Non-Cr paint systems on commercial aircraft – current status and future direction

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Non-Cr paint systems on commercial aircraft - current status and future direction

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ASETSDefense 2014: Sustainable Surface Engineering for Aerospace and Defense, 18-20 Nov 2014, Fort Myer, VA.
Overview
Boeing Commercial Airplanes

Cr$^{6+}$ Overview
Historic & Current use of Cr$^{6+}$
Chromate use and alternatives
Strategy for Sunset Date
Near term systems and qualifications
Gaps and long term developments
Cr$^{6+}$ Overview

Cr$^{6+}$ is a known carcinogen and an excellent corrosion inhibitor

**Carcinogenic**
- REACH Sunset Date 2017-2019
- Hazardous Waste
- OSHA Permissible Exposure Limit 5 $\mu$g/m$^3$

**Gold Standard of Corrosion Inhibitors**

- Paints & Coatings
- Conversion Coatings
- Corrosion Inhibiting compounds
- Sealants

[Diagram showing the process chemistries and the use of Cr$^{6+}$ in different applications]
Historic & Current use of Cr\(^{6+}\)  
Boeing Commercial Airplanes

Cr\(^{6+}\) containing materials have been used on all metal parts, including aluminum, titanium, and stainless steel alloys.

Over 75% of the plane is coated with chromated materials.

Successful Cr\(^{6+}\) reductions via:

- Substrates and Design changes (composite materials, titanium, guidelines, etc.)
- Alternative materials (products and processes)
# Chromate Alternative Successes and Targets

<table>
<thead>
<tr>
<th>Chromated material/process</th>
<th>Alternatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromic acid anodize</td>
<td>Boric sulfuric acid anodize (BSAA), Accelerated sulfuric acid anodize (ASAA)</td>
</tr>
<tr>
<td>Deoxidizers</td>
<td>Ferric/nitric deoxidizers</td>
</tr>
<tr>
<td>Paint strippers</td>
<td>Mechanical, benzyl alcohol based. In work: laser &amp; atmospheric plasma</td>
</tr>
<tr>
<td>Composite primers</td>
<td>BMS10-103</td>
</tr>
</tbody>
</table>
| **Exterior primer (BMS10-72, MIL-PRF-23377)** | BMS10-72 NC  
In work: searching for Cr₆⁺ equivalency                                        |
| **Non-structural interior primer (BMS10-11 Ty I lite)** | In work: XBMS10-147                                                             |
| **Structural interior primer (BMS10-11 Ty I, MIL-PRF-85582, MIL-PRF-23377)** | In work                                                                     |
| Bond primer (BMS5-89, BMS5-137)      | In work                                                                     |
| Assembly level primer                | In work                                                                     |
| BMS10-20 (SAE-AMS-C-27725)           | In work                                                                     |
| BMS10-79                             | In work                                                                     |
| BMS5-95                              | In work                                                                     |
Strategy for Sunset Date
Non-Cr for BMS10-11, BMS10-20, BMS10-72/BMS10-79, BMS5-89

Multidimensional approach:

- **Non-Cr Inhibitor Development**
  - Boeing novel inhibitors, models & screening
  - External materials

- **Paint Vendor**
  - Formulate/re-formulate

- **Continuous Screening**
  - Detail & Assembly
    - 5000 hrs NSS
    - Fluid Resistance
    - Adhesion

- **Qualification Testing**
  - XBMS10-147 Non-Structural Interior
    - Goal 2015
  - Non-Cr BMS10-11 Assembly Structural
    - Non-Cr BMS10-20 Ti bonding
    - Non-Cr BMS10-79 Ti bonding
    - Non-Cr BM55-95 Ti bonding
    - Goal 2016
  - Non-Cr BMS10-11 Direct Replacement
    - Non-Cr BMS10-72 Al bonding
    - Non-Cr BM55-89 Al bonding
    - Non-Cr BM55-137 Al bonding
    - Goal 2018
  - Non-Cr BM55-89 Ti bonding
  - Non-Cr BM55-137 Ti bonding
  - E-Coats

Formulation feedback

**Test top candidates to the spec requirements, match product performance to application.**

**Low-Risk Applications**
- Easy to inspect
- Non-structural
- Low risk of corrosion
- e.g. Payloads, Systems LRU
- e.g. Bond primer for Ti

**Medium-Risk Applications**
- e.g. Assembly primer

**High-Risk Applications**
- Difficult/impossible to inspect
- Life of airplane
- Structural
- High risk of corrosion
- e.g. bond primer for Al
Corrosion Protection System Development

Materials development
- CSIRO, Boeing, Suppliers, universities
- Inhibitor species
- Polymer resins
- Formulation nuances

Testing/evaluation
- Boeing, universities, CSIRO
- Accelerated exposure protocols
- Advanced evaluation techniques

Modeling tools
- Boeing, CSIRO, universities
- Inhibitor mechanisms
- Transport processes
- Service performance prediction
Continuous Screening Overview

Materials Process Example:

Test panel stack-ups:

Screening Tests:
- Dry/Wet Adhesion. BSS7225, ASTM D 714.
- 30 days 120F condensing humidity. BSS7225, ASTM D 714
- 30 day hydraulic fluid soak. BSS7263, ASTM D 714
- 5000 hours in Neutral Salt Spray chamber. BSS7249, ASTM D 714

Candidates that look good in screening, move to production batch testing
Continuous Screening
Medium/High risk zones

Four candidates are moving to production batch testing to BMS10-11 Ty I, BMS10-20, BMS10-72, & BMS10-79

<table>
<thead>
<tr>
<th>Assembly Primer:</th>
<th>Control</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>7075-T6 Bare Al</td>
<td>0%</td>
<td>22%</td>
<td>0%</td>
<td>3%</td>
<td>1%</td>
</tr>
<tr>
<td>Alodine 600</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BMS10-11 Ty I Green</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BMS10-11 Ty I Yellow or Candidate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Detail Primer:</th>
<th>Control</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>7075-T6 Bare Al</td>
<td>0%</td>
<td>33%</td>
<td>0%</td>
<td>1%*</td>
<td>1%*</td>
</tr>
<tr>
<td>Alodine 600</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BMS10-11 Ty I Green or Candidate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*2000 hr exposure
XBMS10-147  
Low-corrosion risk zones

Technical Requirements
▪ Corrosion resistance criteria based on MIL-PRF-23377, but with a wider scribe.
  ▪ Neutral Salt Spray (NSS) for 2000 hrs, no pitting & minimal oxides within the scribe.
▪ Compatibility requirement testing based on application

Opportunities
▪ Interior payloads primer for non-structural parts (brackets, clips, stow-bin rails, etc…) – All models
▪ Systems Line Replaceable Units (LRU), such as ducts, valves, pumps, etc…) – 777X

Status:
▪ 7 candidates tested, top candidate reformulated for improved adhesion (blisters)
  ▪ Reformulation successful, candidate currently in qual testing

Compatiblity requirements by application:
**XBMS10-147**

**Top Candidate**

**Curing Solution Reformulation**
- 5 candidates screened
- Tested Fresh vs Aged 4 months @ 120F
- Chemistry vs mechanical properties

**Liquid Component Testing**
- HPLC
- FTIR
- GPC
- LCMS

**Cured Film Testing**
- Rivets/Fasteners Adhesion
- Wet/Dry Adhesion
- 120F Condensing Humidity
- SEM/EDS

**Top re-formulation proceeding to qual**
- 1st production Batch sprayed Sept 2014

**Curing solution components per reformulation.**

<table>
<thead>
<tr>
<th>Candidate</th>
<th>Initial</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adh. Rivets &amp; Fasteners</td>
<td>FAIL</td>
<td>FAIL</td>
<td>FAIL</td>
<td>PASS</td>
<td>FAIL</td>
<td>PASS</td>
</tr>
</tbody>
</table>

**SEM – focused ion beam paint cross-section at 12,500x mag**

**Stack-up:**
- Substrate: 2024-T3 Clad + Rivets & Fasteners
- Surf Prep: Solvent Wipe
- Primer: Candidate or XBMS10-11 Ty I

**Pass/Fail:**
- 1: FAIL
- 2: FAIL
- 3: PASS
- 4: FAIL
- 5: PASS

**Proceed to Qual:**
- Initial
- 4
- 3
Adhesive Bond Primer
High/Medium/Low risk zones

Overview

- Two candidates selected based on performance over on titanium/sol-gel and aluminum/PAA substrates
- The desired goal is to find a primer that can do both aluminum and titanium bonding at both 250F and 350F processing temperatures

Key Tests

- Wide Area Lap Shear - BSS7202 Type III
- Metal to Metal Peel - BSS7206 Class 1, ASTM D 1781
- Salt Spray – Scribed panels, ASTM B117
- Wedge Crack – BSS7448 ASTM D 3762

Qual & Implementation Goals:

- Boeing Specifications:
  - BMS 5-89
  - MMS350, Ty III
  - MMS307, Type II
  - HMS 16-1111, Ty I
  - HMS 16-1278, Ty 1
  - BMS 5-137
  - DMS 2002, Ty 3 & 4
  - DMS 2169, Ty 1(A)
  - SCGMS56033, Class 2
Electrocoat (e-coat)
Low corrosion-risk zones

**Process:**
- Automated, low waste process which provides uniform paint film thickness.

**Overview:**
- Potential use for complex geometries, such as tubes in low corrosion-risk zones
- One candidate has passed screening tests, with varying degrees of corrosion protection depending on metal alloy.

**Plans to acquire a Pilot Coater in 2015**
Gaps & Long Term Developments

Gaps:

- In-service testing and long term exposure. Will not be accepted until proven in service.
  - 50-100k cycles per commercial aircraft
  - Lifecycle of 20+ years
  - Corrosion observed after 8-10 years in-service for Cr

- Risks associated with unknown failure of primary structure
  - Flight and safety critical components
    - Interaction between corrosion effects and fatigue crack initiation is unknown

- Reliable inspection methods
  - Implement nonchromate systems with increased inspection
  - Understand relationship between corrosion morphology and fatigue initiation/propagation

- Risk based implementation increases manufacturing complexity
  - Ensuring the correct coating system on the correct application

Low-Risk Applications
- Easy to inspect
- Non-structural
- Low risk of corrosion
  - e.g. Payloads, Systems LRU
  - e.g. Bond primer for Ti

Medium-Risk Applications
- e.g. Assembly primer

High-Risk Applications
- Difficult/impossible to inspect
- Life of airplane
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- High risk of corrosion
  - e.g. Bond primer for Al

Current Authorization Needs: List 3 and 4 Chromates

<table>
<thead>
<tr>
<th>Identification</th>
<th>Authorisation Dates</th>
<th>REACH Authorization Needed</th>
</tr>
</thead>
<tbody>
<tr>
<td>List</td>
<td>Substance</td>
<td>CAS</td>
</tr>
<tr>
<td>3</td>
<td>Ammonium Dichromate</td>
<td>7789-09-5</td>
</tr>
<tr>
<td>3</td>
<td>Chrome Trioxide</td>
<td>1333-82-0</td>
</tr>
<tr>
<td>3</td>
<td>Chronic Acid, hydrated forms</td>
<td>7738-94-5 &amp; 15330-68-1</td>
</tr>
<tr>
<td>3</td>
<td>Potassium Chromate</td>
<td>7789-00-6</td>
</tr>
<tr>
<td>3</td>
<td>Potassium Dichromate</td>
<td>7778-50-9</td>
</tr>
<tr>
<td>3</td>
<td>Sodium Chromate</td>
<td>7775-11-3</td>
</tr>
<tr>
<td>3</td>
<td>Sodium Dichromate</td>
<td>7789-12-0 &amp; 10588-01-9</td>
</tr>
<tr>
<td>4</td>
<td>Dichromium tris (chromate)</td>
<td>24613-89-6</td>
</tr>
<tr>
<td>4</td>
<td>Pentazinc Chromate Oxalatehydroxide</td>
<td>49685-84-5</td>
</tr>
<tr>
<td>4</td>
<td>Potassium hydroxystannatedichromate</td>
<td>11103-86-9</td>
</tr>
<tr>
<td>4</td>
<td>Strontium Chromate</td>
<td>7789-06-2</td>
</tr>
</tbody>
</table>

BCA Chemical Risk Management is interested in discussing partnering opportunities in the chromate use application process.