Replacing Hexavalent Chromium

By Paul C. Wynn & Craig V. Bishop

The use of passivations based upon Cr(VI) are under review, because of pending regulatory changes. In this article, alternatives available that are most likely to succeed are examined.

Chromate passivation systems containing hexavalent chromium compounds are extensively used in electroplating and metal treatment processing. They impart many beneficial and essential characteristics to metallic substrates and to deposits obtained from a number of techniques, such as mechanical and electrodeposition.

Cr(VI)-based passivations exhibit a number of desirable characteristics (Table 1). They will passivate the surface of zinc and zinc alloy electrodeposits with a thin film that provides end-user benefits such as color, abrasion resistance and increased corrosion protection. When damaged, these Cr(VI)-based systems possess a unique "self healing" property. This means that soluble hexavalent chromium compounds contained within the passivation films will re-passivate any exposed areas. For the applicator Cr(VI) passivations are easy to use, can be bulk-applied often by a single stage immersion, and are inexpensive to make up and operate.

The need to replace chromates based upon Cr(VI) is gathering momentum. Hexavalent chromium salts are classified as hazardous substances (toxic, sensitizing and carcinogenic); they are environmentally and toxicologically hazardous. It would therefore be desirable to replace these products with a suitable "environmentally friendly," commercially acceptable alternative.

For some time it has been widely accepted that sufficient evidence exists for the carcinogenicity of Cr(VI) compounds in humans and animals. Certain forms of Cr(VI) have been found to cause increased respiratory cancer among workers. This has produced regulatory control for their use and disposal, which has ensured that industry can legally continue to use the technology. This has produced a lack of desire for industry to adopt suitable alternative strategies.

It is interesting to note that not all forms of chromium present a danger to humans. According to some, there are forms of Cr(VI) that may be noncarcinogenic, such as dichromates of sodium and potassium. Cr(III) is an essential nutrient that helps the body use sugar, protein, and fat.[1] An intake of 50 to 200 µg per day is recommended for adults. We should therefore appreciate that not all chromium is "bad," and guard against a witch-hunt.

Table 1
Desirable Characteristics of CrVI Passivates

- Prevents oxide formation
- Provides color
- Slow corrosion in prototypic tests (salt spray, roof top, etc.)
- Provides adhesion for organics (paint)
- Helps prevent corrosion of painted surfaces (creep)
- Conductive
- Thin
- Flexible
- Lubricious
- Easily applied
- Not flammable
- Stable for weeks or months
- Durable
- Resilient (repairs itself)
- Re-hydrated after baking
- Coats in recesses
- Easy to strip
- Inexpensive equipment
- Single tank
- Inexpensive

End-of-Life Directive

The European Union's "end-of-life" vehicle directive[2] aims to reduce waste disposal, through waste prevention from vehicles and ensure where practicable the reuse, recycling and recovery of end-of-life vehicles and their components. The Directive requires introduction of a certificate of destruction for end-of-life vehicles, allowing authorities to control the destiny of end-of-life vehicles, while the automotive manufacturer meets all or a significant part of the take-back costs.

Provisions apply from:

- July 1, 2002 for market vehicles from that date, and
- January 1, 2007 for vehicles before July 1, 2002

A prohibition on the use of heavy metals such as hexavalent chromium in materials and components of vehicles will exist from January 1, 2003.

From 2000, a concession of 2g of Cr(VI) per vehicle has been available, allowing the interim continued use of Cr(VI) because it was recognized that suitable replacement technology is still being implemented. One European-sited auto manufacturer conducted a detailed vehicle tear-down, and established that less than 1g Cr(VI) was present on its vehicles. This is believed to be the first vehicle manufacturer to conduct a physical analysis to assess the current situation.

Biestek and Weber[3] identified the chromium content of chromate coatings, and through their work it becomes possible to calculate the maximum permissible amount of Cr(VI) components. For instance, electrozinc and yellow Cr(VI) has a film weight of 12 mg/dm^2, of which 70 percent is identified as Cr(VI). This equates to 73 ft^2 for 2g per vehicle (see Table 2).

Many technological advances are often driven by the effects of legislation, and the competitive nature of the automotive industry, but there exists tremendous interest in this topic in other industries. Does this finally point to

Table 2
Biestek and Weber

	mg/dm^2	Cr	CrIII	$mgCrVI/dm^2$	$dm^2/2g$	$ft^2/2g$
Zn clear	1	30%	90%	0.27	7407	797
Al clear	3	30%	80%	0.72	2778	299
Al yellow	10	35%	70%	2.45	816	88
Zn yellow	12	35%	70%	2.94	680	73
Mg yellow	15	38%	70%	3.99	501	54
Zn olive	23	42%	70%	6.762	296	32

Table 3
Passivation Strategies to Replace CrVI

- CrIII—Difficult to build thickness on Zn but alloys do allow significant increases in thickness. Colors are 'different.' Fate of CrIII is uncertain.
- Organic Films—Large variety. Coating thickness, uniformity, and color are concerns.
- Inorganics—Salts/oxides of Al, Ti, V, Mo, Wf, Co, Ce, Zr, etc. produce colored coatings. Do poorly in salt spray.
- Oxides—Silicates, phosphates, etc. Complement CrVI, CrIII, and organic coatings. Can't be used alone.
- Organometallics—Stability in water is limited to a few compounds. Very expensive chemicals.
- Multiple Steps—Combinations of the above, very promising, capital expense may be involved.

Table 4
Trivalent (CrIII) Observations

- Salt spray on zinc not quite as good as conventional.
- Iridescent colors aren't identical to CrVI.
- Doesn't repair itself.
- Still has chromium.
- Salt spray on alloys is very good.
- Easy application
- Thin, conductive, very long-lived.
- **In most respects, it is a suitable substitute for hexavalent chromium.**

the end in acceptable use of hexavalent chromium passivation?

Does it Mean "The End?"

The impact of this directive has galvanized the efforts of global automotive companies that supply to the European economy. They are responding to these concerns and pending changes in legislation by evaluating alternatives to Cr(VI)-based passivation systems. One North American-based automotive company has stated that it wants to remove the issue of Cr(VI) completely from its vehicles. This means that it currently plans to specify chromium-free based passivations for new vehicles components from 2005. This, however, leaves the interim problem of Cr(VI) replacement for 2003 compliance.

Alternatives

A group of commercially acceptable alternatives to Cr(VI) products were patented in the 1990s,[4] but until recently the finishing industry showed little interest in this availability. Many strategies to replace Cr(VI) have been proposed (Table 3), but today's interest is now focused upon passivation films obtained from trivalent chromium compounds. In most respects, Cr(III) closely resembles the characteristics of Cr(VI) and is a suitable alternative (Table 4).

Many will be familiar with the clear, blue passivation films on electrozinc deposits, which have been successfully obtained from products based upon trivalent chromium compounds since their commercial adoption in the 1970s. These have developed in reliability and performance in recent times, having found particular favor with alkaline non-cyanide zinc users. Their increased material and process control cost is balanced by their longevity and color consistency. Many end-users have changed their specification requirements in favor of this.

Trivalent Chromium

The adoption of Cr(III) systems would, therefore, be a logical step in the development of replacement technology. Iridescent colors can be achieved, but are different from those obtained from Cr(VI) (Fig. 1). The changing attitude of end-users means that color shade is becoming less of an issue, which greatly assists the finisher to justify installation of these products.

There are some issues with Cr(III) vs. Cr(VI) on zinc. For the end-user, color is not identical to Cr(VI), corrosion resistance is reduced, and there are also no "self healing" benefits. For the finisher, the current crop of products being introduced into the market need to be operated at elevated application temperatures of 30–60°C (86–140°F), although they remain relatively easy to operate. Research and practical experience indicates that the most suitable medium for use of this technology will be zinc alloy deposits.

Corrosion test numbers are significantly better for Cr(III) over zinc alloy than for Cr(VI) over zinc.[5] In fact, high alloy zinc/nickel deposits represent the highest level of performance, even after deposit post-forming and heating. This means that current end-user specification requirements can still be achieved with this technology change; in fact, both white/zinc and red/ferrous protection are improved.

The corrosion performance of chromate passivation films is frequently evaluated by the 5-percent neutral salt spray test which, although recognized as having limitations, is to date the most accepted test method for performance testing. Many companies and organizations have issued their own specifications controlling test conditions—the most obvious change being the adoption of a heat test, typically 120°C (248°F) for 24 hr, prior to salt spray. However, ASTM B117[6] remains the most accepted and recognized test standard. Despite the introduction of other performance tests, such as the Cyclic Corrosion Tests and the Kesternich test DIN 50018, this neutral salt spray standard remains the universally accepted method for defining performance variations between coating systems.

Chrome-free Passivations

Totally non-chromium passivations[5] have been under development for some time, and there exists a number of proposed alternatives. Organic films, inorganic salts, oxides and organometallics have all been proposed as suitable materials. All have problems when used as individual steps, so their individual adoption seems unlikely. The best chance seems to be with the use of a combination of these in a multiple-step process.

After zinc or zinc alloy deposition, the multi-step process requires the

Trivalent (CrIII) colors: iridescent & black.

application of a color, such as achieved from a non-chromium inorganic salt. A bonding layer to provide adhesion is required; an organometallic coupling agent could be used. The film is then dried prior to application of a corrosion-inhibiting top coat such as an acrylate or silicate, followed by a second dry operation (the wet-dry-wet-dry method). Currently, when applied over a zinc alloy, this represents the most suitable non-chromium process. However, even over high alloy zinc/nickel, it is not possible to offer the same level of white corrosion performance compared to that achieved from zinc and Cr(VI).

Summary

There is a growing acceptance that industry will adopt trivalent chromium Cr(III) as an intermediate solution to the replacement of Cr(VI). It offers the best available technology not requiring excessive cost, and when applied over a zinc alloy can achieve suitable or superior corrosion protection against zinc with Cr(VI) passivation. Cr(III) systems over zinc alloy are the easiest to apply and the most enduring. Non-chromium is the ultimate goal, but first, compromises must be made for acceptance of this technology. Of these others most likely to succeed, it will be the multiple-step wet-dry-wet-dry method. *P&SF*

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