Experiences of a First Generation Trivalent Hard Chrome Process
Hard Chrome Introduction
Why hard chrome?
Hard chrome benefits

**Hard chrome** coatings have **many beneficial properties**

Very hard

Superior tribological properties

Chemical resistance

Corrosion resistance

Hard chrome deposits are popular due to the unique properties they imbue standard substrates enabling them **to work** longer, **better** and **under tougher conditions** than they would normally survive in
Hard chrome benefits

Hard chrome plating processes are popular due to their simplicity and robustness

Cheap
Short
Fast
Simple

Hard chrome plating is one of the simplest and cheapest processes in electroplating giving a deposit with excellent physical properties
Typical hard chrome properties
Deposit properties

Although Hard chrome coatings are typically smooth and shiny in appearance they are typically micro-cracked due to a shrinkage in the crystal structure during and shortly after plating.

High hardness of 800 – 1,100 HV 0.05

Typical thickness 8 – 40 µm (5 – 1,000µm)

Micro-cracked structure

Excellent adhesion on metallic substrates
Why Cr(VI) hard chrome alternatives?
Toxicology
SVHC substances

The European Chemicals Agency risk assessment report I.05.16 mentions a large number of risks of negative health effects for Cr(VI) substances

Acute toxicity
Skin, eye, respiratory tract irritation
Skin sensitisation
Occupational asthma
CMR toxicity

ECHA SVHC support document, 2nd Dec 2010 classifies chromium trioxide as a Cat. 1A carcinogen and Cat. 1B mutagen
Legislation
REACH

This legislation requires Cr(VI) substances to be authorised for use.

The sunset date for authorisation is the 21st September 2017.

There are consortia and individual companies making authorisation applications.

<table>
<thead>
<tr>
<th>Name</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium trioxide</td>
<td>1333-82-0</td>
</tr>
<tr>
<td>Chromic acid</td>
<td>7738-94-5</td>
</tr>
<tr>
<td>Dichromic acid</td>
<td>13530-68-2</td>
</tr>
<tr>
<td>Sodium chromate</td>
<td>7775-11-3</td>
</tr>
<tr>
<td>Sodium dichromate</td>
<td>10588-01-9</td>
</tr>
<tr>
<td>Sodium dichromate dihydrate</td>
<td>7798-12-0</td>
</tr>
<tr>
<td>Potassium chromate</td>
<td>7789-00-6</td>
</tr>
<tr>
<td>Potassium dichromate</td>
<td>7778-50-9</td>
</tr>
<tr>
<td>Ammonium dichromate</td>
<td>7789-09-5</td>
</tr>
</tbody>
</table>

April 17 2013: Inclusion in Annex XIV
January 2015: CTAC Finished drafts
May 2015: CTACsub Submissions
March 21 2016: Latest Application Date
September 21 2017: Sunset Date
Why alternatives?
Remove toxic substances

**Cr(VI) substances** are **under immense** regulatory **pressure** due to their toxic nature

**Restriction** of Cr(VI) substances in the future is **to be expected**

Suitable **alternatives** are **required** to offer the same benefits to plated parts

A **Cr(III) hard chrome** process is the most sought after **alternative**

Chrome plate but using benign substances
Requirements of alternatives
Main requirements

No Toxic Substances | Wear Resistance | Corrosion Resistance

Additional desirable features
Cheap, Fast, Short, Simple...
Cr(III) hard chrome
Introduction
Typical Cr(III) issues from literature
Difficult to plate

**Plating direct from Cr(III) solutions is not possible**

- Complexing agents required
- Anodic etching not possible
- Extensive pre-treatment required

Cr(VI) generation at anode
- Measures required to prevent this

- Short bath lifetime
- Macro-cracked deposit

\[
\begin{align*}
\text{Cr}(^{3+}) & \quad \text{OH}_2 \\
\text{H}_2\text{O} & \quad \text{OH}_2 \\
\text{H}_2\text{O} & \quad \text{OH}_2
\end{align*}
\]
1st generation Cr(III) hard chrome
Process Overview
CMR to non-CMR

Hazard Symbols

More complicated bath make-up but...

Major reduction in hazardous substances employed

No ‘skull and cross bones’
## Parameter differences

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cr(VI) process</th>
<th>Cr(III) process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr content</td>
<td>100 - 150 g/l</td>
<td>15 – 30 g/l</td>
</tr>
<tr>
<td>Sulfate</td>
<td>2 – 5 g/l</td>
<td>27 - 55 g/l</td>
</tr>
<tr>
<td>2\textsuperscript{nd} Catalyst</td>
<td>100%</td>
<td>-</td>
</tr>
<tr>
<td>Complexing Agent</td>
<td>-</td>
<td>100 - 300 g/l</td>
</tr>
<tr>
<td>Buffer</td>
<td>-</td>
<td>100%</td>
</tr>
<tr>
<td>Additives</td>
<td>-</td>
<td>100%</td>
</tr>
<tr>
<td>pH</td>
<td>&lt;1</td>
<td>3.5 – 6.5</td>
</tr>
<tr>
<td>CD</td>
<td>20 – 90 A/dm\textsuperscript{2}</td>
<td>20 – 60 A/dm\textsuperscript{2}</td>
</tr>
<tr>
<td>Temperature</td>
<td>50 – 65 °C</td>
<td>45 – 60°C</td>
</tr>
<tr>
<td>Deposition Rate</td>
<td>0.6 – 1.6 µm/min</td>
<td>0.5 – 1.0 µm/min</td>
</tr>
</tbody>
</table>

*Cr(III) hard chrome processes have a larger amount of additives compared to Cr(VI) processes – adding to the cost*
## Plating tank requirements

<table>
<thead>
<tr>
<th>Main Tank</th>
<th>Ancillary Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tank material</strong></td>
<td>Ah meter</td>
</tr>
<tr>
<td>PP (PVDF)</td>
<td>Required</td>
</tr>
<tr>
<td><strong>Anodes</strong></td>
<td>Exhaust</td>
</tr>
<tr>
<td>Inert MMO / Graphite</td>
<td>Required</td>
</tr>
<tr>
<td><strong>Rack material</strong></td>
<td>Filtration</td>
</tr>
<tr>
<td>Ti clad Cu</td>
<td>Required</td>
</tr>
<tr>
<td><strong>Heating</strong></td>
<td>Solution agitation</td>
</tr>
<tr>
<td>Ceramic PTFE Titanium</td>
<td>Required</td>
</tr>
<tr>
<td><strong>Cooling</strong></td>
<td>pH control</td>
</tr>
<tr>
<td>Required</td>
<td>Required Automatic</td>
</tr>
<tr>
<td><strong>Rectifier</strong></td>
<td>Dosing</td>
</tr>
<tr>
<td>12 – 16 V capacity</td>
<td>Required Automatic</td>
</tr>
</tbody>
</table>
Comparison
**Plating speed**

![Graph showing plating speed comparison between Cr(III) and Cr(VI) processes](image)

*Cr(III) process has the same plating speed as a leading Cr(VI) process*
Bath lifetime

Excellent bath lifetimes achieved with good bath stability

- >800 Ah/l
- >200kAg plated
- >6 months

Good process control and long bath lifetimes possible
Hardness

The Cr(III) process has a similar hardness to conventional Cr(VI) hard chrome but less than proprietary Cr(VI) hard chrome processes

- Cr(III) 700 – 850 HV 0.05
- Conventional Cr(VI) 800 – 1,000 HV 0.05
- Proprietary Cr(VI) 900 – 1,100 HV 0.05
Appearance

The Cr(III) deposit is shiny and bright. The deposit is able to take a good polish. Similar appearance to Cr(VI) deposit. More macro-cracks.
Corrosion resistance
Macro-crack solution

The *macro-cracked* structure means minimal corrosion resistance of the part.

To improve corrosion resistance of the part a corrosion resistant base layer is required.

*Nickel underlayer* the favorite choice.

This gives a **step change in corrosion resistance**

>1,000 hours NSST instead of 24 – 200

The process becomes longer due to the extra process steps required.
Superior chloride resistance

The Cr(III) deposit contains a small amount of carbon. This imbues the coating with better chloride resistance compared to Cr(VI) deposits.

Combined with the Nickel underlayer gives the whole coating a completely better class of corrosion resistance.

After 240 hours calcium chloride testing
Cr(III) Process Summary
## Summary overview

<table>
<thead>
<tr>
<th>Process</th>
<th>Conventional Chrome</th>
<th>Proprietary Cr(VI) Hard Chrome</th>
<th>Cr(III) Hard Chrome (+ Nickel underlayer)</th>
<th>Electroless Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Plating Speed</strong></td>
<td>17 - 20</td>
<td>40 - 90</td>
<td>40 - 60</td>
<td>10 – 25</td>
</tr>
<tr>
<td><strong>Hardness</strong></td>
<td>800 - 1,000 HV0.05</td>
<td>900 - 1,100 HV0.05</td>
<td>700 - 850 HV0.05</td>
<td>520 - 750 HV0.1</td>
</tr>
<tr>
<td><strong>Hardness</strong> (annealed 2h@200°C)</td>
<td>750 - 1,000 HV0.05</td>
<td>850 - 1,100 HV0.05</td>
<td>920 - 1,100 HV0.05</td>
<td>930 - 1,080 HV0.1</td>
</tr>
<tr>
<td><strong>Wear Resistance</strong> (Taber Test)</td>
<td>Good</td>
<td>Excellent</td>
<td>≈ Proprietary</td>
<td>10 - 20% of Proprietary</td>
</tr>
<tr>
<td><strong>Corrosion Resistance</strong> (NSST)</td>
<td>Acceptable</td>
<td>Good</td>
<td>Very Good (Due to Ni layer)</td>
<td>Very Good</td>
</tr>
<tr>
<td><strong>Process Control</strong></td>
<td>Easy</td>
<td>Easy</td>
<td>Medium</td>
<td>Medium</td>
</tr>
</tbody>
</table>
Summary

A 1st generation Cr(III) hard chrome process is now a possibility

Release in Autumn 2016

The process is stable, well understood and has a long lifetime

Corrosion resistance requires the use of a Nickel underlayer

Better class of corrosion resistance

The process is longer, more complicated and more expensive than current Cr(VI) processes

A 1st generation Cr(III) hard chrome process can be used as an alternative for Cr(VI) hard chrome, but with some limitations
Thank you

for your attention!

Contact
Global head office
Atotech Deutschland GmbH
Erasmusstraße 20
10553 Berlin – Germany
+ 49 (0) 30 349 85 0
info@atotech.com
www.atotech.com