Arnaud de Vooys

Trivalent chromium plating, anode and cathode

Making packaging steel in the 21st century
ECCS packaging steels

- ECCS = Electrolytically Chromium Coated Steel
- ECCS excels in adhesion to organic coatings (lacquers, polymer coatings)
- ECCS is used in the production of DRD (Drawn & Redrawn) two-piece cans and components that do not have to be welded, such as ends, lids, crown corks, twist-off caps and aerosol bottoms and tops
ECCS electroplating process

Tata makes ca. 200-300 ktonnes/year
Say 200.000.000 m²

Typical coil dimensions:
- Length: 10000 m
- Width: 1.2 m
- Thickness: 0.2 mm

Coating weight:
- 50 – 100 mg m⁻² Cr
- 7 – 35 mg m⁻² CrOₓ

Line speed:
- Up to 10 m s⁻¹

Total rectifier current:
- 50000 A

Deposition time:
- A few seconds
Cr6+ replacement

- ECCS requires hexavalent chromium electrolytes, a.k.a Cr6+
- Hexavalent chromium is considered a hazardous substance
- In response to REACH legislation, Tata Steel R&D has developed an electrolyte based on Cr3+ and formic acid

\[ \text{Cr}_6^+ + 3e^- \rightarrow \text{Cr}^3+ \]
ECCS replacement

How hard can it be?

Pretty hard actually: ECCS works very well

Search for alternatives (brittle, electrochem. active, soluble, poisonous, etc.)

In the end, we went back to Chrome with different application
Characterising Cr layer, FIB-TEM cross section

Smooth part, homogeneous Cr layer

Cr layer, lower density than Fe

50 nm
Characterising Cr layer, FIB-TEM cross section

Rough part

Chrome follows surface roughness

Steel shows surface crack

ION Meeting 2016
Characterising Cr layer, FIB-TEM cross section

Rough part

Steel had small surface crack

Chrome is deposited in the crack

Good “throwing power”
Does it work?

“the proof of the pudding is in the eating”

Cr layer was coated with PET laminate and compared to PET laminated ECCS
Material was shaped into cans, filled with de-aerated brine, sterilised, stored for two weeks and evaluated visually
One danger: the anode

In theory it is possible to oxidise Cr3+ to Cr6+ at the anode (steel coil is the cathode)

Need to check to avoid danger
Results of long-term galvanostatic experiments

<table>
<thead>
<tr>
<th>anode</th>
<th>Cr(VI) mg l(^{-1})</th>
<th>current efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>150 ± 15</td>
<td>ca. 12.6</td>
</tr>
<tr>
<td>MMO + IrO(_2) + Ta_2O_5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

-applied current density = 92 mA (ca. 5000 A m\(^{-2}\)) for 3600 s

Cr6+ is not just a theory, but can happen with the wrong anode
Core of electrolyte is Cr$^{3+}$ and formic acid

$$\text{stable complex} \quad \text{formate} \quad \text{destabilised complex}$$

$$\text{Cr(H}_2\text{O)}_6^{3+} + \text{HCOO}^- \rightarrow \text{[Cr(H}_2\text{O)}_5(\text{HCOO})]^2+$$

Formic acid on Pt

- Reaction 1: formic acid to CO2
- Reaction 2: formic acid to CO, which sticks to the electrode

CO is a poison to the reaction (not just for humans)
Hence the drop in current = drop in reaction rate
Cr$^{3+}$ and formic acid on Pt

- No CO$_2$ formation: Cr(III) complex blocks formic acid
  So it adsorbs, ‘sticks’  $\rightarrow$ Pt does something to Cr$^{3+}$

question: is ‘sticking’ the only thing that happens?
Cr3+ and formic acid on Pt

Mass spectrometer measures no CO2 nor CO → Formic acid has nothing to do with it → Must be Cr3+

Cr3+ oxidation… …uh oh
MMO: sodium sulphate + sodium formate + chromium(III) sulphate

No ‘sticking’ of Cr$^{3+}$ $\rightarrow$ no oxidation of Cr$^{3+}$ $\rightarrow$ no Cr$^{6+}$
Conclusions

- Cr(III)-formate adsorbs strongly on platinum
- Cr(III)-formate is oxidised at platinum
- Platinum is therefore catalytically active for Cr(VI) formation
- Cr(III) adsorption and Cr(VI) formation also occurs in the absence of formate (not shown here)
- Adsorption of Cr(III)-formate is absent on MMO and consequently no Cr(VI) is formed at MMO
21st century ECCS

21st century ECCS formally presented at Tinplate Conference in London (international fair for steel packaging producers and users)

Launch: soon