



ELISHA TECHNOLOGIES Co. L.L.C.
1 HUNTHAUSEN DRIVE
P.O. BOX 280
MOBERLY, MO 65270

A Cathodically-Deposited Mineral Coating for Replacement of Cr (VI) and Cr (III) Treatments of Zinc

Presented at AESF/EPA Conference

February 1, 2001

Nancy Heimann, Operations Manager
Elisha Technologies Co. L.L.C.

PHONE [660] 269-3700

FAX [660] 269-3737

1.0 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 mineral coating 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 mineral coating 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, 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 mineral coating from its inception to the current state of the art. The paper will discuss what is known about the theories and mechanisms as well as discuss the performance attributes that have been observed with this technology. It has been observed that the mineral coating surface provides the following benefits:

- Improved corrosion protection
- Improved paint adhesion
- Environmentally benign alternative to phosphate and chromates
- Improved electrical and heat insulating properties
- ESCA of specific metals

2.0 Patents and Intellectual Property Position

Elisha Technologies Co LLC has a wide ranging patent estate that reflects its diverse research capabilities. The patent estate covers corrosion resistant aerosol sprays, lubricants, greases and gels, improved paint formulations, mechanical systems having improved corrosion resistance, etc. Elisha Technologies began filing patent applications in 1997 to cover the proprietary CM process and related chemistries, proprietary mineral coating surface, and articles having a mineral coating surface. Two U.S. Patents covering the CM process recently issued (U.S. Patent Nos. 6,149,794 and 6,153,080). Numerous other U.S. and non-U.S. patents and patent applications are pending.

3.0 MECHANISM

The original concept behind the mineral coating 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.

Electron Spectroscopy for Chemical Analysis (ESCA) was significant in the determination of both mechanism and characterization of the formed mineral barrier. The shallow sampling depth of 50-100 angstroms for ESCA allowed for the characterization of the barrier itself, rather than the bulk metal layer. Over time, ESCA revealed a progression of species building on top of the metal substrate. ESCA could distinguish the degrees of silicate polymerization, ranging from a simple orthosilicate (SiO_4) to a more polymerized disilicate (Si_2O_7), up to the highly polymerized silica (SiO_2) by examining the silicon (2p) photoelectron energy values.

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 (CM) treatment.

The initial hypothesis of the silicate simply migrating towards the anode using electrostatic forces had to be rethought in light of the surprising performance data. The protection being afforded to the cathode had to be due to some other mechanism. Much like the last discovery of the previous work of mineralization via passive delivery system,

the performance was seen before the mechanism was understood. In an effort to quickly understand the mechanism and effects of corrosion performance, a Six Sigma design of experiment strategy was employed to identify the key factors that effect the mineral coating.

This work identified the following formation process for mineralization.

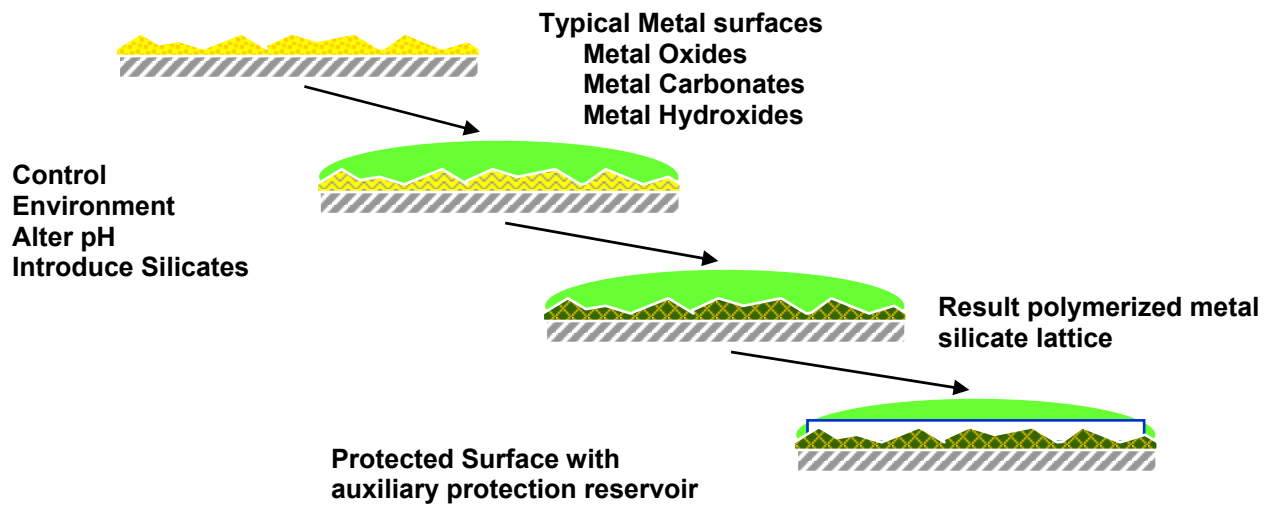


Figure 1: Basis of Mineralization Technology

Additional analytical data, including Scanning Electron Microscopy (SEM) gave visual evidence to the above-illustrated diagram, as follows:

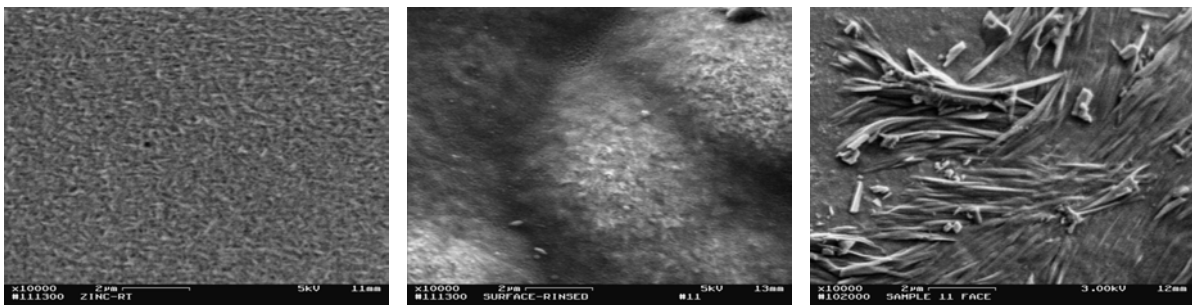


Figure 2: SEM images (from left to right) of 1) untreated zinc plated surface, 2) polymerized metal silicate lattice, and 3) protected surface with silica buildup.

4.0 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 a 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.

4.1 Topcoated 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 mineral coating 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 the mineral coating has a dramatic effect on the overall performance of the coating system, as exhibited in the following pictures:



Figure 3: ASTM B117 Salt Spray Performance of end-fitting fasteners at 3000 hours using coating systems on left: Zinc plate with the mineral coating 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.

4.2 Secondary Forming Tolerance

The mineral coating 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.

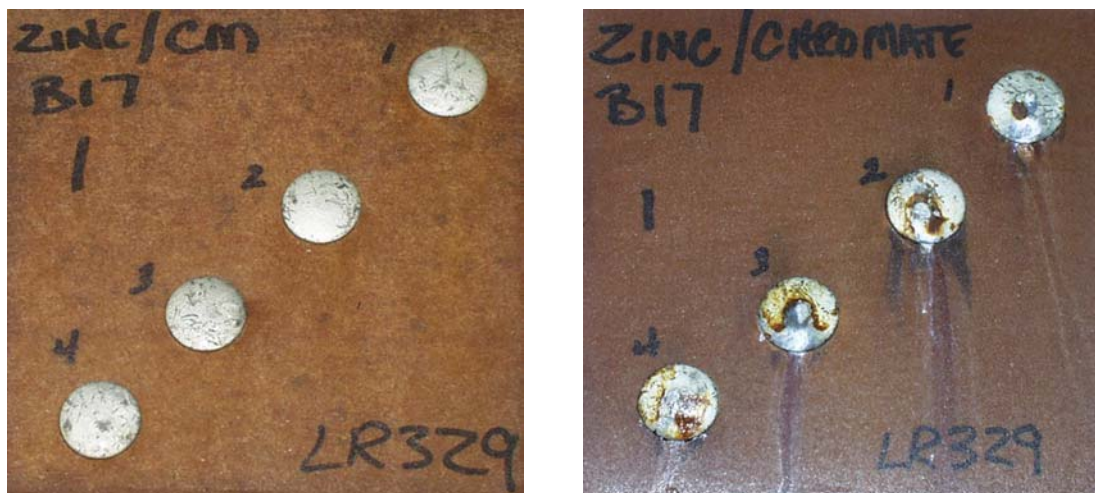


Figure 4: ASTM B117 Salt Spray Performance of “bucked” rivets at 1000 hours using coating systems with and without the mineral coating. Left: Zinc plate with mineral coating topcoated with chromate containing heat-cured epoxy. Right: Zinc plate with yellow chromate (Cr(VI)) topcoated with same chromate-containing heat-cured epoxy.

4.3 Stand-Alone Performance

The mineral coating 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 mineral coating surface is conformal and reacts with the entire surface to form a barrier coating. This is also exhibited by increased adhesion observed when using the mineral coating 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 mineral coating 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.

It is also interesting to note that the white rust data is not extended in a similar ratio to the appearance of first red rust. It is anticipated that additional processes additives, such as lubrication aids (waxes) and sealer coats will be needed. Indeed, experiments have

shown that waxes and “spin-dry” coatings have increased the white-rust performance to beyond 250-300 hours.

Performance of several different cathodic mineralization scenarios are shown in Figure 5.

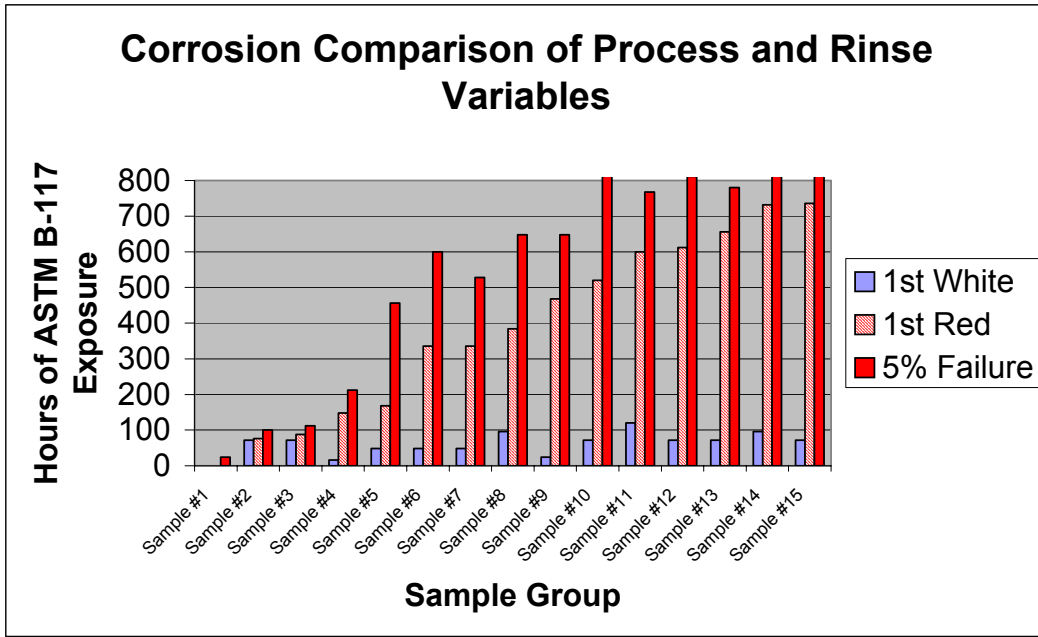


Figure 5: Corrosion Performance (in hours of ASTM B117 salt spray exposure) of 15 different “stand-alone” samples (without additional polymer topcoat).

4.4 Torque Tension Performance

The objective of this testing was to obtain a torque tension comparison between Wilson Garner M10 bolts coated with zinc and yellow chromate and zinc and mineral coating. Torque tension is used to predict repeatable clamp force and is a critical characteristic for many fasteners. The data showed there was less friction on the bolts coated with the mineral coating than the ones coated with yellow chromate. Additional testing is planned and underway.

Torque tension experiments were performed in accordance to test protocol USCAR-11. The experiments were done with an RS Technologies torque tension machine at Magni Industries. Eight samples of each of the two coatings were subjected to forces ranging from 20,000 to 42,300 Newtons.

A comparison of the torque tension data for the samples with zinc with a yellow chromate and those coated with zinc and mineral coating is given in Figure 6.

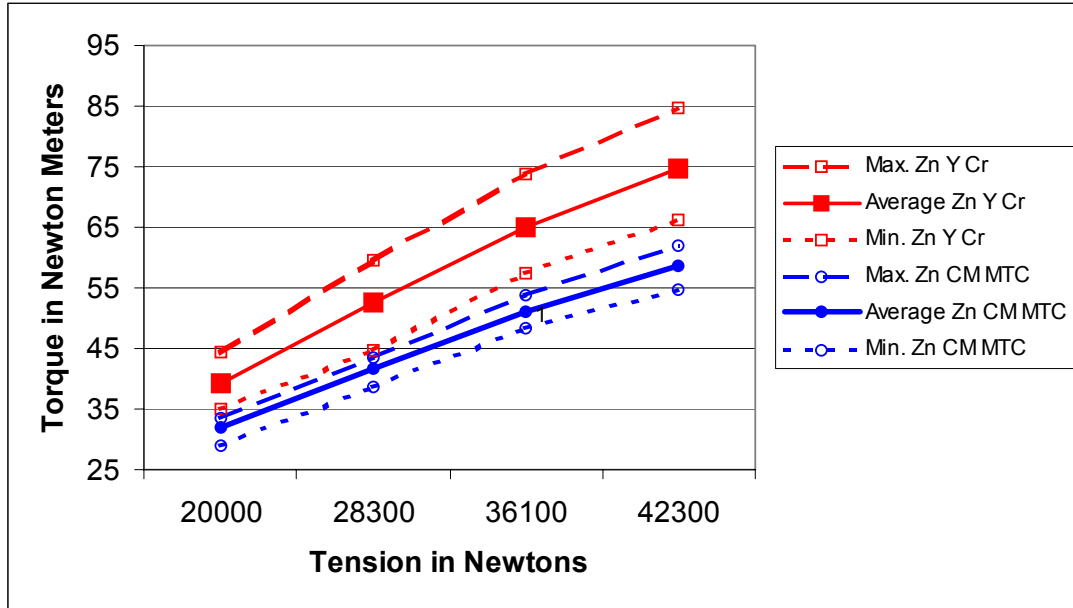


Figure 6 – Torque vs. Tension Comparison for Yellow Chromate and Elisha® EMC™

The standard deviation for the peak torque for the zinc yellow chromate treatment was 5.57 Nm with a three-sigma range of 33.4, and was 2.56 Nm with a three-sigma range of 15.4 for the zinc and mineral coating treatment.

The lower values of torque for the mineral coated bolts indicate that there is less friction on the mineral coated surface than on the yellow chromate surface. The reference coefficient of friction for the mineral coated surface was 0.18 at 28300 Newtons and 0.23 at 28300 Newtons for the yellow chromate surface. Since the three-sigma range for the mineral coating is smaller than that for the yellow chromate, the mineral coating surface allows for a more reproducible torque tension relationship than the yellow chromate. Additional work must be performed to evaluate the impact of lubrication materials.

5.0 Path Forward

Introduced at SAE-Off Highway in September of 2000, the mineral coating represents the only publicized completely chrome-free electrolytic surface treatment for zinc. Work in the 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.

6.0 Acknowledgements

The author would like to acknowledge the input to this work by the Elisha team including Bob Heimann, Wayne Soucie, Bill Dalton, Kay Hawkins, and Eric Netemeyer.

Elisha Technologies Co LLC is a privately held member of the Orscheln Group. Elisha develops corrosion solutions for industry, such as automotive and non-automotive vehicles, chemical, petroleum, marine and wire rope manufacturing. Elisha's patent estate includes 14 US patents issued, allowed, or pending patent applications in the US and internationally.

To learn about Elisha® EMC™ and Elisha's other surface engineering and corrosion solutions, see www.elisha.com.

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