Presented by

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With the support of the FOT members

Pre-treatment for bonding Composites/Metal

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TOPICS

- Introduction
- Metal surface treatment
- Composite surface treatment
- Surface preparation evaluation
- Future Prospects
Original Bonding Process

• Bonding of metallic structure was introduced from the beginning of A300 manufacture
  ‣ Longitudinal Joint (Lap Joint)

• Modification 2727 after MSN 157

• Periodic inspection using service bulletins
  ‣ Longitudinal joints
  ‣ Stringer
  ‣ Doubler
History and Service Experience

• Historical Causes of Failure
  ▸ Improper Surface treatment
  Failure mechanism was determined by Bondline Corrosion in both:
  ▸ laboratory investigations and
  ▸ Service Findings in affected aircrafts

• Corrective Actions
  ▸ CAA - end Pre-treatment
  ▸ Advanced adhesive epoxy films + chromated primer
  ▸ Design changes
State of the Art - Processes

For Bonding Application

1. Alkaline degreasing
2. Alkaline Etching
3. Acid Pickling
4. Chromic Acid Anodizing

Pickling
“grain boundary etching”
Acid Pickling Requirements

- Applicable for Bonding processes
- Performance on all used Al-alloys nearly equivalent
- Activation of Al surfaces
  - Removal of marking inks (still remaining after degreasing)
  - Removing oxide/hydroxide films
  - Desmutting properties
  - No significant roughening of surface; homogeneous, continuous appearance.
- Only by chemical means, non electrolytic process
- Uniform, “pickling” topography
- Metal removal (constant ageing of the batch)
- Surface has to be compatible with post treatments
- No electrochemical deposition of Cu, Zn & Fe from the solution of the Al-surface
- No deposition of metal salts or hydroxides from the solution to the Al-surface
<table>
<thead>
<tr>
<th>Bonding (NOR)</th>
<th>Metal removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alk. Cleaning</td>
<td>Metaclean T 2001</td>
</tr>
<tr>
<td>Alk. Pickling</td>
<td>Almeco 51</td>
</tr>
<tr>
<td>Acid Pickling</td>
<td>CSA</td>
</tr>
<tr>
<td><strong>In total</strong></td>
<td><strong>~ 4-6 µm</strong></td>
</tr>
</tbody>
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Anodising Requirements (i)

- General Requirements
- Applicable for Bonding processes
- Oxide layer not to be easily damaged by manual handling
- No significant impact on damage tolerant behaviour
- No significant impact on fatigue behaviour
- Performance on all Al-alloys used in production
- Homogeneous oxide layer for all alloys, exceptional case: high Silicon containing alloys (>2%)
- Detectable, non contacted method should be mandatory
Anodising Requirements (ii)

Process Requirements

- Chemical solution (bath) should be stable for extended periods
- Quality easily controlled by defined levels

Oxide layer Requirements

- Hydrolysis products must have no deleterious effects
- Stability against manufacturing environment for defined time intervals
- Oxide layer covering the substrate completely with low electrical conductivity
- Compatibility with waterborne primers

Adhesion/Corrosion requirements

- No adhesion failure to substrate or primer
- Oxide layer must be as porous as possible
- Bondline-Corrosion resistant
Chromic Acid Anodising: Porous Structure

**CAA**: 40V, 25 min + 50V, 5 min Bengouth Cycle

- oxide layer with wide pores
- sealable
- good adhesion for bonding
- good corrosion behaviour

Section of CAA specimen. Anodic layer app. 4μm

Porous structure
Bonding-Primer (i)

• Material Properties
  ‣ One component epoxy system
  ‣ Low VOC (less 250g/l), 10 to 30% solid content
  ‣ Not 100% water based (application aspects)
  ‣ Containing corrosion inhibitors
  ‣ No hazardous substances which require special protection
  ‣ Coloured material for quality control purposes (thickness control)
  ‣ Storage time at least 12 month at RT (or +4°C)
  ‣ Work life at least 15 to 30 days (30°C/75% R.H.)
  ‣ Compatible with all qualified structural bonding adhesive film or paste (use as standard primer)
  ‣ Compatible also with 175°C curing adhesives and basic primer/top coats
  ‣ Penetration of bonding primer in oxide layer (viscosity behaviour)
**Bonding-Primer (ii)**

- **Mechanical Properties**
  - Multiple curing (up to 5 times) without any degradation in performance
  - Primer layer thickness tolerance between 2 and 15 µm without degrading the quality of adhesive joint (e.g. peel load)
  - Fulfill the requirements AIMS 10-01-001 and 10-01-002 together with the appropriate adhesive film or paste.
  - Bondline corrosion:
    - 90 days: \( \leq 10\% \)
    - 180 days: \( \leq 20\% \)
    - 300 days: \( \leq 30\% \)
  - Work life at least 15 to 30 days (30°C/75% R.H.)
  - Resistance to filliform corrosion (EN 3665)
  - Good adhesion on surface oxide layer
Critical Issues

• Replace current situation by a chromate free process
  ‣ Pre-treatment
  ‣ Primer

• What are the real criteria for implementation
Objectives

- Current projects intend to find systems for preparing the surface of carbon fibre composite elements before bonding.
- Especially focused on:
  - Structural bonding
  - Elements with big size areas to be bonded
  - Parts made off thermoplastic matrix composites
- The aim is to develop automated technologies
  - Reproducible
  - Accurate
  - Quality assessed
  - Easy to control and inspect
  - Ecologically favourable
  - Applicable for automation
Composite Surface Treatments

- Composite structures can have bonded joints fabricated by three different processes:
  - Secondary bonding
  - Co-bonding
  - Co-curing
- Surface preparation is a critical step in any bonded joint and must be clearly defined before any bonding is performed.
- Particularly important for:
  - Secondary and co-bonding processes.
Composite Surface Preparation Methods

- Peel ply
  - Dry
  - Wet
- Peel ply + additional surface preparation
- Plasma and Corona treatments
- Abrasion by means of blasting techniques
Peel Ply Surface Preparation

- Widely used within AIRBUS

- Probably the most effective and repeatable pre-treatment at the present time
**Peel Ply Surface Preparation**

- **Object**
  - Finding more efficient peel ply to be used as a pre-bond treatment without subsequent abrasion.
  - Understand factors affecting good or bad peel ply behaviour

- **Recent Works**
  - Investigation of different dry peel ply
    - Nature = Nylon / polyester
    - Different Weave patterns
    - Weave surface treatment
  - Evaluation of wet peel ply
  - The best peel ply depends on the laminate type as well as the adhesive used.
Composite Surface Treatments

WET PEEL PLIES

LAMINATE: 8552/AS-4 UD
ADHESIVE: FM 300 K .05
FRACTURE TOUGHNESS (G_{IC})
Plasma and Corona Treatments

• Object
  ‣ Basic research on the effects of different types of source of plasma as well as corona discharge.
  ‣ Mainly focused on the thermoplastic matrices composites.

• Testing
  ‣ Shear strength Dry, Hot / Wet and exposure in hydraulic fluid.
  ‣ Toughness (\(G_{IC}\)), Dry, Hot / Wet and exposure in hydraulic fluid.
  ‣ Micro analytical investigations.
Plasma and Corona Treatments

• **Intermediate conclusions**
  ‣ The study of different physical based pre-treatments showed for ND plasma a significant increase of shear strength as well as the fracture toughness energy after dry and hot / wet testing.

• **Further activities**
  ‣ Analysis of the pre-treated surface.
  ‣ Analysis of interphase.
  ‣ Mechanical tests on the resulting bond line.
Abrasión de medios de pulido

- **Object**

  - Define the best parameters to define a suitable and efficient pre-bond treatment by blasting techniques.
Preliminary Tests Conclusions

- **Treatment of carbon tape laminates**
  Dry blasting surface preparation increase the $G_{IC}$ and SLS test results values.
  Failure mode are predominantly cohesive.
  Using appropriate blasting parameters, carbon fibres of the laminates are not damaged.

- **Treatment of non-crimp fabric laminates**
  First investigation confirms the same trend.
  Application of grid blasting increase the shear strength and the fracture toughness energy.

- **Further activities**
  - Investigations of different grid materials and processes variables (e.g. distance, angle) on different substrate has to be performed.
  - Optimum dry blasting parameters shall be determined in future tests.
Critical Issues

- Which criteria does the modified surface have to fulfill?
- Do we have to require a type of failure mode? A measured strength or both?
  - How to predict long term durability with coupons?
- Any change must be checked by additional testing e.g. extensive compatibility tests.
- Determination of release test to monitor batch to batch consistency.
- Define storage condition for laminate as well process step durations' (e.g. assembly time).
- Study effects of pre-bond humidity.
  - Laminate
  - Honeycomb
Moisture pick-up in Nomex honeycomb

Moisture Pick-up in Nomex honeycomb to MLG Door (Hus 195)
(Drying @62°C then moisture pick-up in clean room @195, 20-21°C/45-47% RH)
Surface Preparation Evaluation

• Deep”academic” work has been performed regarding test methods for adhesives and adhesive joints that could eventually be applied to assess the surface preparation quality of composite adherents for bonded, co-bonded and co-cured composite joints.

• There is very little published scientific work concerning the evaluation of adhesive joints between composite materials.

• Most of the existing work is related to standards or international committees for standardization.
Mechanical test methods

– Peel stress test methods are more sensitive to surface preparation than shear stress methods.
– Actually the most sensitive existing test method still seems to be the $G_{IC}$ DCB test in all its different configurations.
– $G_{IC}$ DCB test method is expensive, difficult to prepare and test correctly.

› Final conclusion
– Existing test methods do not fit exactly with the requirements demanded.
– For composite it’s necessary to develop a new “simple and reproducible” test to evaluate the quality of the structural bonding.
Physical test methods

- No direct correlation has been found between percentage of Si and mechanical behaviour of the bond line by means of $G_{IC}$.

- No direct correlation has been found between percentage of F and mechanical behaviour of the bonding line by means of $G_{IC}$ in the percentages found in the laminate.

- Direct correlation has been found at higher values of F content (due to other ancillaries contamination).

- Direct correlation has been found between failure mode and extractable residue.
Future Prospects

• Surface preparation
  ‣ Metal: substitution of chromate (Surface treatment + primer)
  ‣ Composite: enhancement to peel ply or replacement

• Adhesive
  ‣ Stability in out time and pre-bond humidity

• Inspection
  ‣ NDI for weak interface detection
  ‣ Strong request to define the equivalent to the wedge test for composite.
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