Aerospace Non Chrome Corrosion Inhibiting Primer Systems

Roger Brown, Akzonobel Aerospace Coatings
# Aerospace Non Chrome Corrosion Inhibiting Primer Systems

**Author:** Akzonobel Aerospace Coatings, 1 East Water, Waukegan, IL, 60085

**Abstract:**
ASETSDefense 2009: Sustainable Surface Engineering for Aerospace and Defense Workshop, August 31 - September 3, 2009, Westminster, CO. Sponsored by SERDP/ESTCP.
Overview comments and a historical perspective on non chrome systems

A quick test;

Technology development for replacement of chromated primers in aerospace has been in progress at Akzo and competitors for:

a) Forever  
b) Since Orville and Wilber at Kitty Hawk  
c) At least 20 years  
d) Any and all of the above

Presently at AkzoNobel Aerospace roughly 30% of lab resources are devoted to this technology, and this is the longest continuous running project in the company.

Aerospace is the only Akzo market still permitted to formulate with chromate pigments
## Why?

### Why is chrome so difficult to replace?

- Excellent protection of aluminum
- Protection mechanism of chromates is well suited to the substrate and the industry
- Long, positive use history
- Very wide compatibility
  - To common alloys
  - To resin types
- Universal pigment
- Has “always worked” mentality in the industry

### Why is the replacement initiative gaining strength?

- Recent changes in hazard evaluation and detection/monitoring standards
- General increased awareness of HSE issues in our industry
- REACh and similar regulations
- Strong position taken by the Department of Defense
State of the industry

• Essentially all OEMs in the aerospace field currently have active programs to reduce or eliminate chromates.

• There is significant debate as to the safety and performance of chrome III versus chrome VI.
  
  • **AkzoNobel position is that chrome is chrome.**

• There a handful of NC products approvals to OEM and military specifications.
  
  • These approvals still require chromate containing materials to be somewhere in the final coating stack up if corrosion resistance is part of the specification.
  
  • Pretreatments
  
  • Wash primers
  
  • Intermediate primers
Issues with non-chrome system approvals

- Accelerated testing results versus the known life of the current chromated systems
  - Question of risk / liability / cost
  - Example of Aviox CF
- Specification testing is built around the “known”
  - Salt fog testing / cyclic testing
  - Leachability mechanisms versus cathodic protection
- Less “universality” of non-chrome systems
  - Larger number of product needed, both finished goods and pigments
  - Probable higher costs
AkzoNobel Aerospace Non-Chrome Technologies

• Aviox CF
  • Conventional non-chrome pigmentation, acetoacetate/ketamine resin technology

• Aerowave Primer Systems
  • Water based 2k epoxy / amine systems
  • Chromated and non chromated technologies
  • VOC = 250 gr/l

• Corrosion inhibitive engineered nano particle coatings
  • Briefing Wednesday at 9:00 by Jeannine Elliot of TDA

• Commercial exterior decorative non chrome primer
• Magnesium metal based systems
Research Request: Development of CF Primer System to Commercial OEM Specifications

Parameters and Objectives

• Exterior decorative EOM system to meet BMS 10-72/AMS 3095 requirements
  • Commercially available pretreatment (sol gel)
  • Meet or exceed application, appearance, and cure capabilities of current (SrCrO₄) primer
  • HAPS free, VOC compliant world wide
  • Meet all HSE specifications, TSCA, REACH, Akzo
  • Strippable
  • No weight increase over current system
  • Meet specification requirements for corrosion, not performance norm of chromates
OEM CF Primer – Development and Optimization

• Multiple ‘starting blocks” (~ 20 beginning pigmentations)
  • Aviox CF
  • Previous CF efforts
    • Failed in comparison to chromate controls
    • Innovative group/basic research designed materials
  • Focus on 2024 as primary substrate
    • Verification on 7075, other alloys
  • Screening evaluations:
    • NSS
    • Filiform
    • Cure studies
    • Each study contains;
      • Positive and negative controls
      • Primer only and topcoated samples
OEM CF Optimization/ Down Selects

• Usual issues found to be true
  • Good NSS ≠ Good filiform ≠ Good cure ≠ Good application properties
  • Down select process is to minimize ≠ and move to a balance of all properties
  • Project life to date is ~ 30 months, 3-5 dedicate research staffers
    ➢ Formulation meeting initial product profile
    ➢ Based on unique, patent pending pigmentation technology
    ➢ Currently in qualification approval test programs
## Corrosion Resistance Test Updates

### Neutral Salt Spray Testing

<table>
<thead>
<tr>
<th>System</th>
<th>1000 hours</th>
<th></th>
<th></th>
<th>2000 hours</th>
<th></th>
<th></th>
<th>3000 hours</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scribe</td>
<td>Field</td>
<td>Scribe</td>
<td>Field</td>
<td>Scribe</td>
<td>Field</td>
<td>Scribe</td>
<td>Field</td>
<td></td>
</tr>
<tr>
<td>Neg Control</td>
<td>Bl</td>
<td>Dk</td>
<td>Co</td>
<td>Bl</td>
<td>Bl</td>
<td>Dk</td>
<td>Co</td>
<td>Bl</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>100</td>
<td>60</td>
<td>0</td>
<td>10</td>
<td>100</td>
<td>100</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>20</td>
<td>70</td>
<td>10</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Pos Control</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>10</td>
<td>5</td>
<td>0</td>
<td>5</td>
<td>20</td>
<td>5</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>10</td>
<td>70</td>
<td>10</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Test System</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>5</td>
<td>5</td>
<td>0</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>20</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>

Bl = blistering,  
Dk = scribe darkening,  
Co = white corrosion in scribe  
Values are % of space defect occurs
2000 hrs NSS (ASTM B-117)
2024 T3 Clad, AC-131

Chromated reference
New Technology
Negative reference
Progression during NSS up to 2000 hrs

500 hrs  1000 hrs  1500 hrs  2000 hrs
Filiform corrosion on 2024 T3 Clad, AC-131
720 hrs

New chrome free

Chromated reference
Magnesium Rich Primer Concept MgRP

• Project of AkzoNobel in conjunction with North Dakota State University to utilize magnesium powder as the primary pigment for chromate replacement

  • Fundamental research at NDSU, headed by Dr. Gordon Bierwagen

  • License, development agreement with AkzoNobel Aerospace

  • Concept similar to known electrochemical protection of steel by zinc

  • Significant departure from traditional methods and mechanisms of corrosion protection for aerospace
MgRP Technology

Parameters and Objectives

• Question the validity of accelerated testing designed for inhibition due to leaching materials: however, the goal is to provide an excellent coating for the intended use and pass the specification.

• Testing conducted both as primer only and as topcoated system, but with emphasis on system

• Accept premise that zero chrome is the only possible answer

• Utilize only commercially available pretreatments

• Run consistent testing, including uniform scribe as detailed by CTIO

  • Scribe width = 30 mils
  • Scribe depth= 9 mils (into metal)
  • All scribes by Hermes engraver method
MgRP Early Development Issues

Significant studies carried out to correlate:

• Salt fog results to electrochemical data/cathodic protection
• Early blistering in salt fog versus no failures in 36+ months in multiple field exposures
  • Battelle
  • CTIO
  • NAVAIR
  • Multiple Akzo sites

Accelerated testing issues:

• Primer only testing
  • Surface whitening of the panel
  • Clean, bright scribes, no field blisters
• Topcoated panel testing
  • Some whitening in scribe
  • No pitting or corrosion products in scribe
  • Occasional blistering along scribe
Technology Optimization- Results

Determination of test failure causes

- Observations
  - Blistering occurred within the primer, not at the metal
  - Cyclic test results>> full wet exposure testing
  - Mg particle pretreatments minimized whitening of primer only testing
- Work direction/ result
  - Resolve issue of too much activity of the magnesium metal
  - Resulted in patent pending system utilizing synergistic technology which
    - Controls magnesium activity
    - Provides 2° corrosion inhibition mechanism
    - Maintains full non chromate character of the system and
      - ensures complete protection of the substrate equal to or
        surpassing commercial chromate systems,
Improved MgRP formulation versus previous generation MgRP, 2000 hours NSS, 2024-T3

Previous generation MgRP over PreKote

Improved MgRP over PreKote
Improved MgRP formulation over PreKote versus chromate primer over CCC, 2000 hours NSS, 2024-T3
### 2000 Hours NSS
Topcoat: Aerodur 5000, Substrate: 2024-T3

<table>
<thead>
<tr>
<th>Previous generation MgRP over PreKote</th>
<th>Improved MgRP over PreKote</th>
<th>Chromate Primer over CCC</th>
<th>Negative Control over PreKote</th>
</tr>
</thead>
</table>
![Previous generation MgRP over PreKote](image1)
![Improved MgRP over PreKote](image2)
![Chromate Primer over CCC](image3)
![Negative Control over PreKote](image4)
2000 hours B117, Aerodur 5000 topcoat, PreKote treated 2024-T3
2000 hours B117, Aerodur 5000 topcoat, PreKote treated 2024-T3, Stripped Panels
Current Technical Status

1. New generation product commercially available
2. On going joint full testing programs with CTIO, NAVAIR, Military contractors, and commercial OEMs
3. Full health, safety, and environmental impact evaluations have been completed by Akzo and by third party risk assessment firm with positive results
4. Technology has been fully upscaled for production at Akzo’s Waukegan, Illinois site
5. Supply chain logistics for raw materials and finished goods has been fully established
MgRP Continuing Work

• NDSU/ Akzo continuing research project for full characterization of the technology and mechanisms of protection

• OSD sponsored university research on correlation of salt fog to “real” data

• Completion of military and commercial specification testing and approvals

• Evaluation of alternative physical forms of magnesium pigment

• Evaluation of magnesium alloy pigments

• Continued optimization and development of magnesium rich product line