Replacing Chromates

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Elisha Technologies developed new way to protect metals from corrosion using only silicates, common sand-like minerals found in the earth's crust. No chromium. No phosphate. Just better performance without environmental or regulatory worries.
A pilot line was installed to validate chromate replacement over zinc plating. This paper details the capabilities of the pilot line and documents the better adhesion, better heat tolerance, better flexibility and better stress performance of the environmentally friendly EMC™ coating.

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Since its inception in 1993, one company has actively pursued the development of mineralization technology. This process forms a thin mineral film on the surface of metals used as protection, decoration, insulation, and other untapped applications. The mineral coating surface has been shown to improve corrosion resistance of zinc systems even when used without a polymer topcoat system. 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.

1.0 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. In addition, this paper will highlight recent construction of a full capability zinc plating, mineralization processing, topcoating pilot line.

2.0 Performance

The mineralization technology 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.

2.1 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 1: 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.

2.2 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 mineralization technology coating.

Figure 2: 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.

2.3 Torque Tension Characteristics

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 preformed 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.

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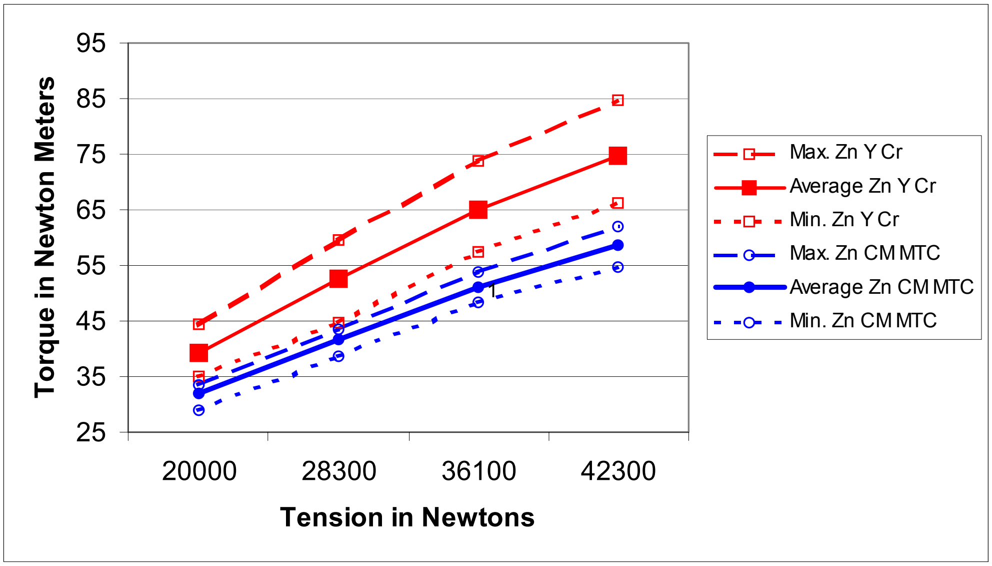


Figure 3 – Torque vs. Tension Comparison for Yellow Chromate and Elisha® EMC™

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.

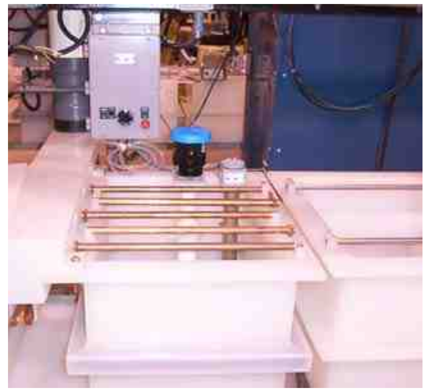
The lower values of torque for the mineral coated bolts indicate that there is less friction on the mineral coated surface than on the yellow chromate surface. The reference coefficient of friction for the mineral coated surface was 0.18 at 28300 Newtons and 0.23 at 28300 Newtons for the yellow chromate 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 Pilot Line Design and Construction

In order to validate the mineralization process on commercially available processes, it was necessary to design, construct and install a pilot line to zinc plate and apply the mineralization coating. Various topcoats can be added to duplicate actual applications.

The zinc plating process has the typical preparation (cleaning, rinsing, activation) and three commercially available zinc processes. These are non-cyanide alkaline zinc, acid chloride zinc, and a zinc alloy. If requested, a company's exact chemistry can be duplicated to validate the mineralization process.

The tanks were designed as single cell barrel process tanks and arranged to quickly adapt to two-cell rack plating process tanks. A center anode bar is added and the cathode bar is relocated and another added to provide a two cell rack plating arrangement.



The support structure is stainless steel and each module is in a separate dip pan. The first module is the loading / cleaning module which includes soak clean and electro clean.

Module 2 is an acid activate and a triple counter current rinse. The rinse tanks use permanently mounted stainless steel bars arranged to support the plating barrel or two racks.

The zinc plating module has three separate tanks for three separate chemistries. This allows non-cyanide zinc, acid chloride zinc and a zinc alloy bath to be immediately available. A workbar storage was provided below the ventilation hood for ease of bar storage and retrieval. Hose reels are located to provide D.I. water make-up to the tanks. All heated tanks are reinforced with metal box beams completely encased in polypro for corrosion protection.

Following the zinc plating is a three stage counter current rinse. In order to maintain maximum flexibility, all tanks are as similar as possible including the rinse tanks. The 3-stage rinse is by separate, externally plumb tanks.

Three holding tanks with a “cover provide the turn around point and work surface between zinc plating the the mineralization coating.
Prior to the mineralization coating is an acid activation and three stage rinse module.

Two mineralization tanks were arranged in the line and a third, spare tank provided for maximum flexibility. The parts are then transferred to a spin dryer basket.

If parts are being transferred from a barrel to spin dryer basket, a chute is provided to facilitate rapid loading.

Immediately after mineralization coating, parts go to a spin dryer, then rinse, then another spin dry. An unloading station is then provided.The original concept behind the mineral coating project was to extend Mineralization technology beyond a “passive” coating delivery system to an “actively”

It has been observed that the mineral coating surface provides the following benefits to samples processed in this line:

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

6.0 Patents and Intellectual Property Position

There is 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. Patent applications were began in 1997 to cover the proprietary mineralization technology process and related chemistries, proprietary mineral coating surface, and articles having a mineral coating surface. Two U.S. Patents covering the process were 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.