



## ELISHA ENGINEERED SURFACES™

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### Zero Chrome Electrolytic Surface Treatment for Metallic Surfaces- Part I

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#### **Abstract**

Elisha Technologies Co LLC announces its latest achievement in surface engineering know as Cathodic Mineralization. Cathodic mineralization is a proprietary electrolytic process, similar to electro-galvanization, that is operated by immersing a metallic (or an electrically conductive) component within an electrolyte containing water and a silicate solution. The electrolyte can be tailored by adding water-soluble dopants. A current is passed through the electrolyte such that the component is employed as the cathode. Under these conditions, the component/cathode interacts or reacts with the electrolyte to form a "mineral-like" layer. The mineral layer is so thin that it will not affect the dimensions of tolerance sensitive parts. The mineral layer can replace chromating, as well as phosphating for steel, stainless steel, electro or mechanical plated zinc, zinc/aluminum alloys and other metal or metallized parts.

#### **1. Introduction**

##### ***1.1 Background***

Since its inception, Elisha Technologies Co, LLC has actively pursued the development of mineralization technology. Mineralization technology is the process of forming a thin mineral film on the surface of metals used as protection, decoration, insulation, and other untapped applications. Elisha Technologies has been successfully developing a corrosion resistant coating process based on silicate chemistry known as cathodic mineralization (CM) and has coined the term Elisha Mineral Coat (Elisha® EMC™) to describe the new surface. Among the many advantages of the process are:

- the solutions and rinse waters are environmentally benign.
- the process forms a amorphous smooth surface that exhibits corrosion protection, topcoat adhesion improvement, and greater lubricity.
- the process that forms the protective mineral barrier is simple and elegant.

Much of the success of the Elisha® EMC™ surface chemistry can be attributed to the reaction mechanism. This mineral reaction mimics chemistries found in nature and is tailored to metal finishes. The process acts as an interface between the metal and silicate by binding the silicate components with the metal ions from the substrate surface. This electrolytic method offers many advantages including a simple application and two forms of surface protection.

## ***1.2 Nature***

Some of the properties of the Elisha® EMC™ surface are those shared by nature itself. This makes the coating both unique and potentially adaptable. Nature has a process known as shallow hydrothermal alteration, formerly known as epithermal metasomatism, in which the elements of a mineral structure can be modified using an aqueous solution rinse. Because this process is limited to the Earth's upper crust, minerals can be modified at very low temperatures and pressures. Through the exchange of specific ions, this process can modify the properties of the mineral itself. One of the objectives of the CM process is to create a mineral-like lattice tailored to different substrates or conditions to which substrates must be exposed. Geyselite is another example of how nature produces minerals near the Earth's surface using steam from a geyser without the use of extremely high pressures or temperatures.

Perhaps the most important CM similarity to nature is the inorganic lattice, which forms. Most of the minerals formed in nature utilize some type of crystalline structure based on a silicate and/or aluminate structure. In these arrangements, the silicon and aluminum atoms are arranged in a tetrahedral structure. The octahedral sites can be occupied by supporting metal cations, which may include iron, zinc, aluminum, calcium, sodium, boron, and zirconium, among others. The cation placement will be dependent upon size, charge, density, and environment.

Like nature, silicate chemistry also provides various backbone structures. The silicate structure can polymerize to differing degrees; from the very basic monomeric orthosilicate to the highly structured framework silicates found in zeolites. Partial polymerization is also evident in dimerized silicates known as disilicates, to linear chains, including pyroxenes. Silicates can be further polymerized dimensionally to include ring and sheet structures all the way up to the three dimensional framework structures. The structure's rigidity increases as the degree of polymerization increases, eventually assuming brittle characteristics seen in some glasses. The lower degrees of polymerization provide a more malleable structure, yet not as tightly bound as the higher degree silicates.

The CM process creates unique inorganic lattices similar to those found in natural minerals. One of the goals of the CM process is to tailor the lattice using silicates and metal ions such as iron or zinc to form a partially polymerized lattice much like those formed in the natural silicate systems. The CM barrier uses the same basic structure of the inorganic lattice, but applies it uniquely to the surface of the metal to be protected.

## ***1.3 Scope of Paper***

This paper will discuss the development of the Elisha® Electrolytic Mineral Coat (EMC™) from its inception to the current state of the art. The paper will discuss mechanism, development of suitable anodes, and scale-up to the commercially viable process.

## 2. Mechanism

The original concept behind the Elisha® EMC™ Project was to extend the Elisha Mineralization technology beyond a “passive” coating delivery system to an “actively” controllable surface mineralization system. Previous work in the passive systems had shown that silicates delivered through either a urethane coating or an oil-based gel could chemically bond with metal surface to form a metal silicate layer. Utilizing an environment set up with relatively higher amounts of silicate to that of molecular oxygen results in the metal silicate formation dominating. The passive process was diffusion-limited in two aspects. First the silicate was required to diffuse through the organic carrier. The second limiting factor was the diffusion of the metal and/or silicate through the newly formed metal silicate layer. A 200-angstrom thick mineral layer could take from hours to days to form.

One of the intended purposes of the cathodic mineralization method was to use EMF potential to drive the silicate to the metal surface rather than depending on the diffusion rates of the carriers. The original hypothesis was to use the working metal piece as the anode so that its positive charge could drive the migration of the negatively charged silicate species within an aqueous solution to the metal surface, thus increasing the reaction rate and thickness of the film. Initial testing showed that the anode, which was expected to show improved protection, did not show any improvement in salt spray. However, by chance the cathode was also tested and was found to improve corrosion performance 5 fold over the control and anode panels. This initial observation sparked the investigation of what is now known as the Cathodic Mineralization treatment.

The focus of this paper is on proper anode selection and solution chemistry.

## 3. Electrochemical Anode performance and Solution Chemistry

### 3.1 Iron anodes

Two types of water have been used in cathodic mineralization process experiments. The first is deionized Type I water with an approximate resistance of 18 mega ohms. Another is laboratory grade distilled Type IV water from Culligan. This water matches closely with the water presently used at Elisha Technologies laboratories. The bath consisted of 0.1021 g of FeCl<sub>3</sub> and 349.98 g of N. Sodium Silicate solution dissolved in one of the two experimental water. The process beaker volume with the solution was fixed at 3.5 liters. We used one cathode panels mineralized on both sides using two iron anodes on either side. The panel area is 3”X6” with actual coating area of about 33 square inches.

Notation used in experimental runs and graphs: 0507-A1-ISON0

0507 indicate the date identification

A1 – solution A used first time (usually 15 minutes each run)

ISON0 – Iron Solid New 0<sup>th</sup> time

ISU1 – Iron Solid Used electrode First time (no cleaning of the surface)

ISC1 – Iron Solid Cleaned First time

Figure 1 shows the data from Iron Anodes in de-ionized water – Solution A. You will notice from run 0507-A1-ISON0 to 0507-A3-ISU2 a significant decrease in current. After three runs the anodes had developed a hard deposit on them. First, they were cleaned with a polishing cloth and then were rerun. As you can see in run 0507-A3-ISU2/0511-A9-ISC1 the current dropped from about 10 amps to 7.8 amps. The anodes were obviously not cleaned very well, so they were cleaned with sand paper. After the anodes were cleaned (run 0507-A3-ISU2/ 0513-A10-ISC2) the current went back to

where they had started in run 0507-A1-ISNO. What we learned from Solution A is that 1.) Iron anodes can not be used consecutively without thoroughly cleaning them and 2.) de-ionized water does not make that much of a difference as you will see in Figure 2.

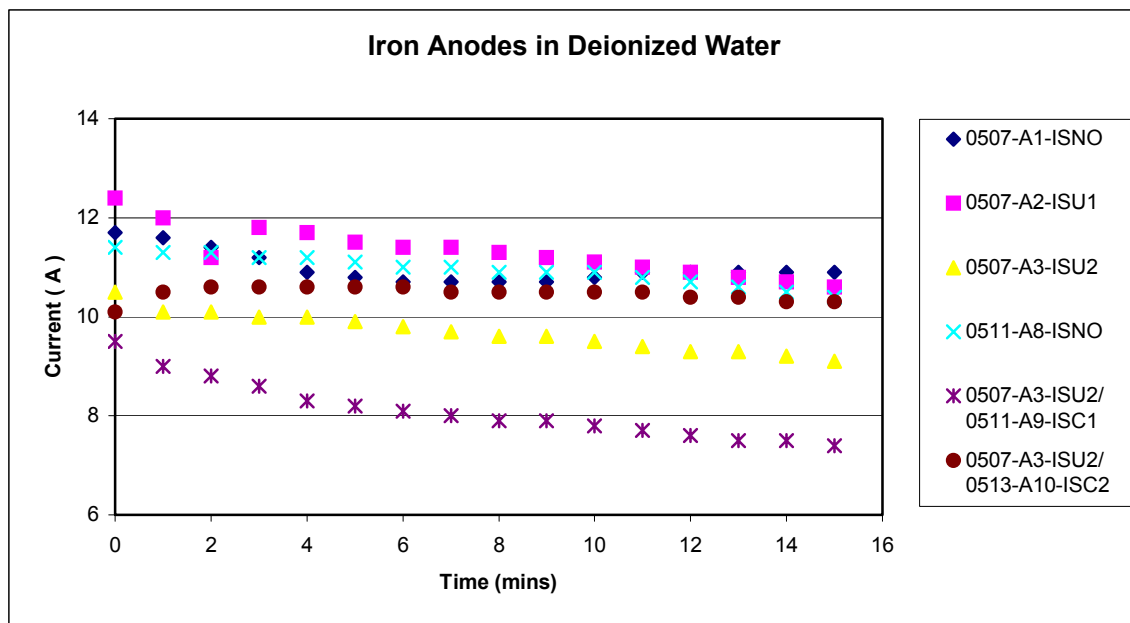


Figure 1 Iron anodes in deionized water

Figure 2 shows the data from solution C that was done using distilled water. After three runs the anodes were cleaned with sandpaper. If you compare Figure 1 with Figure 2 you will notice that the drop in current between the first run and the third run is less in distilled water than in deionized water. Hence, using deionized water over distilled water does not make that much of a difference. As in Solution A the current in run 0519-C3-ISU3/0519-C4-ISC1, which had been cleaned with sandpaper, had come back to where it started in the first run 0519-C1-ISNO.

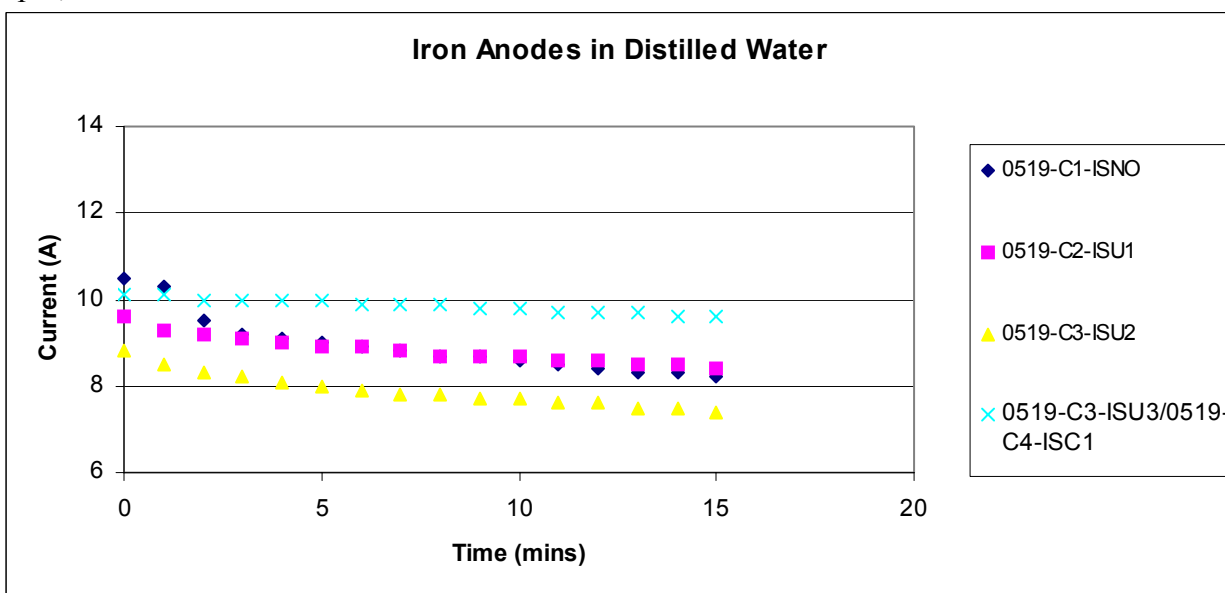


Figure 2 Iron anode in distilled water

However, as we saw in solution A, iron anodes will not have a consecutive current through out each run unless the anodes are cleaned. From the data collected in solutions A and C using iron anodes,

we elected to approach the cathodic mineralization process using a different electrode. Platinum was our next consideration for the anodes. Similar to the iron anodes, we tested the platinum anodes first in solution A (deionized water) and also in solution C (distilled water) to observe any difference.

### 3.2 Electroplated Platinum/Titanium (Pt/Ti) Anodes

Figure 3 shows the data for electroplated platinum/titanium anode in deionized water, solution A. From run 0507-A4-PSNO to run 0507-A7-PSU3 the current remained relatively steady during the runs even though the current had decreased between them. The decrease in the current is also less than the drop in current using iron anodes.

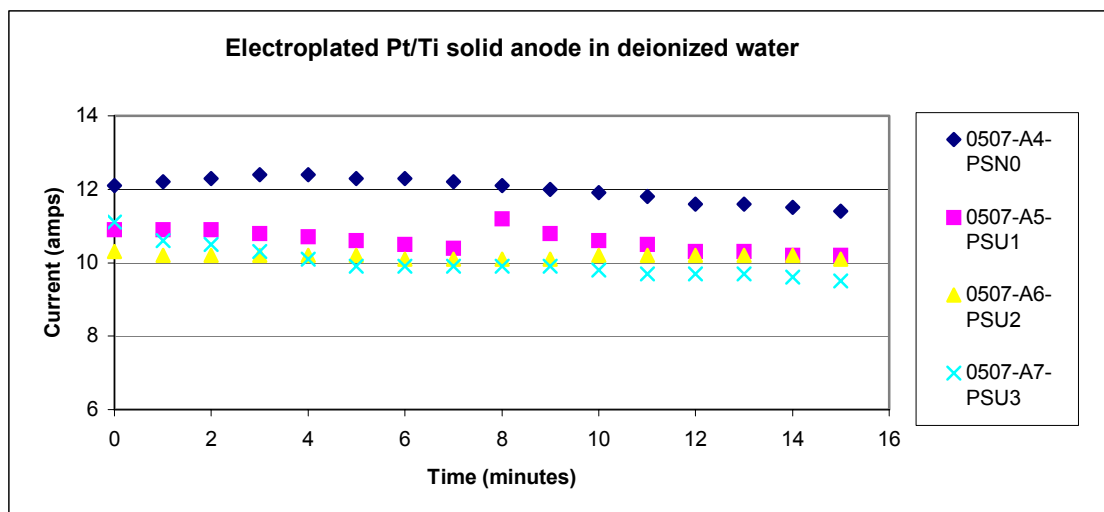


Figure 3 Electroplated platinum/Titanium (Pt/Ti) solid anode in deionized water-solution A

Figure 4 shows the data for electroplated platinum/titanium anode in distilled water, solution C. In solution C, runs five to nine were done using the same platinum anodes from solution A. The anodes had been cleaned before the first use. During the four runs in solution C the platinum anodes had developed a whitish deposit. There is a noticeable difference between solution A and C. In solution A the current between runs decreases as shown in Figure 3. However, in solution C the current is unsteady in that the current will decrease then it will come back to where the first run started. This is shown in Figure 4 where you can see that in run 0522-C8-PSU3 the current comes back relatively close to run 0507-A7-PSU3/0522-C5-PSC1.

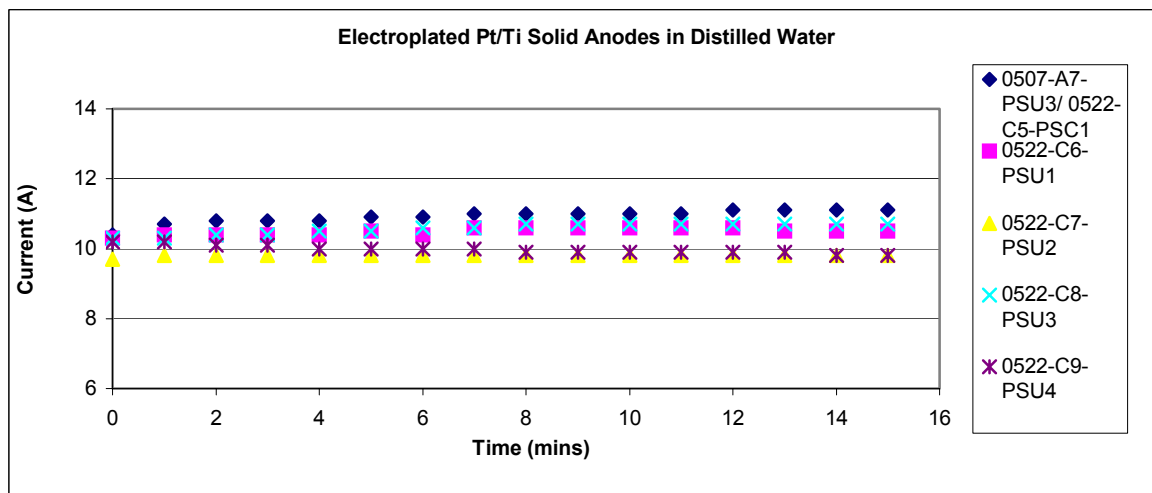


Figure 4 Electroplated platinum/titanium (Pt/Ti) anode in distilled water, solution C

The Figures 3 and 4 show that the platinum anodes run better in distilled water than in deionized water and also platinum anodes run better than the iron anodes. During the five runs in solution C there was a formation of deposit on the anodes that were scraped off and analyzed. These precipitates do show presence of silicate.

Figure 5 shows the data in solution D (distilled water). There were six runs completed using the same platinum anodes that were cleaned twice.

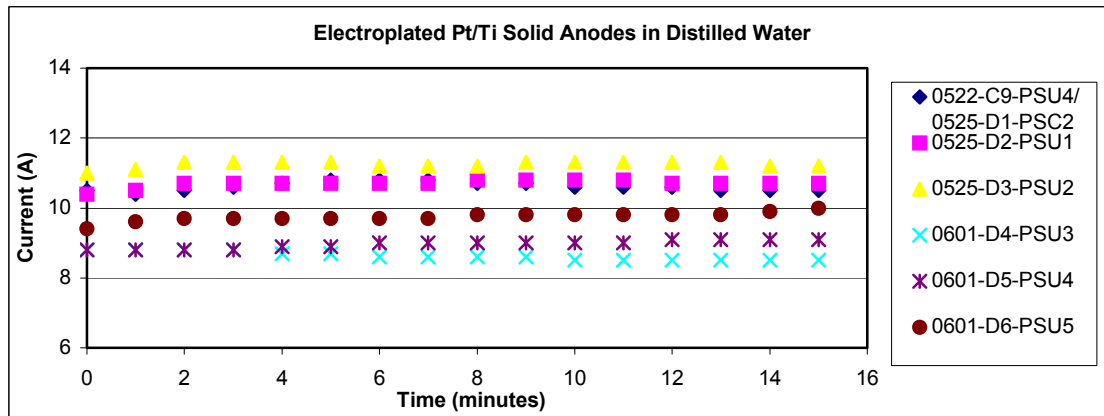


Figure 5 Electroplated Platinum/Titanium (Pt/Ti) solid anodes in Distilled Water- Solution D

Figure 5 shows the current is relatively steady during each run. Also, between runs 0522-C9-PSU4/0525-D1-PSC2 and 0601-D6-PSU5 the current also comes back close to where it started. The current between runs does not steadily decrease but instead it increases during the third run and the sixth run. After the six runs done in solution D there were no deposits that formed in any of the runs.

Solution E (distilled water) used the same platinum anodes that were used in solution D without any cleaning. There were three runs done in this solution. At no time during these runs there was any visual deposits form on the anodes. But the anode always shows weight gain. Similar to solutions C and D the current does not decrease steadily but at the end of the three runs comes back to the first run.

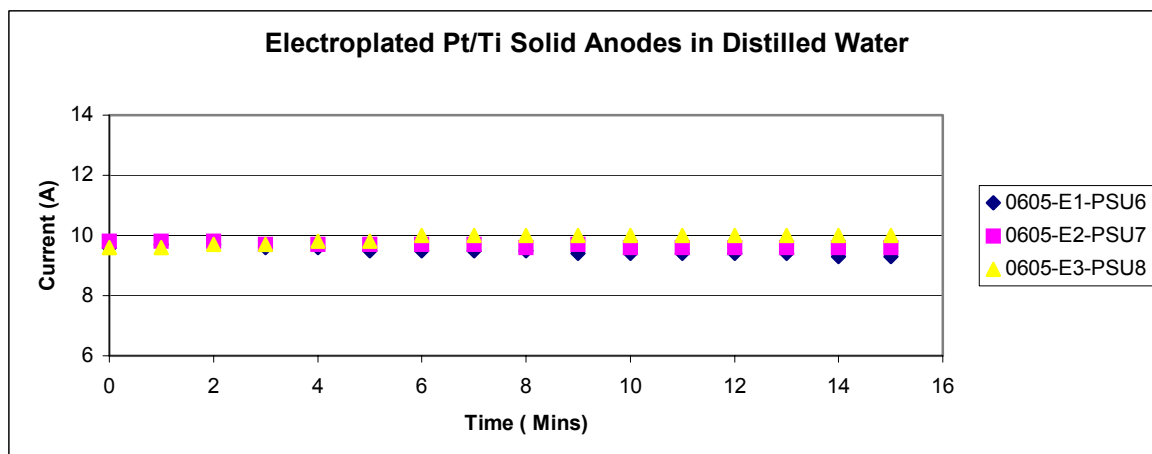


Figure 6 Electroplated Platinum/Titanium (Pt/Ti) Solid Anodes in Distilled Water- Solution E

### 3c. Platinum clad niobium solid anodes

These anodes were very smooth and lighter than the platinum anodes used in previous solutions. We believed that smoother surface might reduce even further any non-visual deposit formation and in turn keep the anodes from gaining weight. The lighter and foil type of anode structure will also be beneficial for barrel plating configurations. There were six runs in solution F (distilled water). A crystalline deposit had formed on the anodes during the six runs. The deposit had also formed in the solution. We estimate that the deposits were forming on the anodes, but because they are so smooth they were not sticking and would fall back into the water.

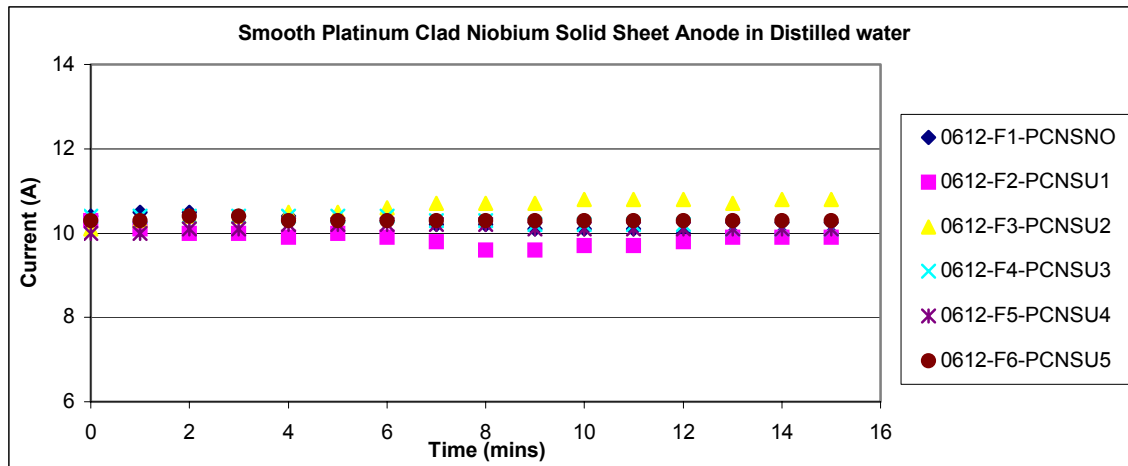


Figure 7: Platinum Clad Niobium Solid Sheet Anode in Distilled Water- Solution F

Graph shows that the current is similar to the current with the platinum solid anodes in that through out the runs the current does not steadily decrease but returns to where the first run started. Even though deposits had formed on the anodes the current does not decrease steadily like the iron anodes.

### 3d Platinum clad niobium mesh anode

We also used a platinum mesh anode in solution G (distilled water). There were six runs done in this solution using the mesh anodes. Through out the six runs there was no formation of deposits on the anodes.

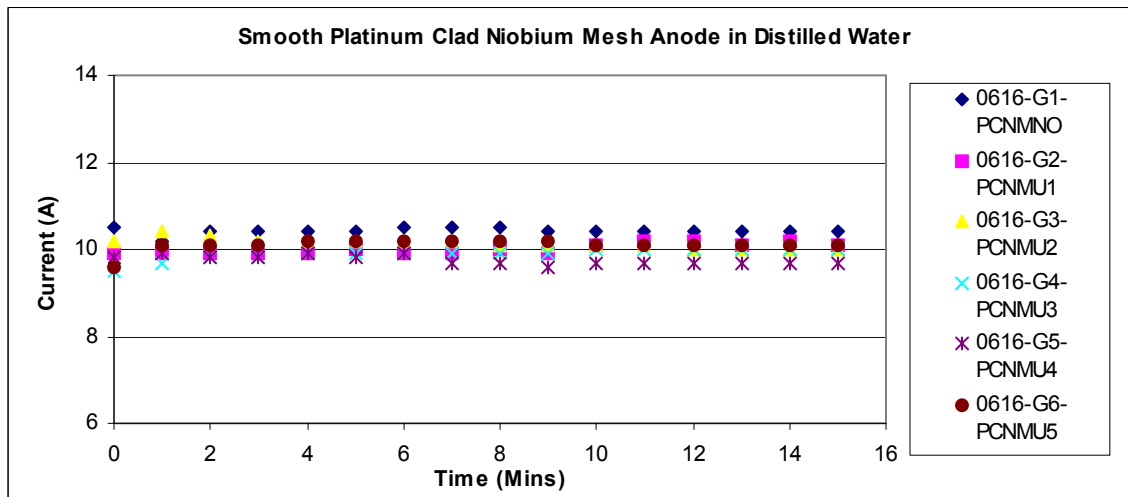


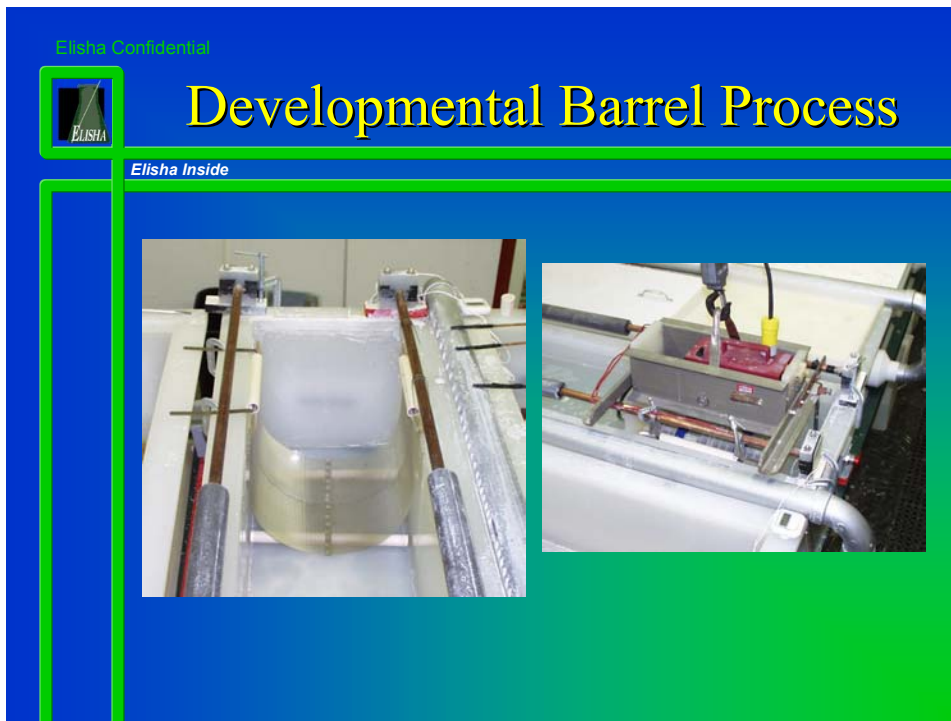
Figure 8: Smooth Platinum Clad Niobium Mesh Anode in Distilled Water- Solution G

Similar to solution F the current in Figure 8 returns to where it started between the first and last run, however there was no formation of visual deposit on the anode. But once again, we observed anode weight gain. Also the range of the current 9.6 – 10.5 is also similar to the range in current in solution F. Overall, the mesh formation seems to be the best anode used for plating because 1.) There was no deposit forming on the anode and 2.) The current was relatively stable during the runs and did not steadily decrease between the runs. Our later life time studies (not within scope of this paper) revealed that these anodes needs chemical cleaning after certain number of experimental runs to maintain the current within certain optimal range.

#### 4. Scaled-up laboratory pilot barrel and full scale barrel

Modern electroplating manufacturing technology is concerned with mass production, automation, quality, and flexibility. Mass production is important for low cost manufacturing. It requires machines that will process parts at a high rate while meeting all the specifications requirements. Barrel plating were the first plating device to dramatically increase productivity. There is no racking or unracking of parts and barrel machines usually requires less space, and they are easily automated minimizing operator attention. The choice of barrel plating also depends on the type of parts.

We have successfully implemented a laboratory pilot barrel of 800 SI cathode parts area and 270 SI anode areas. The anode is the platinum clad niobium mesh. We also implemented a full-scale barrel 9000SI cathode parts area and 1734 SI anode area. We have attached photographs of both systems.





**Figure 9. Photographs of Barrel Process**

## **5. Performance**

The Elisha® MTC™ tie-coat provides an improved surface on articles by managing the surface chemistry and affecting a new surface through chemical reaction and interaction. The mineral-like surfaces are formed, when mineral-forming precursors are delivered to the surface of metal or metal-coated articles. The substrate usually contributes donor ions to react and/or interact with delivered precursors, forming thin surface structures. These surfaces may exhibit engineered characteristics including, but not limited to, corrosion resistance, temperature resistance, flexibility, coating adhesion, and chemical resistance.

### *5.1 Top coated Performance*

The mineral can be topcoated with a wide range of commercial coatings such as a silane, heat-cured epoxy, carbonate, alkyds, latex, among other solvents, or water-based coatings. Although the mineralization process is chromate-free, the chromate-free status of the entire coating system will be dependent upon the content of the topcoat. In other words, the Elisha® EMC™ tie-coats can reduce chromate usage when topcoated with a chromate containing coating, or eliminate chromates altogether when used without a topcoat or when topcoated with a chromate free coating.

The mineral is extremely beneficial when employed as an inorganic mineral tie-coat for improving the bond between metal and organic topcoats. Improving adhesion with EMC™ has a dramatic effect on the overall performance of the coating system, as exhibited in the following pictures:

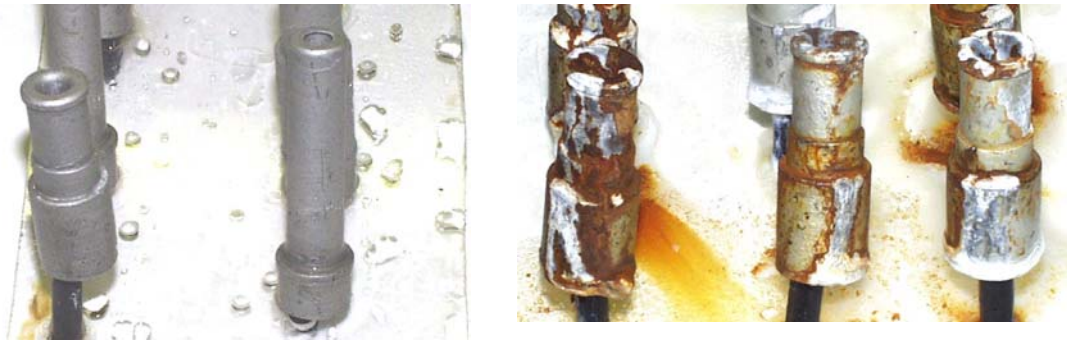


Figure 10: ASTM B117 Salt Spray Performance of end-fitting fasteners at 3000 hours using coating systems on left: Zinc plate with Elisha® EMC™ topcoated with chromate-containing heat-cured epoxy, and on right: Zinc plate with yellow chromate (Cr(VI)) topcoated with same chromate-containing heat-cured epoxy.

### 5.2 Secondary Forming Tolerance

The Elisha® EMC™ surface has also been shown to be tolerant of secondary forming of fasteners, such as rivets. This is explained by the significant adhesion improvement observed, but may also be the product of the extreme thinness of the EMC™ coating.

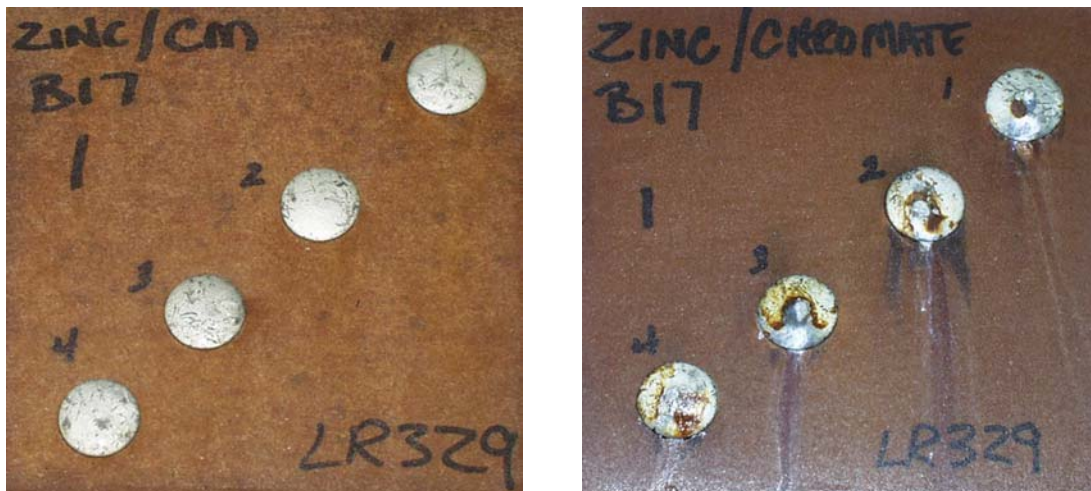


Figure 11: ASTM B117 Salt Spray Performance of “bucked” rivets at 1000 hours using coating systems with and without Elisha® EMC™. Left: Zinc plate with Elisha® EMC™ topcoated with chromate containing heat-cured epoxy. Right: Zinc plate with yellow chromate (Cr(VI)) topcoated with same chromate-containing heat-cured epoxy.

### 5.3 Stand-Alone Performance

The EMC™ surface has also been shown to improve corrosion resistance of zinc systems even when used without a polymer topcoat system. Various adaptations of the basic cathodic mineralization process can be used to achieve a variety of performance specifications of hours in ASTM B117 to first white, hours in ASTM B117 to first red, and to 5% red rust failure.

Variations in the cathodic mineralization process include secondary rinses and additives to the bath chemistry. An interesting result is the overall extension of first red rust duration over a typical zinc surface. A zinc control surface will exhibit first red rust at 24-48 hours. Depending upon the exact mineralization process used, the first evidence of red rust can be extended to several hundred hours. This is thought to occur for several reasons.

It has been shown in earlier work by the author (NACE Paper 97266) that the mineralized surface reduces the instantaneous rate of corrosion by a factor of ten. It has also been shown by surface analytical methods such as SEM and ESCA that the EMC™ surface is conformal and reacts with the entire surface to form a barrier coating. This is also exhibited by increased adhesion observed when using EMC™ surface with polymer topcoats. Based on these observations and an understanding of the corrosion chemistry of zinc, the mode of protection of zinc with the Elisha® EMC™ surfaces is, therefore, two-fold. First, the mineral provides a barrier coating to reduce the attack of corrodants on the surface of zinc. Secondly, the mineral incorporates the surface of zinc into the mineral reaction and therefore removes the galvanic ability of zinc to sacrificially corrode.

## **6. Summary and Conclusions:**

Introduced at SAE-Off Highway in September of 2000, the EMC™ coating represents the only publicized completely chrome-free electrolytic surface treatment for zinc. Work in Elisha® cathodic mineralization process is continuing to pursue commercial avenues for this technology. The first applications are for zinc-plated fasteners that must survive secondary mechanical processing.

Work at CHEMIONIC is continuing and we expect to present the next part of this paper in near future.

## **7. Acknowledgement**

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