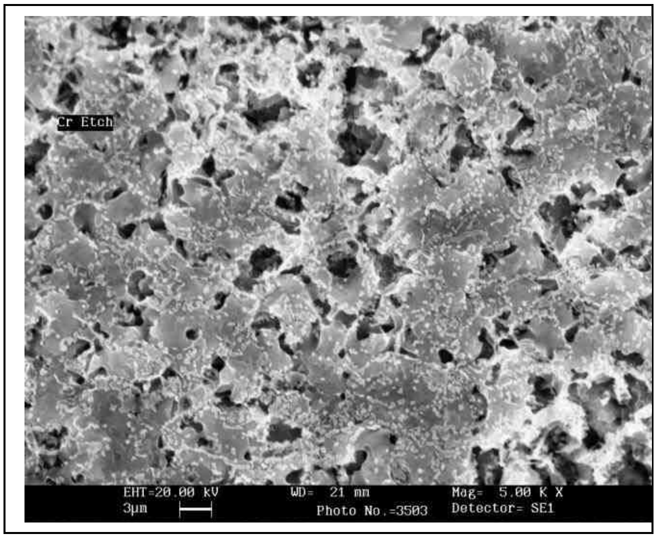

Figure 4. Chrome/Nitric Etch 5000X

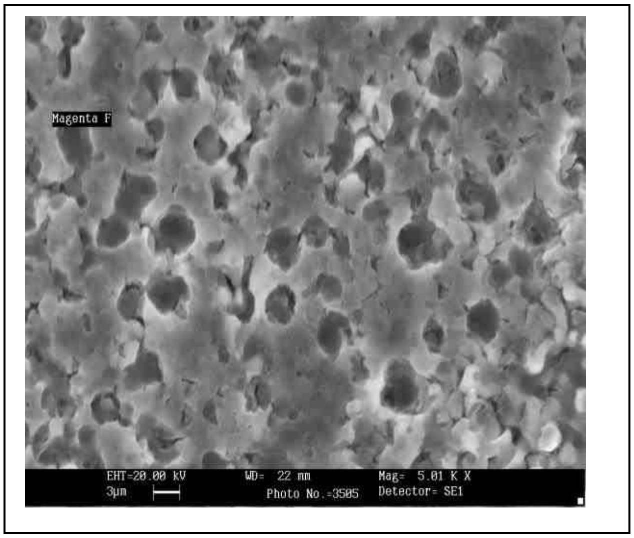

Figure 5. Alkaline etch 5000X

The next step is to form a chemical film or displacement film, on the surface of the magnesium. In this process of directly plating EN on magnesium, magnesium fluoride, MgF_2, is formed on the surface. Displacement films are used to protect the surface of active metals that will form oxide films on which plated metals would not adhere. Aluminum, beryllium and magnesium are good examples where use of a displacement film prior to electrodeposition will provide superior adherence of the electrodeposited metal. A zinc displacement film works well on all these metals; in addition, stannates work on aluminum and fluoride chemical film works on magnesium as a pretreatment for electrolytic or electroless plating.

Looking at the thermodynamics of the formation of magnesium fluoride on magnesium, Figure 6, we see that MgF_2 is formed over a wide pH range. The pH range is from 0-13. Only in very high alkaline solutions, with fluoride present, you will not form the MgF_2 on the surface. The thickness of the MgF_2, Figure 7, is approximately 4.6µm (0.18 mils) which is about 20 times thicker than an alloy zincate on aluminum.[4]

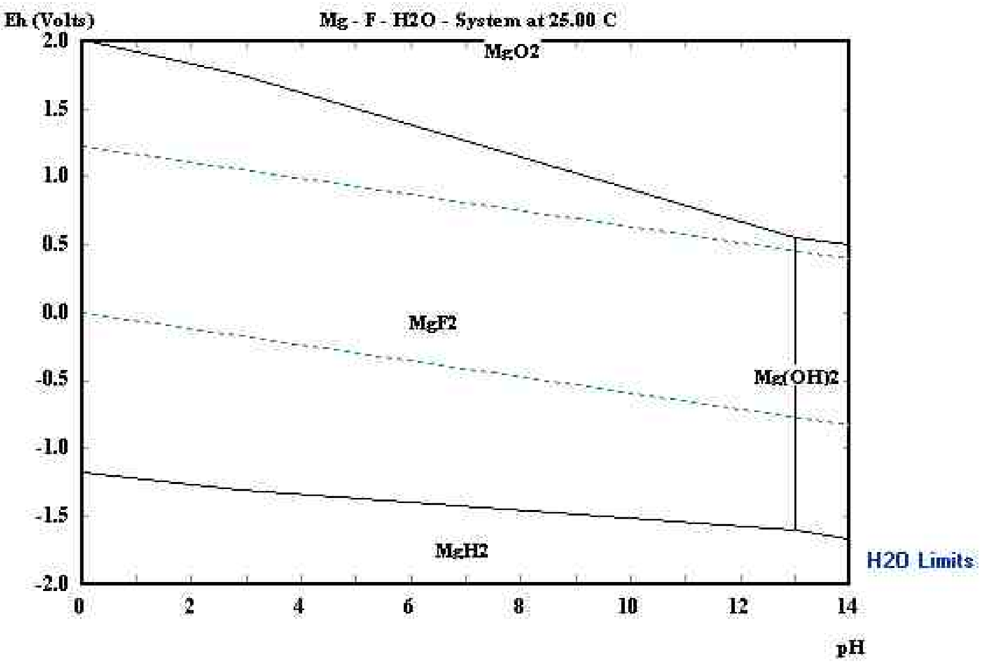

Figure 6. Potential – pH Diagram of Mg-F-H_2O system.

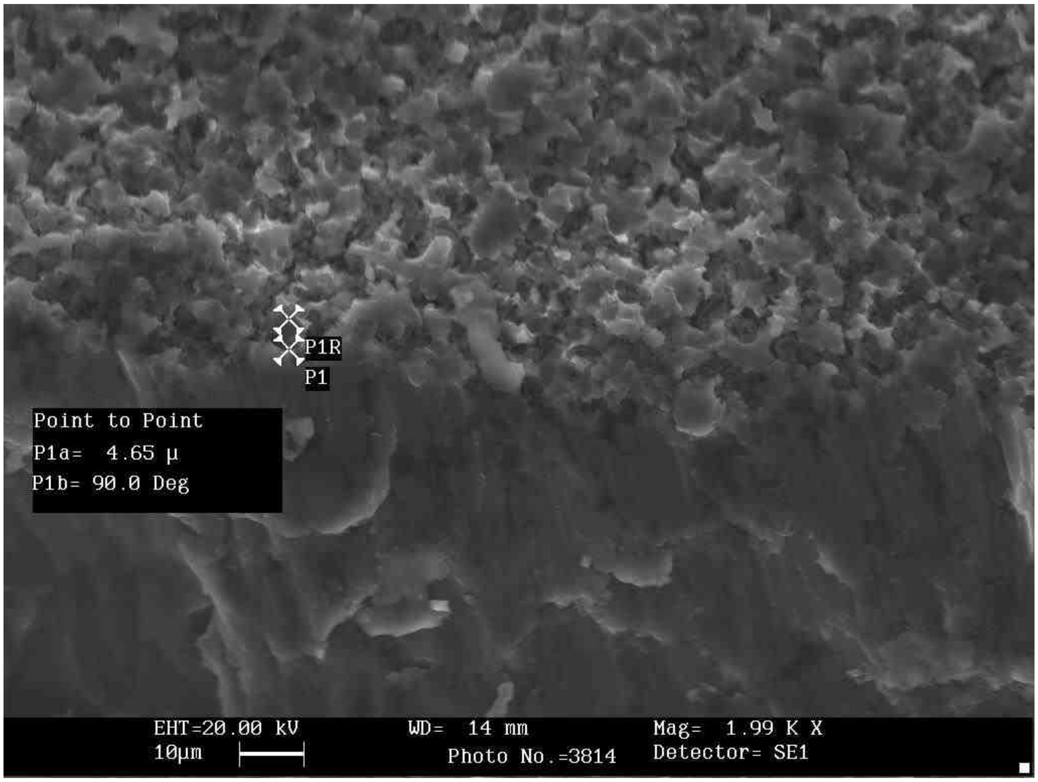

Figure 7. Cryofracture of Magnesium panel with MgF_2 on the surface 2000X

After the formation of the displacement coating on the magnesium alloy, in this case MgF_2, the part is ready for further processing. The next step is electroless nickel plating onto the magnesium substrate. A special electroless nickel solution is needed to process magnesium. This electroless nickel solution needs fluoride present to inhibit the dissolution of the magnesium so the electroless nickel can plate onto the surface of the magnesium. Figure 8 shows the open circuit potential (OCP) of a magnesium AZ-91D panel in an electroless nickel solution with and without fluoride. From this we can see that with the addition of fluoride the OCP of magnesium is lowered by 0.15 V. This lowering plus the addition of fluoride inhibits the formation of magnesium hydride (MgH_2), Figure 6.

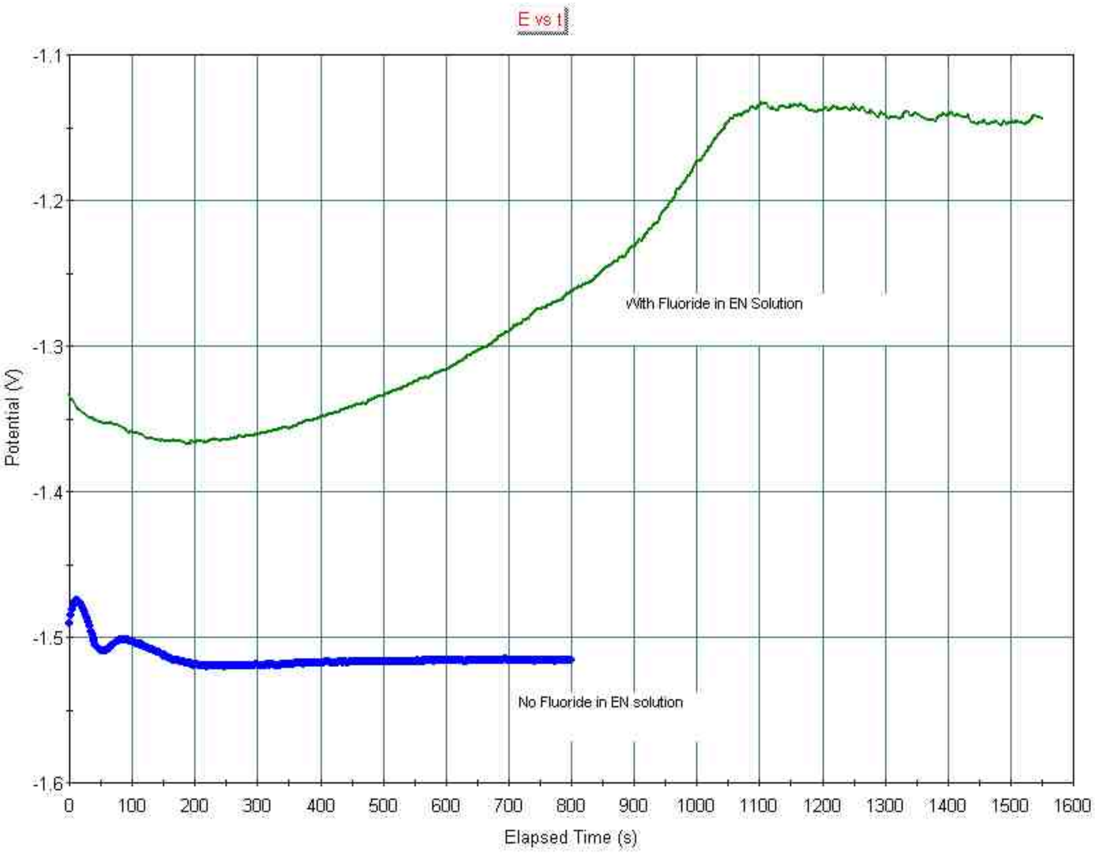

Figure 8. Open circuit potential of AZ-91D in electroless nickel solution with and without Fluoride.

As stated earlier this electroless nickel deposit is only used as a barrier coating to protect the magnesium substrate from further processing solutions and not for corrosion protection by itself. This electroless nickel chemistry is designed to produce an electroless nickel coating with 3-7% phosphorus depending on solution age.

Cross section of a part plated in electroless nickel-copper-nickel-chromium is shown in Figures 9A and 9B. The optical microscope picture, Figure 9A, shows a dark line between the electroless nickel and the substrate. Evaluating this dark line with a scanning electron microscope (SEM) the dark line disappears and the magnesium is etched away more than the electrodeposited coatings.

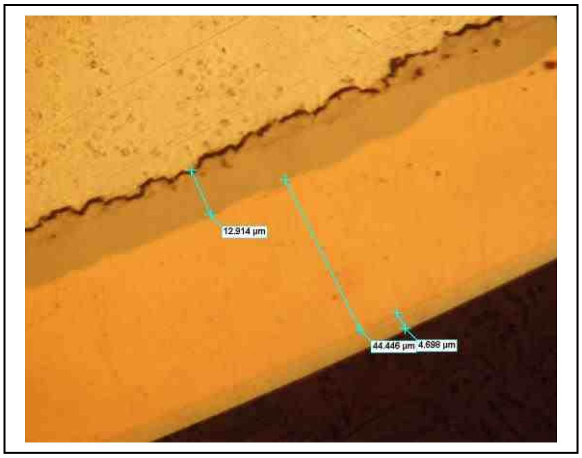

Figure 9A. Optical image of cross section 1000X.

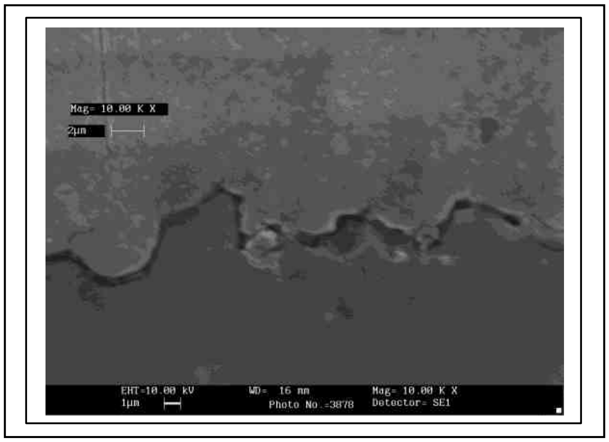

Figure 9B. SEM of cross section, 10,000X.

The polishing compounds used to polish the mount seem to dissolve the magnesium substrate faster than the electroless nickel-copper-nickel-chromium electrodeposits. Using other methods to check the adhesion of the electrodeposit to the magnesium substrate, ASTM B 571-97 [5], we evaluated bending the panel, baking at 200°C (392°F) for 30 minutes than quench in ice water and reverse sawing the panel. These entire tests showed excellent adhesion of the coatings to the magnesium substrate.

Corrosion resistance, especially on cast material, is dependent on the substrate. Typical cast defects are porosity, gross segregation, flux inclusions or other imperfections that would tend to cause porosity in the plated coating. Figures 10A and 10B show typical defects in cast parts. Figure 10A shows the surface of an AZ-91D magnesium casting with porosity. Figure 10B shows a cross section of the same casting showing gross cracking in the deposit. Salt spray data shows that other coatings need to be applied after the special electroless nickel coating to achieve any meaningful hours. With 12µm (0.5 mils) of the special electroless nickel corrosion of the base metal can be seen in less than three hours of neutral salt spray, Figure 11 A shows the corrosion pits. Figure 11B shows salt spray of a AZ-91D panel plated with 18µm (0.7 mils) of high phosphorus electroless nickel over 7.6µm (0.3 mils) of the magnesium special electroless nickel process. This panel was in salt spray for 300 hours without showing any signs of corrosion. Other parts are being tested now but with copper-nickel-chromium on the surface.

In addition to salt spray testing electrochemical testing was done to evaluate the porosity of the special electroless nickel deposit. Several panels were run with various times to obtain different thickness. Previous studies have shown that 30 minutes of plating, about 6µm (0.25 mils) produced a deposit that was pore free as measured by Tafel plots.[6] In these experiments the open circuit potential of an area of 1 cm² was measured in a 5% NaCl solution, the same as the neutral salt solution used in the salt spray cabinet, per ASTM B 117. Figure 12 shows the open circuit potential measurements of three AZ-91D panels plated with various thicknesses of the special electroless nickel solution. The initial rest potential of all three panels are very similar in potential, 0.42±0.03V. This shows that the magnesium panel is encapsulated well enough that the salt solution does not penetrate the electroless nickel immediately. With 6µm (0.23 mils) of electroless nickel it takes about 600-700 seconds in the 5% NaCl solution to penetrate the coating. Once the salt solution penetrated the coating we can see a significant change in potential from –0.42 V to –1.22 V. With 8µm (0.3 mil) of electroless nickel it takes about 1800 seconds to see a significant change in potential and at 2500 seconds we are completely through the electroless nickel coating. The main difference we see between the 6µm thick deposit and the 8 µm thick deposit is the shape of the curve. The 6 µm thick coating showed a significant increase in potential in a very short time whereas the 8 µm thick deposit change was very gradual until it reached the critical point when the coating failed. The 11µm (0.43 mils) thick deposit did not show any sign of failure over the 3600 seconds the test was performed. This indicates that the coating, under these test conditions, is more robust than the thinner coatings in protecting the substrate.

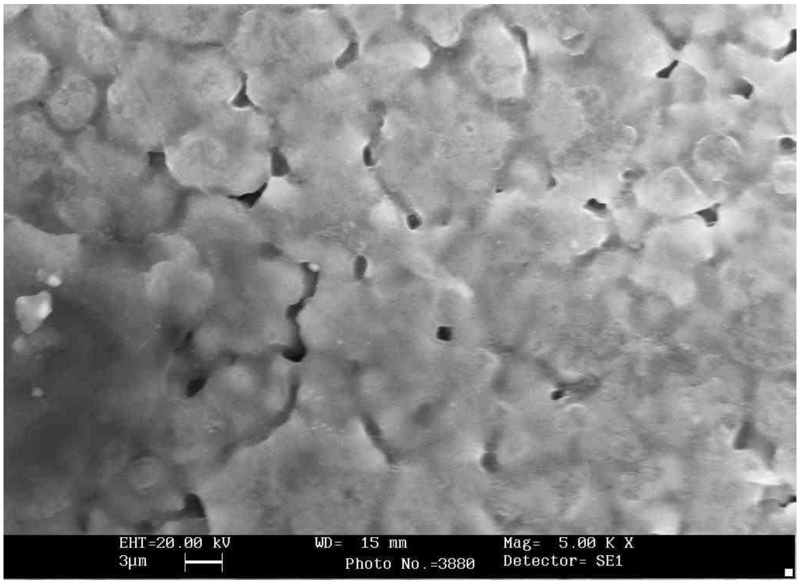

Figure 10A. Surface of raw casting. 5000X

Figure 10B. Cross-section of raw casting. 400X

Figure 11 A. Special EN 12 µm on Mg.24 Hrs salt spray

Figure 11B. High P EN over Mg special EN 300 Hrs salt spray.

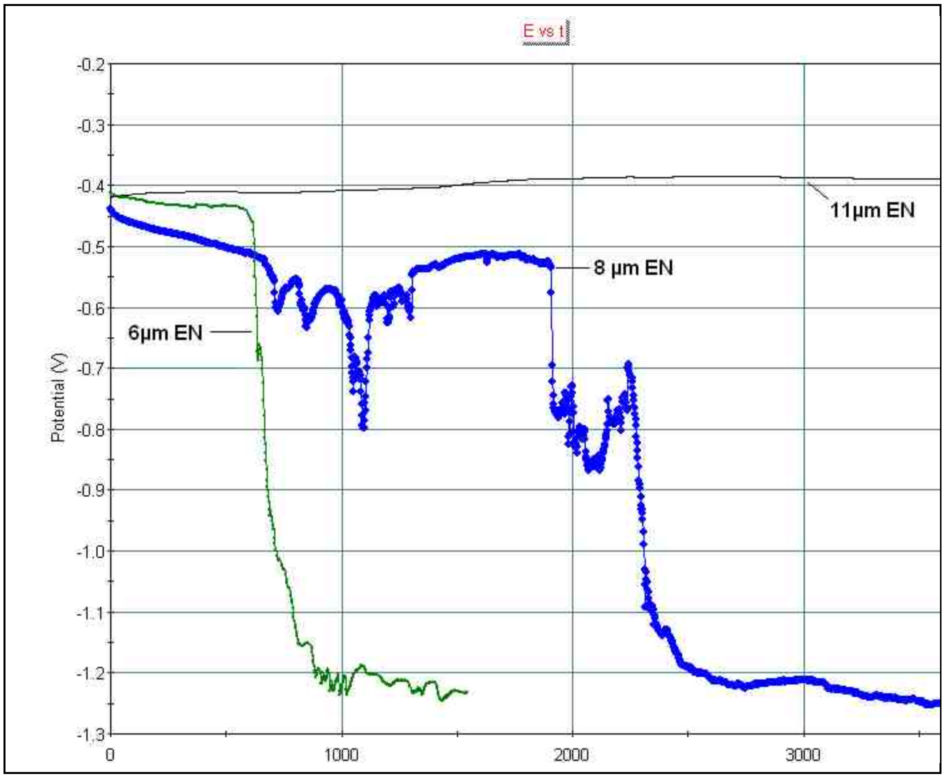

Figure 12. Open circuit potential of electroless nickel on AZ-91D panel.

Conclusion:

Direct electroless nickel deposition on magnesium alloys offers benefits to the conventional zincate treatment. The direct procedure eliminated the need for rectifiers and a cyanide copper strike which, in turn, simplifies racking and tank design; also, more parts can be plated at the same time with the direct EN on magnesium.

With the non-chromium etch there is more control on the etch rate of the magnesium alloy that is being processed. This gives more process control of the non-chromium etch as compared to the chromium based etch. In addition the non-chromium etch uses less hazardous chemicals than the chromium etch. The non-chromium etch produces a much finer etch which in turn produces a part that has a much smoother surface finish.

Corrosion resistance was measured by salt spray and electrochemical methods. The salt spray data showed that the special electroless nickel is not very corrosion resistance by itself. Incorporating a high phosphorus electroless nickel layer over the special electroless nickel for magnesium the corrosion resistance increased dramatically. Electrochemical data showed that with a thicker initial electroless nickel coating the salt spray solution took longer to penetrate the special electroless nickel coating. The corrosion resistance of the duplex coating, with a good substrate, should produce salt spray hours consistent with the type of electroless nickel on the surface.

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