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Zinc Conversion Coatings
TECHNICALLY speaking

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Historical Perspective and New Developments Regarding Conversion Coatings and Seals for Zinc Deposits

Producing quality parts that meet a customer’s aesthetic and corrosion protection demands is what every zinc metal finisher strives for. Ongoing changes in government regulations in both the United States and abroad have made it increasingly difficult for the zinc metal finisher to satisfy a customer’s needs while adhering to new policies.

As globalization becomes more and more widespread, metal finishers will have end users across the world, and the parts they finish must be capable of meeting the regulations of the country where the product will be used. Chemical suppliers have invested significant resources, resulting in the development of new conversion coatings and seals that allow the zinc metal finisher to overcome the challenge of new regulations while meeting customer needs.

REGULATIONS IMPACTING CONVERSION COATINGS AND SEALS FOR ZINC

It is well known that, for many years, hexavalent chromium [Cr(VI)]-based conversion coatings were the preferred choice for the corrosion protection of zinc. The relatively low cost, ease of use, self-healing properties, and finish color options were the main reasons for its widespread use. In addition, the demands for corrosion protection were lower in the past—48 to 96 hours to 5% white corrosion through the typical neutral salt spray test (ASTM-B117) was usually sufficient.

Although Cr(VI) has many advantages, it has been documented as a known carcinogen and is toxic to the environment. OSHA’s permissible exposure limit (PEL) for Cr(VI) is 5 μg/m³, measured as a time-weighted average over an 8-hour period. The limit was established in 2006 and was a decrease from the previous PEL of 52 μg/m³ originally recommended in 1943 and adopted by OSHA in 1971. It is higher than a PEL of 0.25 μg/m³ requested by the both interest group Public Citizen and the United Steelworkers Union, and higher than OSHA’s original goal of 1 μg/m³.

OSHA found that implementing such a low limit could cause financial difficulty for the electroplating industry, and would be impossible for hard-chrome electroplaters to achieve. Public Citizen and the United Steelworkers continued to fight to have the limits reduced to 0.25 μg/m³. Recently, the 3rd U.S. Circuit Court of Appeals upheld the 5 μg/m³ PEL for Cr(VI).³

In addition, the European Union has implemented several directives. Regulations on the Restriction of the use of Hazardous Substances in electrical and electronic equipment, more commonly known as RoHS, set limits on the amounts of cadmium, lead, mercury, hexavalent chromium, polybrominated biphenyls (PBB), and polybrominated diphenyl ethers (PDBE) that can be used to manufacture electronics and electrical devices. The limits currently are 1,000 ppm or 0.1% by weight for all materials except cadmium, which is lower at 100 ppm or 0.01% by weight. The RoHS directive made it impossible for parts processed using Cr(VI) to be used in devices sold in Europe, except for certain military and medical exemptions.

The End of Life Vehicle (ELV) directive also prohibits use of the same materials for the automotive industry. In addition, the Waste Electrical and Electronic Equipment (WEEE) directive makes it the responsibility of the manufacturer to properly dispose of all products made using the hazardous materials listed in the RoHS legislation. These directives were implemented to provide an incentive to manufacture products without the use of hazardous materials.⁴

Cobalt has some environmental restrictions. Preliminary studies have shown that it may be a carcinogen to humans and causes respiratory problems with acute
exposure to high levels. It is used in many of the trivalent chromium [Cr(III)]-based conversion coatings to enhance corrosion protection. During 2008, the worldwide prices of cobalt were drastically affected due to a shortage in the global market. This economic phenomenon forced most of the chemical suppliers to research new technologies by looking at both raw material substitutes and reducing cobalt concentrations in their formulas. The final products needed to be comparable to the previous formulations and achieve similar or improved performance results. While cobalt currently does not have any PELs, replacement products are now available in anticipation of changes in future regulations and to combat possible cost increases on conversion coatings.

**CHROMIUM WASTE TREATMENT**

As mentioned earlier, Cr(VI) is toxic, and if untreated effluent water containing Cr(VI) is directly discharged into the environment, public health would be seriously affected. Such a scenario would be a violation of both local and federal laws. The EPA limits the release of total Cr into stream water to 0.1 ppm, and many local regulations have more stringent limits for both Cr(VI) and Cr(III). Therefore, effluent water treatment is necessary for metal finishers.7

Treatments for removal of chromium from effluent water may include: anaerobic bio-filter beds that use microorganisms to extract chromium from the solution; ion exchange resins that selectively remove metal ions of chromium, zinc, iron, and others; active carbon filtration, which absorbs some metals and organic contaminants from waste water; and chemical precipitation, which is the most commonly used method. The chemical precipitation method occurs in two phases: first reduction of Cr(VI) to Cr(III) and second the precipitation of Cr(III). Common reducing agents used in the first phase are sulfur dioxide (SO₂), sodium bisulfite (NaHSO₃), sodium meta-bisulfite (Na₂S₂O₅), and ferrous sulfate (FeSO₄). The following equation illustrates the reaction that takes place when sulfur dioxide is used:

\[ 3\text{SO}_2 + 2\text{H}_2\text{CrO}_4 + 3\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{(SO}_4)_3 + 5\text{H}_2\text{O} \]

It is necessary to control the reaction by maintaining the pH between 2 and 3 using sulfuric acid (H₂SO₄).

The second phase to precipitate the Cr(III) is accomplished by increasing the pH. Typically, calcium hydroxide [Ca(OH)₂] or sodium hydroxide (NaOH) is added to the effluent to maintain a pH above 8.0 for the precipitation of chromium hydroxide to occur. The following equation illustrates this reaction using calcium hydroxide:

\[ \text{Cr}_2\text{(SO}_4)_3 + 3\text{Ca(OH)}_2 \rightarrow 2\text{Cr(OH)}_3 + 3\text{CaSO}_4 \]

Chelating agents in Cr(III) conversion coating formulations can complicate the waste treatment process by slowing the precipitation of chromium hydroxide. To solve the problem, other chemicals, including ferric chloride, ferric sulfate, aluminum chloride, or aluminum sulfate salts, can be substituted instead.
Cr(VI) was significantly higher at 52 µg/m³. These first-generation Cr(III) hydroxides.\(^8\) Replacing Cr(VI) conversion coatings with Cr(III) conversion coatings can simplify the waste treatment process by eliminating the reduction reaction described in the first phase.

**REPLACEMENTS FOR HEX-CROME CONVERSION COATINGS**

Cr(III) conversion coatings were available in the 1970s but were not as effective in the protection of zinc when compared with Cr(VI). Sales of these products were minimal because, at that time, the PEL for conversion coatings used peroxides, typically hydrogen peroxide, in the formulations as oxidizing agents.

The working conversion coating needed to contain 3–35% hydrogen peroxide solution by volume, and required constant replenishment. In addition, these conversion coatings would require additional amounts of the peroxide due to losses of 0.1–0.4% volume of hydrogen peroxide per hour of downtime. The rate of consumption of hydrogen peroxide was depended on the amount of zinc in the solution. Therefore, as the concentration of zinc ions increased, the consumption of peroxide increased.

This was a significant cost to the electroplater, especially for a product that gave dismal results in neutral salt spray testing. The cost, lack of environmental laws— in addition to the in situ production of Cr(VI) during the formation of the conversion coating—are reasons why the product was not preferred.\(^9\)–\(^11\)

Second-generation Cr(III) conversion coatings ended the use of strong oxidizing agents like hydrogen peroxide and incorporated the use of both known complexors and chelators of Cr(III). This includes, but is not limited to, fluorides, oxalic acid, and malonic acid. Moreover, other transition metals were incorporated into the formulation— particularly cobalt. These formulations were introduced in the late 1990s to early 2000s when regulations for Cr(VI) were increasing and electroplaters were scrambling to find products that met both OSHA’s PEL and the RoHS, WEEE, and ELV directives. As previously noted, stricter limits for both Cr(VI) and total Cr were implemented during this time period.\(^11\)

Second-generation Cr(III) conversion coatings still had some per-
formance disadvantages when compared with Cr(VI), including, but not limited to, loss of corrosion protection, tight operating ranges, low scratch resistance, and high operational costs. Furthermore, if chelating agents were used, it made waste treatment difficult. Figure 1 shows neutral salt spray results per ASTM B117 to 5% white corrosion of Cr(VI) conversion coatings versus second-generation Cr(III) coatings.

Although there were significant disadvantages, especially in barrel-plated parts, the results show that in most cases the Cr(III) conversion coatings were comparable to Cr(VI) conversion coatings. Third-generation Cr(III) conversion coatings were similar to their second-generation counterparts, but with the addition of nanoparticles to the solution. Advantages of the system were increased hours in neutral salt spray to white corrosion and self-healing properties previously lost from Cr(VI) conversion coatings. Figure 2 shows a comparison of second- and third-generation trivalent chromates.

Current research has led to new innovations in conversion coatings. A Cr(III) conversion coating without cobalt is available as future regulations change or cobalt costs increase. Another commercially available yellow Cr(III) conversion coating is stable in UV light. Lastly, there are black conversion coatings that do not contain chromium. These formulations are proprietary, and little information is available to the public regarding their performance properties. Figure 3 shows typical salt spray results from these formulations.

**SEALS USED WITH CONVERSION COATINGS**

Parts can be processed through a seal after the conversion coating is applied. The coating is applied using either a dip or spray application, usually no longer than one minute and then typically dried without rinsing. Some advantages of using seals are increased corrosion resistance of parts by an additional 50-100 hours to white corrosion in neutral salt spray (Fig. 4), as well as providing uniformity of appearance. A disadvantage is the topcoats can leach the color from the conversion coating previously applied to the part.

Most of the coatings available are based on silicates. Some also contain inorganic compounds in their formulation. Patents exist on using silicates as a conversion coating replacement. However, higher standards from automotive and other industries have made this application very difficult as a replacement for conversion coatings.

Various torque tension specifications for fasteners can be met using proprietary waxes in the formulation of the topcoat. The waxes are either water-soluble or form emulsions. Different formulations are made to meet the requirements specified by the individual customer. In some cases, custom products can be made.

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- Aluminium anodizing
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CONCLUSIONS
The added cost and step of waste treatment, government regulations, and lower performance characteristics are all reasons for zinc metal finishers to switch from using conversion coating based on Cr(VI). Significant progress has been made in the development of both Cr(III) and non-Cr conversion coatings as replacements. Topcoats can give additional corrosion protection and other benefits not previously seen in Cr(VI) conversion coatings, and they can help meet torque tension requirements from a customer’s specification. As regulations change and end-user specifications become more challenging over time, chemical suppliers will continue the development of new products to meet future customer needs.

NOTES

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