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DEVELOPMENT AND COMMERCIALIZATION OF NON-CHROME ELECTROLYTIC SURFACE TREATMENT FOR METALLIC SURFACES

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Presented at
Cadmium, Chromium and Nickel Alternatives: An Information Exchange
Seven Spa Resort, Champion, Pennsylvania
September 26, 2000

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INTRODUCTION

Elisha Technologies Co., L.L.C. has discovered ways to grow high performance thin silicate-based mineral films on metallic or metallic coated substrates at low temperature and ambient pressures in conventional electrolytic baths. The work to date has been predominately on zinc; however, other substrates, including lead, stainless steel, steel, and gavlalume are being studied. The subject process, developed over the last several years, converts naturally passivating oxide films into unique complex oxides. Protection and enhanced surface characteristics are afforded without the use of hexavalent or trivalent chromates.

ELISHA MINERAL TIE COAT

Driven by growing environmental concern and industrial mandates to reduce, and in some cases, eliminate chromate conversion coatings, Elisha Technologies has developed Elisha® mineral tie-coat (MTC™). The MTC™ mineral is formed through a patented electrolytic process, which is chromate and phosphate free. Under many observed conditions, the MTC™ surface has shown to outperform chromate competitors.

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 and temperature resistance, flexibility, coating adhesion, and chemical resistance.

MIMICKING NATURE

Elisha Engineered Surfaces™, including the MTC™ surface, is a unique method of mimicking the epithermal metasomatism process found in nature to form surfaces that were previously only found in remote locals, or extreme environments. Further, the surface can be engineered, with unique combinations of reactants and using similar nature-mimicking processes, to produce complex mineral-like surfaces that do not exist in nature.

Nature continues to build and altar particularly in the earth's crust where silicon, iron and oxygen are most abundant. P. M. Dove and J. D. Rimstidt outlined several low temperature hydrothermal systems through known thermodynamics and kinetics, with particular emphasis on the effects of ion and compounds that catalyze and inhibit reaction rates in aqueous systems. The mineralization process improves upon naturally occurring mechanisms and forms a mineral-like surface not found in nature. A graphical representation of the process of mineralization is illustrated in Figure 1.

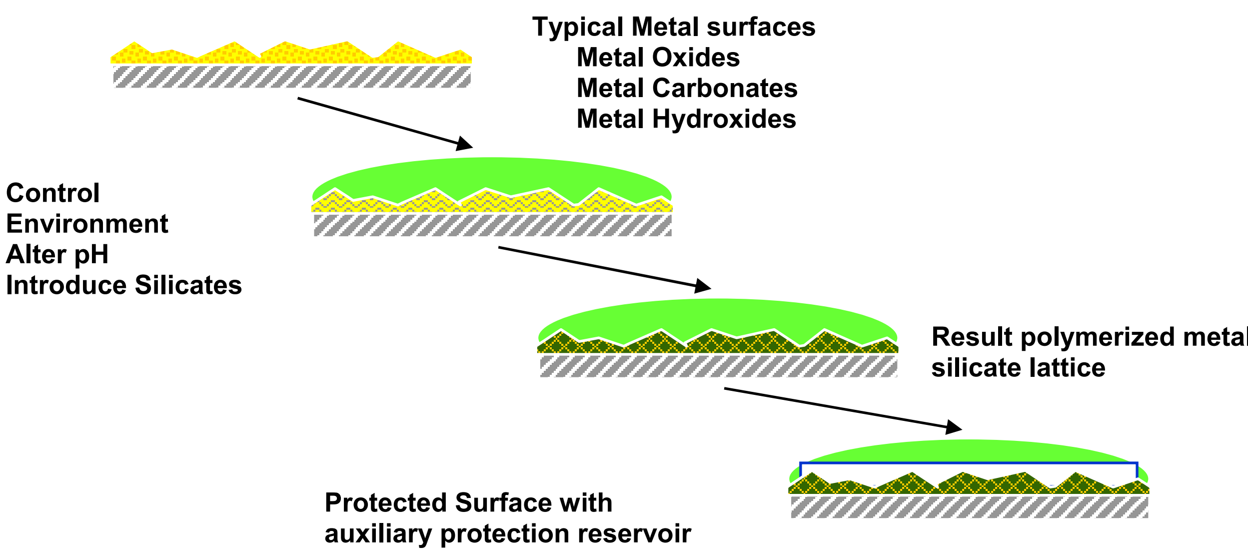


Figure 1: Basis of Mineralization Technology

THIN FILMS

The MTC™ mineral is a thin film (less than 10,000 angstroms) surface. The most prevalent processes for forming thin films has been high cost ion or electron beam sputtering, plasma, physical, or vapor deposition of metal coatings on varied substrates. Lower cost surface treatments currently available are iron and zinc phosphate, as well as, chromate and non-chrome post rinse coating used in the paint industry, but these low cost substitutions do not perform as well as the MTC™ surface.   A scanning electron micrograph image is shown in Figure 2.

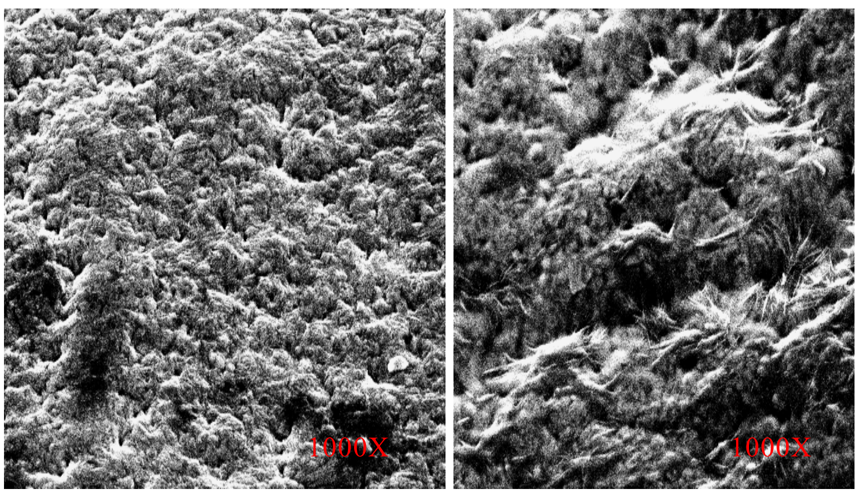


Figure 2: SEM of Electrogalvanized Untreated (left) and Electrogalvanized with MTC™ (right).

The mineralization process forms a tightly adhering mineral in place of the surface oxide. The MTC™ mineral layer is typically less than 2000 angstroms *(less than 1/1000th of a sheet of paper)* and will not affect the dimensions of tolerance sensitive parts. A cross sectional scanning electron micrograph (SEM) shows relative thickness in Figure 3.

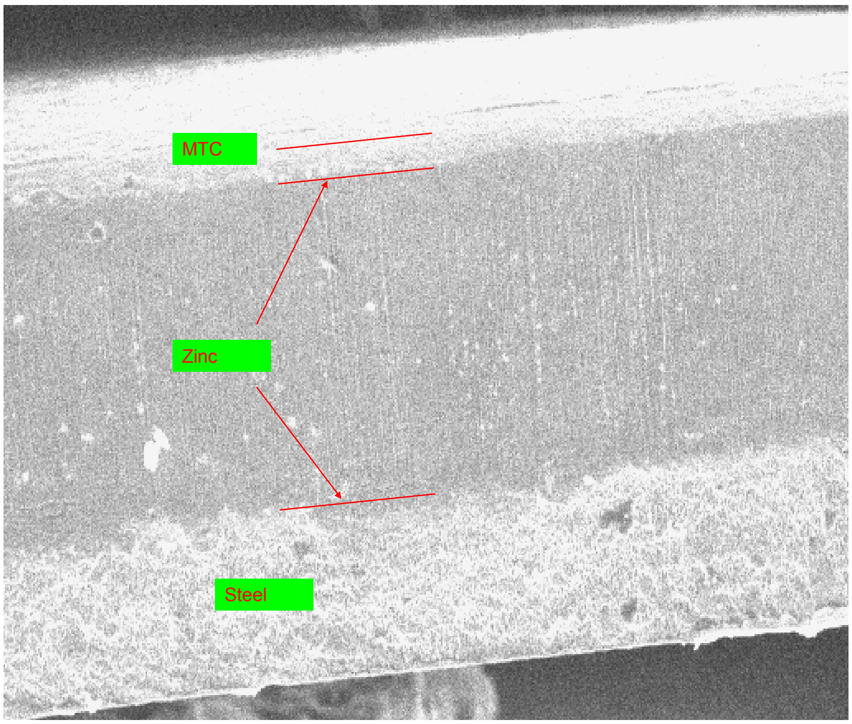


Figure 3: SEM Cross-Section of Zinc Plate with the MTC™ process.

The mineral layer can replace chromate for electro or mechanical plated zinc, as well as beneficial coatings for steel, stainless steel, zinc/aluminum alloys and other metal or metallized parts. The mineral is extremely beneficial when employed as an inorganic mineral tie-coat for improving the bond between metal and organic topcoats.

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 MTC™ tie-coats can reduce chromate usage when topcoated with a chromate containing coating, or eliminate chromates altogether when used without a topcoat or topcoated with a chromate free coating.

PROCESS

The process, to form the MTC™ surface, is similar in set-up to electro-galvanization, but very different in performance, worker exposure concerns and environmental regulatory obligations. The process is accomplished by immersing a metallic (or an electrically conductive) component within an electrolyte containing water and a silicate containing solution. The electrolyte can be tailored by adding water-soluble additives. A current is passed through the electrolyte such that the component is employed as the cathode. Under these conditions, the part's surface interacts or reacts with the electrolyte to form a mineral layer. Components and parts such as fasteners, rivets, bolts, and nuts can be processed in conventional barrel plating systems, as shown in Figure 4.

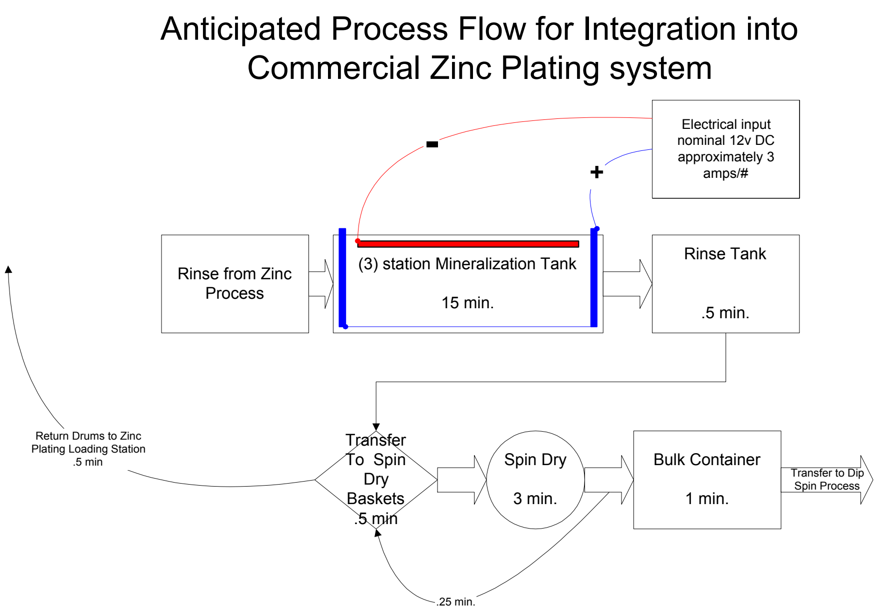


Figure 4: Typical Process Flow

Rack plating can process larger parts such as brackets, channel stock, weldments. Brush plating is a viable option for large surfaces or when immersion is not practical. Coil work is in development and holds great promise.

WASTE STREAM ISSUES

This technology offers the opportunity to eliminate tri & hex chromate and phosphate conversion coatings and their associated hazardous waste streams and related harmful risks. The electrolytic process that forms the MTC™ tie-coat does not generate a hazardous waste stream.

PERFORMANCE

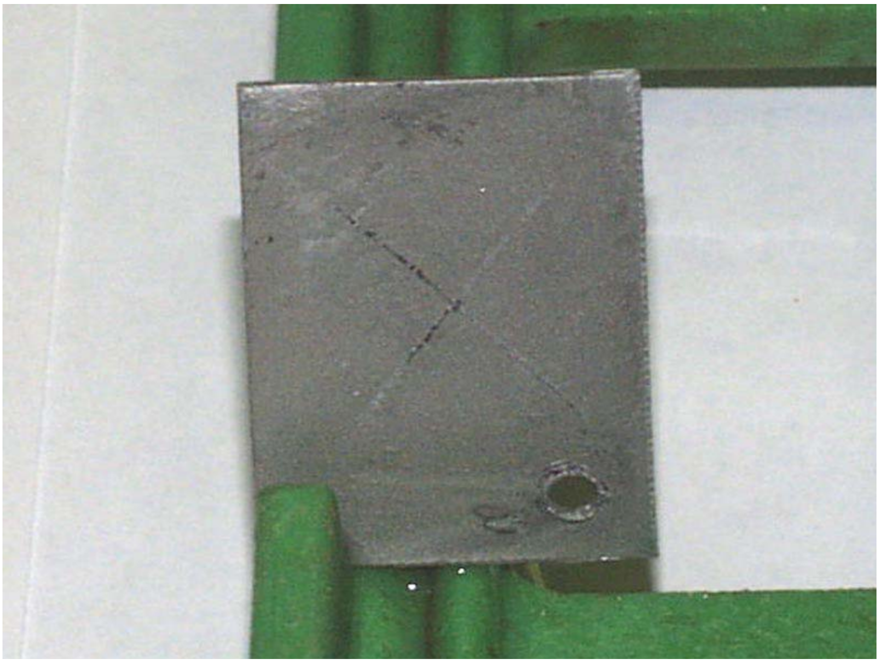
In addition to solving environmental problems caused by chromate/phosphate, the mineral tie-coat offers:

- Better Corrosion Resistance – in some cases doubling or tripling the ASTM B-117 performance of high performance topcoatings, including chromate-containing topcoats. The topcoat material used in the following illustration is a heat-cured epoxy that contains approximately 1% chromate.

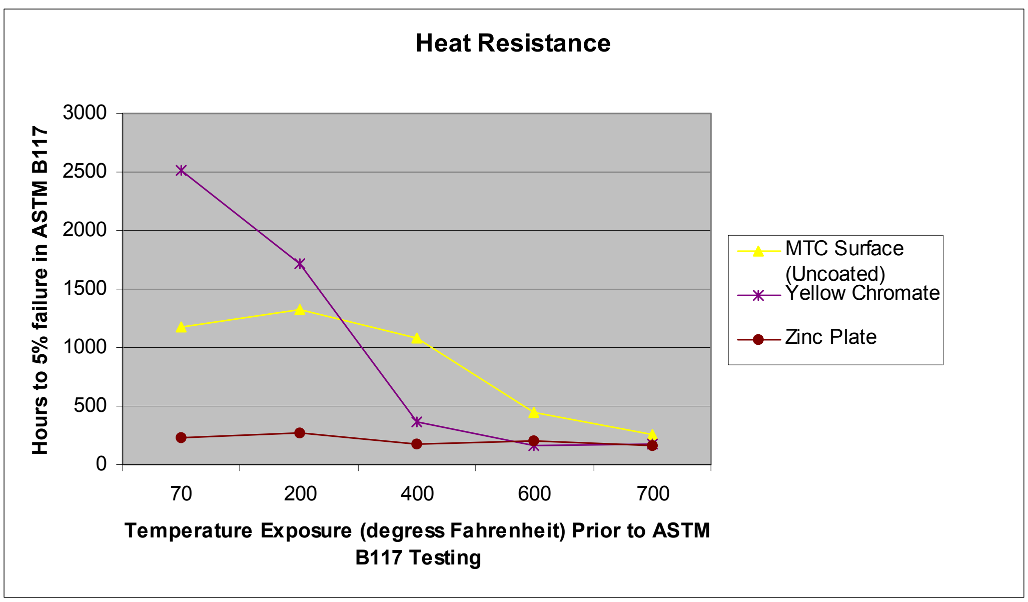
Conventional Zinc,Yellow Chromate, Heat Cured Epoxy topcoat After 3000hr ASTM B-117 Exposure

Zinc Electroplate With Elisha MTC™ and Heat Cured Epoxy Topcoat After 3000hr ASTM B-117 Exposure

- Better Adhesion to a Wide Range of Topcoats – via the advanced surface mechanical and chemical adhesion of the mineral tie-coat to coatings. Dry paint adhesion testing was performed per ASTM D3359 Method B (Cross Cut Taper Test) and the Elisha® process treated parts exhibited no loss of paint adhesion (5B Rating). Additionally, the corrosion performance is exceptional, as illustrated in the following picture of a scribed panel coated with the same topcoating as the previous figure at 3000 hours of ASTM B117 exposure.

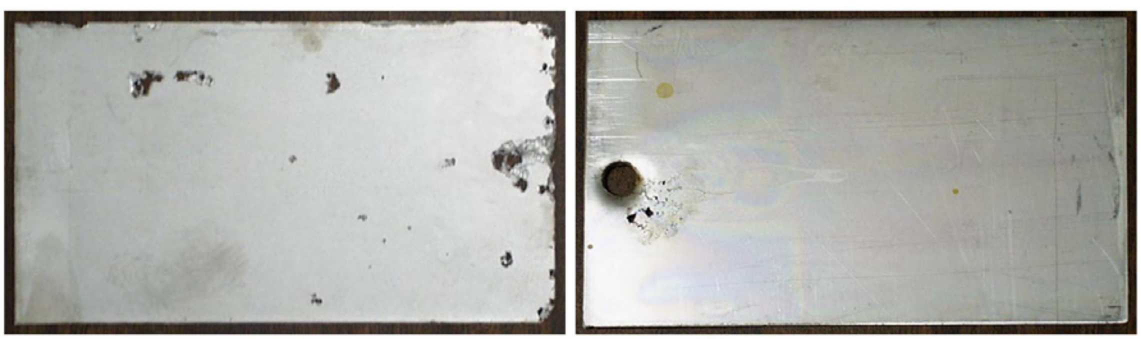


- Better Heat Tolerance – The Elisha MTC™ surface (uncoated) can withstand typical coating cure temperatures with no deterioration of corrosion performance. As illustrated in the following graph, chromate is highly sensitive to heat exposure



- Better Coating Surface Flexibility allows for greater functionality and survives secondary operations, such as "bucking" for rivet fasteners. The following photos show samples that sustained secondary forming (bucking of rivets) after 1008 hours exposure in ASTM B117 Salt Fog. The coating system used in this example is zinc plate, tie-coat, then high performance topcoat. The topcoat used is a heat-cured epoxy that contains 1% chromate. The left photo illustrates yellow chromate used as a tie coat, and the right photo documents the performance of MTC™ tie-coat.

- Better Stress Crack Corrosion (SCC) Performance exhibited by stainless steel SSC reduction of 50% on uncoated stainless steel. Additionally, ASTM G-48 testing indicated dramatic improvement in pitting resistance. Treated 304SS exceeded 120 hours of exposure without pitting. Typical 304 stainless steel experienced through hole pitting in 48-72 hours of exposure as documented in the following illustration.



304SS Control MTC™ Processed 304 SS

INTELLECTUAL PROPERTY

Multiple patents have been issued in the U.S. and abroad covering the mineral formed, as well as the process. Elisha Technologies Co., L.L.C. is a privately held member of the Orscheln Group, and develops corrosion solutions for industry, such as automotive, chemical, petroleum, marine and wire rope manufacturing. Elisha's patent estate includes 14 US patents and other issued, allowed, and pending patent applications in US and internationally, covering its corrosion technology and products. The U.S. Patent Office has issued patents and Notice of Allowance directed to the process and product of the subject technology.

INDUSTRIAL ACCEPTANCE

Coating systems that include the MTC™ tie-coat are currently undergoing durability testing automotive original equipment manufacturers. The current testing is focused on MTC™ coating systems because of the potential to completely eliminate chromate from the coating system (when used in conjunction with a chromate-free topcoating). Elimination of chromates in automobile manufacturing is consistent with the goals and requirements of the automakers' global environmental standards, which have been driven by the European Union End-of-Life Vehicle Directive. The testing for automakers is focused on high-performance coating systems for fasteners.

The acceptance into automotive is based on corporate environmental drivers as well as increased performance. Additionally, the MTC™ coating systems are being accepted into non-automotive markets, based solely on dramatic increases in topcoating performance.

FUTURE WORK

The current application of the Elisha coating is as a tie-coat. However, work is on going to explore the addition of other elemental cations into the lattice mineral structure to accomplish improved white rust performance on zinc, increased performance on other substrate metals, and as an adhesion promoter for metal-containing substrates.