Knowledge–based anticipation and substitution of coatings and surface treatments

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Auto industry response to ELV, RoHS, etc.

- The industry coordinated, and did a good job of eliminating the use of Cd, chromates, and lead–free solders
- RoHS and ELV were painful, but looking back at them they were specific rules covering specific materials
  - Sometimes hard to find alternative materials
  - But you knew whether or not they were problems
- Changes improved industry REACH position
  - Eliminated Cr⁶⁺, Cd, Pb
REACH in one page

- **Registration**: Every chemical must be registered, including toxicity and use
  - Can only be used if registered **for that use**

- **Authorization of SVHCs (Annex XIV)**
  - Eliminate Substances of Very High Concern (SVHCs)
  - You can only use them if authorized (expensive, limited duration, until a clean substitute found)

- **Restriction** (e.g. Cd, Hg, Pb)
  - Use can be limited, forbidden for certain applications, or forbidden entirely

The only chemical exempt from REACH is “perfectly safe” water – responsible for a higher human toll than any other (except TNT?)
REACH is a different kettle of fish

- It covers everything
- You never know what will be hit tomorrow
- SVHCs can be authorized for use, but authorization is expensive and limited
- There are lists of SVHCs
  - But chemicals are dropping from the market, not because they are a problem, but because they are not worth registering, or nobody registered them for your application
  - Some chemicals are likely to drop from US market if lose EU market
Some rough statistics

- It is likely to be possible to substitute most organics.
- There are few good alternatives to many inorganics.
- Even fewer for metals such as Cr and Zn.
Why worry about coatings?

- Because coatings have to protect against corrosion they often fall afoul of Legg’s Law.
  
  Legg’s Law: “Any material active enough for corrosion control will be a health and environmental hazard.”

- Even if the coating is benign, the process chemicals to deposit it may not be:
  - Chrome plating uses chromic acid which has recently been proposed for authorization under REACH.

- Coating industry critical but small:
  - Chemicals for coatings are minor uses not worth the cost and risk for large chemical companies.
  - Coating formulators, users have limited funds to bear REACH costs.
    - Conversion coatings were only registered at 11th hr as market too small for large producers.
Coatings likely to be a problem

- Cd and chromates – no longer used in auto
- Organics of all sorts as so many minor and trace constituents critical to performance
  - Paints, sealants, adhesives
- Ni plates
  - Most Ni salts classified as SVHCs by "read-across"
  - Several Co salts on candidate list for authorization
- Long term we see pressure building on
  - Every corrosion control material
    - Mn, Mo, Zr, Ce, Cr\(^3+\)
  - Cu (Ag is a better conductor anyway!)
  - Nanoparticle–filled coatings
  - Zn plating (what do we need steel for?)
**REACH supply chain issue**

- **Chemical**: 1,000 Tonnes/yr Defined as SVHC
- **Minor side product**
- **Liability risk, registration cost**
- **Authorization cost?**
- **Decision**: Register as intermediate (internal use only)

- **Chemical Supplier**
- **Formulator**
- **Other chemicals**
- **Options**:
  - Find new supply
  - Register ($$)
  - Authorization? ($$$)
  - Reformulate ($$)
  - Withdraw

After Scott Fetter

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What are the practical effects of materials regulation?

- Classifying more and more chemicals as SVHCs
  - Chemicals drop from market as soon as put forward as SVHCs
- Many chemicals will no longer be sold as not worth the cost/risk of registration, even at 1,000 tonne/yr level
  - Many more will be lost as go to 100, 10, 1 tonne levels

<table>
<thead>
<tr>
<th>Chemical</th>
<th>%</th>
<th>Brian Norton, SUR/FIN 2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy Resin</td>
<td>31.30</td>
<td></td>
</tr>
<tr>
<td>Strontium Chromate Pigment</td>
<td>20.00</td>
<td>At Risk: SVHC Listing</td>
</tr>
<tr>
<td>Other Colour Pigments</td>
<td>3.38</td>
<td></td>
</tr>
<tr>
<td>Anti-Settlement Agent</td>
<td>1.17</td>
<td>At Risk: Volume/Cost</td>
</tr>
<tr>
<td>Dispersing Agent</td>
<td>0.50</td>
<td>At Risk: Volume/Cost</td>
</tr>
<tr>
<td>Extender</td>
<td>17.30</td>
<td></td>
</tr>
<tr>
<td>Aromatic Hydrocarbon</td>
<td>15.85</td>
<td>At Risk: Solvent Emissions</td>
</tr>
<tr>
<td>Esters</td>
<td>10.50</td>
<td>At Risk: Solvent Emissions</td>
</tr>
</tbody>
</table>

- List of SVHCs will constantly increase
- Even completely benign chemicals are being lost from the market as a result of REACH
- Constant uncertainty, high R&D cost, high qualification and implementation costs
What can we do about it?

- Minimize risk, cost by better test and design methods
- Use databases to identify alternatives
- Plan on how/when to change
- Keep on top of technology/material developments
- Keep on top of technology/material developments
- Anticipate from lists, databases, suppliers
- Be aware of chemicals used to make them
- Be aware what is in your products
### Electroless Ni-B Restricted Substances

<table>
<thead>
<tr>
<th>Substance Name</th>
<th>CAS Number</th>
<th>Amount</th>
<th>Declaration Amount (%)</th>
<th>Substance Rating</th>
<th>Legislation Name</th>
<th>Legislation Rating</th>
<th>Effective Date</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>7440-02-0</td>
<td>main</td>
<td>100</td>
<td>Ban or with conditions</td>
<td>TU Directive 2013/39/EU (Amendment Directive)</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Coating</td>
</tr>
<tr>
<td>Chromium</td>
<td>12036-17-5</td>
<td>main</td>
<td>10</td>
<td>Caution</td>
<td>CERCLA Hazardous substances</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Coating</td>
</tr>
<tr>
<td>Nickel Nitrate</td>
<td>13517-78-1</td>
<td>main</td>
<td>10</td>
<td>Caution</td>
<td>CERCLA Hazardous substances</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Coating</td>
</tr>
<tr>
<td>Sodium Nitrate</td>
<td>1313-82-4</td>
<td>main</td>
<td>10</td>
<td>Caution</td>
<td>CERCLA Hazardous substances</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Coating</td>
</tr>
<tr>
<td>Silver Nitrate</td>
<td>7440-54-6</td>
<td>main</td>
<td>10</td>
<td>Caution</td>
<td>CERCLA Hazardous substances</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Coating</td>
</tr>
<tr>
<td>Thallium oxide</td>
<td>12034-49-1</td>
<td>main</td>
<td>10</td>
<td>Caution</td>
<td>CERCLA Hazardous substances</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Coating</td>
</tr>
<tr>
<td>Thallium nitrate</td>
<td>7440-05-4</td>
<td>main</td>
<td>10</td>
<td>Caution</td>
<td>CERCLA Hazardous substances</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Coating</td>
</tr>
</tbody>
</table>

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Email: klegg@rowantechnology.com
# What is in the coating? Granta Coatings Database

<table>
<thead>
<tr>
<th>Substance name</th>
<th>CAS number</th>
<th>Amount</th>
<th>Declaration Amount (%)</th>
<th>Substance rating</th>
<th>Legislation name</th>
<th>Legislation rating</th>
<th>Effective date</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>7440-02-0</td>
<td>main (10-100%)</td>
<td>100</td>
<td>Banned with conditions</td>
<td>EU Directive 96/62/EC Ambient Air Framework</td>
<td>n.a.</td>
<td>Banned with conditions</td>
<td>June 27, 2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>REACH Annex XVII - Restrictions (filtered)</td>
<td>n.a.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CERCLA hazardous substances</td>
<td>n.a.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>EPCRA Section 313, Toxic Chemicals</td>
<td>n.a.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>The EPA's List of Lists (LoL)</td>
<td>n.a.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Thallium</td>
<td>7440-28-0</td>
<td>main</td>
<td>100</td>
<td></td>
<td>NTP - Report on Carcinogens (RoC)</td>
<td>Caution</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ASD-STAN Declarable Substances List</td>
<td>Caution</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>EPCRA Section 304, Extremely Hazardous Substances</td>
<td>Caution</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>REACH Annex XVII - Restrictions</td>
<td>Banned with conditions</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GADSL</td>
<td>Banned with conditions</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Joint Industry Guide (JIG)</td>
<td>Caution</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Often the problems will not be the major constituents, but the essential minor or even trace chemicals.
Anticipating change

- Lists
  - 67/548/EEC, List of Lists, SIN
  - REACH Annex XIV Candidates
  - Suppliers
- Similarity to existing SVHCs
- Database
  - Shows current restrictions
  - Potential for future restrictions
- Some changes unanticipated
  - Especially as register smaller quantities (so far only 1,000 tonne)

I’ve got them on the list, They’d none of them be missed
Keeping up with technology

- NASF (National Assoc for Surface Finishing)
  - Coating technologies
  - Environmental regulations US, EU
- Trade magazines
- ASETSDdefense covers alternatives to Cd, Cr$_6^+$, VOCs for military and aerospace
  - Not very useful for most commercial automotive
- Coatings database for comparisons
- We are considering whether there is enough of a market to provide service for keeping up with regulations and materials alternatives
Granta Coatings Database provides performance and usage data. Coatings never as well-defined as bulk materials and alloys.

<table>
<thead>
<tr>
<th>Performance</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Maximum service temperature</strong></td>
<td>1800 °F</td>
</tr>
<tr>
<td><strong>Galvanic potential (sea water)</strong></td>
<td>-0.54 to -0.2 V (estimate)</td>
</tr>
<tr>
<td><strong>Corrosion resistance type</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Coating corrosion rate (seawater)</strong></td>
<td>Medium</td>
</tr>
<tr>
<td><strong>Corrosion: B117 hours to red rust</strong></td>
<td>240 hr</td>
</tr>
<tr>
<td><strong>Corrosion: Beach weeks to red rust</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Corrosion: G85 hours to red rust</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Strain-to-failure</strong></td>
<td>High</td>
</tr>
<tr>
<td><strong>Hardness</strong></td>
<td>650 to 1300 HV</td>
</tr>
<tr>
<td><strong>Electrical resistivity</strong></td>
<td>15 to 140 μohm cm</td>
</tr>
<tr>
<td><strong>Hydrogen embrittling?</strong></td>
<td>No</td>
</tr>
<tr>
<td><strong>Hydrogen bakable?</strong></td>
<td>Not Applicable</td>
</tr>
<tr>
<td><strong>Environmental embrittlement?</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Reduces VOCs?</strong></td>
<td></td>
</tr>
</tbody>
</table>
Planning

- Most alternatives are more expensive, often not as effective (at least not at first), process often requires more care, better QC
  - E.g. Zn sealers: \( Cr^6+ \rightarrow Cr^3+ \rightarrow \text{non-Cr} \rightarrow \text{organic} \)
    - How long will each option last in EU then US?
    - How broad a supply base?
    - Should you migrate to the next closest option for better availability, lower cost and technical risk?
    - Hold out for better performance, lower cost?
    - Wait and see what everyone else does?
    - Or make a big jump in hope it will last longer in the market and maybe give you “green” kudos?
More efficient testing

- Testing and redesigning are expensive
- How do you know a new material will work?
- Wear and corrosion tests very poor indicators of service performance
  - Even worse when alternatives work differently so mechanisms are not the same
    - \( \text{Cr}^{6+} \ vs \ \text{Cr}^{3+} \ vs \ \text{Ce} \) as corrosion inhibitors
    - Hard Cr vs E–Ni composite vs thermal spray for wear
- People are trying to develop better tests (esp corrosion), but will be 5+ years
  - Really hard to do a 2–yr service test in a month
Predictive design

- We have data and models to predict stress, thermal properties
- But all we have for corrosion are rules of thumb for corrosion
- One of the biggest problems is galvanic corrosion between dissimilar materials
  - Rules of thumb not much use as change coatings and their surface treatments
    - On galvanic chart where is Zn vs Zn8Ni vs Zn15Ni vs Al vs Zn/Al–filled polymer vs Mg rich primer?
      - With Cr³⁺ vs Mn vs Zr vs Mo inhibitor?
These data are very old and only for flowing seawater. Most systems have static water condensation or seawater accumulation. Currently we rely on half-century old galvanic data for our coatings. New coatings and treatments require better data to use them successfully.
What if you connect an EN plated plug to a Cd plated socket?

What if water accumulates around the connector, not over the whole backplane as in B117?

Al backplane corrodes right at socket

Electroless Ni

Zn15Ni on socket corrodes to protect electroless Ni on connector

Al backplane

What if you connect an EN plated plug to a Cd plated socket?

What if water accumulates around connector, not over whole backplane as in B117?

Great! Now, what will EN-PTFE do? We have no data for that yet
Integrating performance data, corrosion prediction, design

Website: www.rowantechnology.com  Email: klegg@rowantechnology.com
Environmental regulations will make coatings and corrosion control increasingly difficult
Toward a brave new Cr-free, Zn-free world

- No Zn
- = no steel use
- = no industrial society
- But we can all become great artists again!