# **Coating Systems That Complement and Can Replace Chromates are Based on Zirconia**

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### Abstract:

For zinc plate and other substrates, coatings based on Group IV-A metals (titanium, zirconium, and hafnium) have now been developed. These systems use relatively innocuous chemistries in balance with effectiveness in protection. Parts treated with this technology pass long-term salt spray requirements. Bare corrosion protection, paint adhesion, and conductivity are obtained simultaneously. The final processing stage forms a stable inorganic polymer. In ASTM B-117 testing, zinc plated parts with trivalent chromate, and sealed with a Zirconia product pass at over 500 hours of exposure. Parts processed with Zirconia solutions alone meet many salt spray and other requirements.

#### **Background:**

Zinc metal deposits are used to coat ferrous substrates in order to retard the substrate from rusting. Zinc metal retards the substrate from rusting by acting as a sacrificial coating. The zinc deposit acts as the anode where oxygen is generated, and the ferrous substrate becomes the cathode where hydrogen is generated. Therefore, while the zinc deposit dissolves, the ferrous substrate is in a reduced state, and cannot be oxidized. As a result, the steel substrate will not rust as long as zinc is present.

In addition to the zinc deposit, hexavalent chromate conversion coatings are used to polish and smooth the zinc deposit to improve the brightness of the deposit. Also, the chromate conversion coating will increase the corrosion protection of the steel substrate. The chromate conversion coating is developed by the acid portion of the chromate reacting with the zinc, and hydrogen is generated. The generated hydrogen reduces a portion of the hexavalent chromium in the solution to form trivalent chromium. During the formation of this film, the pH rises at the interface of the film and zinc deposit. The rising pH causes the trivalent chromium to precipitate onto the zinc deposit forming a gelatinous film. As the gelatinous film forms, a small amount of the hexavalent chromium is entrapped in this film. The more hexavalent chromium trapped in the coating, the better the corrosion protection. The gelatinous film is then cured by using heat to remove a portion of the water, which in turn forms a barrier coating on the zinc deposit. The more hexavalent chromium trapped in the coating the better the corrosion protection.

Along with hexavalent chromate conversion coatings, trivalent chromium conversion coatings are also used. In the past, hexavalent conversion coatings were preferred over trivalent except for alkaline zinc deposits. Blue-bright or clear hexavalent conversion coatings on alkaline zinc deposits tend to turn yellow over time. The typical trivalent coatings do not yield the same corrosion protection as hexavalent due to the lack of hexavalent chromate being trapped in the coating. The unique feature of hexavalent conversion coatings is the ability to be self-healing against abrasion and scratches. This self-healing property is due to hexavalent chromium sealing pores and scratches as it is trapped in the conversion coating during the forming of the film on the zinc deposit.

As hexavalent chromium became more under pressure by OSHA and the EPA because of its high toxicity, the focus was turned to developing better trivalent conversion coatings to improve corrosion protection. The European ELV (End of Life Vehicles Directive) and RoHS (Restriction of Hazardous Substances) mandates further drove this focus. The automotive industry requested that hexavalent chromium be replaced, and trivalent chromate formulations became more prevalent in the zinc coating industry. In order to develop better corrosion protection, other metals had to be incorporated in the formulations to take the place of hexavalent chromium. To further increase the corrosion protection, the ambient operating temperature was raised to over 100°F to develop thicker coating thicknesses. The industry was then able to supply trivalent chromium coatings that yielded over 100 hours neutral salt spray corrosion testing.

Especially for the automotive industry, the 100 plus hours salt spray was not enough corrosion protection. In order to supply corrosion protection of 500 plus hours salt spray protection, organic coatings and organic coatings with silica were introduced as a topcoat for chromate coatings. There are several draw backs with these topcoats from curing times, excessive coating in threads making them difficult to use on assembly lines, and contamination of process tanks when rejected parts are stripped and re-plated.

## New Coating Systems:

Keeping in mind the customer complaints of the problems associated with organic coatings, our company was introduced to the co-author of this paper, and the work developed to replace chromate conversion coating on aluminum using Group IV-A metals (titanium, zirconium, and hafnium). Our discussions led to two primary goals:

- 1. Incorporate this chemistry to enhance the performance of trivalent chromates, and
- 2. Adapt this chemistry to replace the use of trivalent chromium all together.

These coatings are based on chemistries that have few issues with regard to waste disposal (in some areas neutralization prior to sewer is all that is required). They are relatively safe for the workplace and drop-in to existing equipment. No exotic conditions or equipment are required.

The primary chemistry is based on USP 5,759,244 and the simple concept that excessive fluoride in coatings with Group IV-A elements will inhibit formation of a metal oxide matrix.<sup>(1)</sup> Initial work was done on aluminum alloys. The Figure 1 below suggests a simple form of the barrier produced on drying.<sup>(2)</sup>

<u>Al</u> Aluminum Substrate	<u>Al<sub>2</sub>O<sub>3</sub></u> Aluminum Oxide	<u>Al<sub>x</sub>OZr<sub>y</sub></u> Alumino-zirconate	<u>ZrF<sub>n</sub>O</u> m Oxyfluro- zirconate	<u>M<sub>a</sub>O<sub>2</sub>M<sub>b</sub>O</u> 2 Oxy-metal[oid] Seal
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Figure 1: Hypothetical oxide gradient ( $M_{a,b}$  = metal and/or metaloid element, a may equal b).

These fully aqueous, cost-competitive coatings based primarily on zirconates have been developed to compete with chromate conversion coatings. In processing, an activation layer is formed over the metal or metal oxide surface to be treated. This layer incorporates components that can act to "heal" the final over-lying film and also promote attachment of a final inorganic "sealing" layer. The final stage in this process forms a stable inorganic polymer. The coatings have been shown to considerably enhance paint adhesion. At the same time, unpainted aluminum alloys shows no pitting in ASTM B-117 salt spray in over 500 hours of exposure. Conductivity and long-term paint performance are superior in head-to-head testing with other chromate alternatives.<sup>(3)</sup>

Now, analogous systems have been developed to provide protection to zinc plate. The products developed so far are used in conjunction with trivalent chrome to get passage of 1000 hours in salt spray. Fully non-chrome systems for protection of zinc plate give considerable life in B-117 testing. The goal for the next generation of completely non-chrome protection of zinc plate is passing 500 hours of B-117 testing.

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<u>Stage 1</u>	Stage 2	Time to "Failure"		
Non-chrome	No seal	< 100 hours		
Trivalent chrome	No seal	$\leq$ 100 hours		
Trivalent chrome	Zirconia seal	$\leq$ 500 hours		
Trivalent chrome	Zirconia/trichrome seal	$\geq$ 500 hours		

Table 1: Zirconia and trivalent chrome systems.

Panels and parts are processed in solutions at 80-110  $^{\rm o}F$  and dried for 10 minutes at 140  $^{\rm o}F.$ 

1. U. S. Patent 5,759,244 "*Chromate-free conversion coatings for metals*," June 2, 1998, C. E. Tomlinson.

2. C. E. Tomlinson, "*Coatings that Compete with Chromates*," *Proc. AESF Annual Conf.* (2003).

3. "*Recent Alternatives to Chromate for Aluminum Conversion Coating*," National Center for Manufacturing Sciences (April 2002), www.ncms.org.

# Biography

Charles Tomlinson received his bachelors in Biology from Ball State University in 1978 and a master's degree from BSU in chemistry in 1991. He has several patents in the area of surface treatment that are related to zirconates. He has worked as Senior Research Chemist, Editor, and Consulting Chemist and in other capacities for companies such as Ball Corporation, Union Carbide, Circle-Prosco, Huethig Publishing and American Analytical Laboratories. In 1997 he founded Natural Coating Systems, LLC with the specific aim of researching, developing and licensing effective, environmentally sound coating chemistries. Natural Coating Systems has several market-specific licensees and has joined efforts with Benchmark Products, Inc. to develop zirconia chemistries for protection of zinc and zinc plate.

# Biography:

Steven Erwin is technical director at Benchmark Products, Inc., P.O. Box 68809, 5425 West 84<sup>th</sup> Street, Indianapolis, IN 47268. After graduating from the University of Evansville with a BA in chemistry, Erwin spent several years as a quality control and plating bath analyst for a major supplier. He later joined Evansville Plating Works and subsequently became plant manager. In 1982, Erwin joined Benchmark Products as a field technical service representative; he became technical director in 1988. Erwin holds a Class "C" license in the State of Indiana for treatment of industrial wastewater.