Trivalent passivation systems - Meeting legislation and exceeding performance requirements
By Alan Gardner, global marketing manager, MacDermid Industrial Solutions

Introduction
Zinc and zinc alloy plated coatings are applied to fasteners in order to give sacrificial corrosion protection to the base metal. However, these sacrificial coatings are very susceptible to corrosion themselves particularly in conditions of high humidity. Corrosion products formed on zinc type deposits are generally referred to as ‘white rust’. Prevention of white rust is usually achieved by application of a conversion coating, traditionally based on hexavalent chromium compounds. These treatments convert the metal surface into a complex mixture of chromium (including hexavalent) compounds giving excellent corrosion resistance.

Hexavalent chromium compounds, however, have long been recognised as carcinogenic. This, coupled with the need to increase the recyclability of vehicles (ELV Directive) and consumer electronics (RoHS) led to the adoption of trivalent based passivation systems in the middle of the last decade, but the story isn’t yet finished as today new regulations, including REACH (SVHC), are raising questions which may be answered by new developments in passivation technology.

Why pasivate?
The primary advantages of hexavalent systems included ease of use, low cost, ability to passivate various deposits (including zinc alloys) and colours. Draw backs consist of factors such as poor application in the supply chain, no advancements to improve corrosion resistance and extremely poor resistance to thermal shock.

Conversely trivalent passivates, which offer at least the same resistance to white corrosion, have exceptional thermal shock resistance, a traceable supply line (www.zinklad.com) and continued advancements to increase corrosion resistance. The various finishes, film thicknesses and relative concentrations of chromium compounds can be seen in the table below.

What is a passivate?
Passivate films are complex films consisting of chemicals such as:

- Oxides of hexavalent chromium (hexavalent based formulations).
- Oxides of trivalent chromium (both hexavalent and trivalent formulations).
- Oxides of divalent metals such as cobalt.
- Organic complexants (some trivalent formulations).
- Water.

Depending on the finish desired, a combination of these will be blended to achieve different characteristics (i.e. blue, iridescent, black). The film will evenly coat the zinc layer providing a barrier coating. This can be seen in Figure 1. A film of some 300nm sits homogenously on the zinc layer.

<table>
<thead>
<tr>
<th>Type</th>
<th>Film thickness nm</th>
<th>Cr6+ (mg/dm²)</th>
<th>Cr3+ (mg/dm²)</th>
<th>Total Cr (mg/dm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clear (trivalent)</td>
<td>25 - 80</td>
<td>Zero</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Iridescent (trivalent)</td>
<td>200 - 400</td>
<td>Zero</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Iridescent (hexavalent)</td>
<td>250 - 500</td>
<td>0.7</td>
<td>2.0</td>
<td>2.7</td>
</tr>
<tr>
<td>Black (hexavalent)</td>
<td>250 - 100</td>
<td>0.7</td>
<td>9.3</td>
<td>10.0</td>
</tr>
</tbody>
</table>

How passivates protect the zinc layer
Zinc is a reactive metal, which gets oxidised (corroded) in the presence of humidity and oxygen. Unlike nickel or stainless steels, the formed zinc oxide is a soft, voluminous and porous corrosion product, which does not prevent further corrosion through the zinc layer (see Figure 2). Therefore, the zinc metal needs protection by chemically formed mixed metal oxide films. The passivate films are hardly soluble in water or water based salt solutions used as anti-freezing agents, thus provide a tough barrier coating.

Thermal shock
Thermal shock tests involve subjecting components to high temperatures [e.g. 150°C for one hour] before neutral salt spray testing (ASTM B117). This is to simulate the conditions ‘underhood’ where very high temperatures are encountered on components that are located near to the engine. Trivalent passivates perform very well in this test. The older hexavalent passivates lose some 90% of their corrosion performance. This loss of performance is due to dehydration and ‘cracking’ of the passivate film.
Trivalent passivates

Trivalent passivates are generally distinguished in two groups: thin film (typically blue passivates) and thick film (typically iridescent or black passivates).

Figure 3 - Types of trivalent passivation

1. The typical passivate film thickness of a thin film passivate is about 80nm – 100nm resulting in an even blue appearance and prevents zinc corrosion between 24 hours – 72 hours in NSS tests.

2. Thick film passivate films form about 4 – 5 times thicker films (thickness between 300nm – 400nm) resulting in an iridescent appearance and prevent white corrosion in neutral salt spray in excess of 72 hours for zinc, 120 hours for zinc-iron and 150 hours for zinc-nickel.

Table 4 – Comparative values to 5% white rust for passivated coatings

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Zinc</th>
<th>Zinc-iron</th>
<th>Zinc-nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hours to white rust</td>
<td>&gt;72</td>
<td>&gt;120</td>
<td>&gt;150</td>
</tr>
</tbody>
</table>

Market adoption

So which industries have adopted these systems? Before the year 2000, trivalent chromium passivates were almost exclusively for zinc plated finishes designed to have ‘chrome-like’ appearances. This would include fasteners for internal automotive trim and domestic hardware, performance passivation for exterior automotive and construction fasteners being the domain of yellow, green and black hexavalent chromium.

Figure 5 - Before 2000, most zinc plated components were passivated in trivalent chromium for a ‘chrome-like’ appearance

After the year 2000 iridescent ‘thick film’ systems were introduced. Testing by leading automotive companies confirmed their suitability as replacements. During the last decade most American, European and Japanese companies have now replaced hexavalent based passivates and specify exclusively trivalent. This includes specifications such as GM 3044 & 4700, Ford WSS M21 P17 & P51, Renault 01 71 002 and VW TL 153, 217 & 244. Fasteners for other industries such as construction and hardware followed, driven by their concerns and also the reduction in platers offering older hexavalent passivated finishes.

Future developments

Future developments will be based on reducing the environmental impact and eliminating metals, such as cobalt, which are now becoming a concern. In respect of the longer term, passivation systems which are completely free of chromium are currently being investigated with the aim of improving performance, cost and ecological impact.

High temperature versus lower temperature technology

The first generation of trivalent thick film passivates operated at 60°C – 70°C. This temperature range had been required to form the needed passivative film thickness at the fixed immersion times range (60 seconds – 90 seconds) of existing plating lines. Although these passivates delivered high performance, their operating costs were higher due to the heating input required.

Recently, new organic and inorganic complexants have been developed. These increase the film formation rate at lower operating temperatures (30°C - 40°C). The advantage is the similar higher performance at lower operating costs.

Cobalt free - Beside mixed oxides of zinc and trivalent chrome, passivative films contain small amounts of cobalt zinc oxide and cobalt chrome oxide. These oxides increase the hardness and temperature resistance of passivative films. By the addition of small amounts of cobalt compounds, the thermal shock resistance of the passivative film is increased to 150°C.

However, cobalt salts are under threat of regulation. The European CLP (classification of cobalt salt) classifies the toxicity of several cobalt salts to carcinogen cat. 2. Therefore an increasing interest on cobalt free passivates has been observed in Europe.

Since 2003, high performance cobalt free, trivalent chromium passivates have been commercially available for zinc-nickel deposits. Today the first cobalt free black passivates have been introduced, also for zinc-nickel deposits. Research continues to develop similar systems applicable to zinc plated deposits, particularly in respect to being resistant to thermal shock tests.

Chromium free passivates - At this time, the replacement of trivalent chrome to non-chrome technologies is being tested in indoor applications such as electronic components that are used in dry environments. Several patents and publications on non-chrome conversion coatings indicate further research on this topic, particularly to develop passivates for higher volume fastener applications such as automotive and construction.

Summary

Environmental directives have driven the change from hexavalent to trivalent passivates in the last decade. Typically these new systems, which are a complex combination of organic and inorganic chemicals, offer superior corrosion resistance. This is particularly true when they are subjected to thermal shock treatments. Available in colours such as blue, iridescent and black, they retard the formation of white corrosion products and therefore the onset of base (red) metal rusting. Originally used in lower performance requirements, they are now the dominant technology for high performance fastener coatings.

However, the story does not end there. Already new trivalent chromium passivation solutions operate at lower operating temperatures than the original systems. Additionally new directives are driving further change in passivated coatings. Materials that will be restricted include cobalt salts. Already the first non-cobalt passivates are being introduced into the market, particularly for zinc-nickel coatings.

Additionally developments in total non-chromium passivates is underway, with interior applications such as electronic fasteners already under going in-house testing.

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