DEPARTMENT OF DEFENCE
DEFENCE SCIENCE & TECHNOLOGY ORGANISATION
DSTO

Bond Durability of Grit-blast and Silane treated Metallic Adherends Bonded with Room Temperature Curing Adhesives

Andrew Rider

DSTO-TR-1187

Bond Durability of Grit-blast and Silane treated Metallic Adherends Bonded with Room Temperature Curing Adhesives

Andrew Rider

Airframes and Engines Division
Aeronautical and Maritime Research Laboratory

DSTO-TR-1187

ABSTRACT

The "Australian Silane Treatment" has been successfully used for bonded repairs carried out at RAAF Airbases for a number of years. This surface treatment has provided a reliable and non-toxic alternative to surface pre-treatments recommended in Structural Repair Manuals (SRM) for metallic adhesive bonded repairs. Generally, however, the silane treatment has only been applied in bonded repairs involving the use of high temperature curing structural adhesives. The purpose of the study detailed in this report was to examine the feasibility of extending the application of the silane pre-treatment to metallic repairs involving the use of room temperature or paste adhesive systems employed in a range of airbase repairs. Wedge style durability tests were conducted for a range of metallic adherends and room temperature curing adhesives. The durability performance of the grit-blast and epoxy silane metallic adherend pre-treatment was compared with standard pre-treatments recommended in a range of SRMs. Generally, the data indicated that the grit-blast and silane pre-treatment offered either improved or similar performance to the SRM alternative pre-treatments on the basis of results from wedge style durability tests conducted at 50^{0}C and 100% relative humidity.

RELEASE LIMITATION

Approved for public release

DEPARTMENT OF DEFENCE
DEFENCE SCIENCE & TECHNOLOGY ORGANISATION
DSTO

AQ F02-01-0076

Published by

DSTO Aeronautical and Maritime Research Laboratory
506 Lorimer St
Fishermans Bend, Victoria 3207 Australia

Telephone: (03) 9626 7000
Fax: (03) 9626 7999

AR-011-949
July, 2001

APPROVED FOR PUBLIC RELEASE

Bond Durability of Grit-blast and Silane treated Metallic Adherends Bonded with Room Temperature Curing Adhesives

Executive Summary

The Royal Australian Air Force (RAAF) has been using a procedure known commonly as the "Australian Silane Treatment" for a number of years in the repair of adhesive bonded structure. The process involves grit-blasting and application of an epoxy-silane coupling agent to the metallic surface prior to application of a film based adhesive. Typically, the adhesives used are cured at high temperatures ranging between 120°C and 170°C. The development of the C5033 RAAF Engineering Standard has enabled the successful and reliable application of the grit-blast and silane treatment for bonded repairs using elevated temperature curing adhesives over a number of years. The C5033 Standard is not applied for the bonded repairs carried out using room temperature curing or paste adhesives. Whilst the fundamental chemistry of the elevated and room temperature curing epoxy adhesives are essentially similar, the physical changes that the adhesives undergo during the curing operation are very different. The purpose of the work detailed in this report was to examine the feasibility of applying the grit-blast and silane treatment to bonded repairs of metallic components using room temperature curing or paste adhesive systems. Currently a range of pre-treatments is recommended in Structural Repair Manuals for bonded repairs involving paste adhesives and metallic components. Examination of these recommended pre-treatments in comparison with the grit-blast and silane treatment was undertaken to determine if the grit-blast and silane treatment could replace the range of treatments currently used. The use of a single pre-treatment method for bonded repairs to metallic components using paste adhesives has the potential to improve the strength, durability and reliability of the bonded repairs which can then lead to reduced maintenance costs associated with Bonded Structure. The innocuous nature of the grit-blast silane treatment will also offer substantial health and safety advantages for technical personnel in comparison with current treatments that involve the use of toxic chemicals such as chromium.

A range of paste adhesives currently used in bonded repairs was examined together with a range of metallic substrates typically present in aircraft structure. The grit-blast and silane treatment of the metallic adherend prior to bonding was compared with a simple abrasion procedure and a chemical treatment using a proprietary paste compound called Pasajell. The adhesive bond durability determined from wedge test experiments carried out at 50°C and 100% relative humidity indicated that the grit-blast and silane treatment performed as well or, in the majority of cases, substantially better than the current methods being applied in depot or field repairs. Surface analysis of the failed wedge test samples revealed that the fracture typically propagated at the

adhesive to aluminium interface and that the introduction of silane coupling agent increased the hydrolytic stability of the adhesive bonds, thereby increasing the adhesive bond durability.

It is expected that these results can be used to expand the application of the grit-blast and silane procedure currently prescribed in C5033 to bonded repairs involving the paste adhesives and aluminium alloys examined in this report. The use of the grit-blast silane procedure should significantly increase the reliability, strength and durability of paste adhesive bonded repairs involving aluminium.

Author

Andrew Rider
Airframes and Engines Division

Andrew Rider joined Airframes and Engines Division at DSTO in 1988 as a Professional Officer Class 1. He has a Bachelor of Applied Science in Chemistry from Swinburne University of Technology and a PhD in Physical Chemistry from the University of New South Wales. He is currently employed as a Research Scientist and works within Airframes and Engines Division. He is involved in research to understand degradation mechanisms involved in bonded structure and repairs used on F-111 and F/A-18 fighter aircraft.

Contents

1. Introduction

The "Australian Silane Treatment"[1] is a surface pre-treatment procedure used on metallic adherends in bonded repairs performed by the Royal Australian Air Force (RAAF). The process involves the grit-blasting of the metallic adherend with alumina grit followed by the application of a 1% aqueous solution of epoxy-silane, prior to adhesive bonding. The RAAF have developed their own standard[2] for bonded repairs using the grit-blast and silane surface treatment which pays particular attention to bonding procedure detail and the need for staff training and supervision. Typically, the silane pre-treatment procedure has been employed in cases where bonded repairs involve the use of high temperature curing structural adhesives, such as FM73, 120^0C cure, and FM300, 177^0C cure.

The purpose of the work detailed in this report was to examine the feasibility of extending the grit-blast and epoxy silane pre-treatment to metallic bonded repairs that use room temperature curing or paste adhesives. The grit-blast and silane surface treatment was assessed in comparison with two typical surface pre-treatment procedures recommended in aircraft Structural Repair Manuals (SRM) for bonded repairs to metallic components using room temperature curing adhesives. The most critical aspect of adhesive bonds formed between metallic components is the long term maintenance of strength in hostile environmental conditions. Typically, moisture has been shown to be the most detrimental factor affecting adhesive bonds and the Wedge Test [3] is regularly used to assess the potential durability of adhesive bonds formed with metallic components. The Wedge Test is also used by RAAF[2] to train technicians involved in adhesive bonded repairs as it provides a rigorous assessment of the quality of the applied surface pre-treatment. On this basis, the relative performance of the grit-blast and silane pre-treatment was assessed using the Wedge Test.

2. Experimental

2.1 Surface Pre-treatments

2.1.1 Grit-blast (GB)

The following steps were used in the grit-blasting of the metallic adherend surfaces:

a. solvent degrease with methyl ethyl ketone (MEK)

b. scotchbrite abrade (one direction only) with distilled water

c. debris removal using lint free tissues wet with distilled water

d. oven dry 15 mins at 110^0C

e. grit-blast at 450 kPa

2.1.2 Scotchbrite (SB)

The following steps were used in the scotchbrite abrasion of the metallic adherend surfaces:

a. solvent degrease (MEK)

b. scotchbrite abrade (one direction only) with distilled water

c. debris removal using lint free tissues wet with distilled water

d. oven dry 15 mins at 110^0C

2.1.3 Grit-blast + Silane (GB+Silane)

The following steps were used in the grit-blasting and silane treatment of the metallic adherend surfaces:

a. solvent degrease (MEK)

b. scotchbrite abrade (one direction only) with distilled water

c. debris removal using lint free tissues wet with distilled water

d. oven dry 15 mins at 110^0C

e. grit-blast at 450 kPa

f. dip 15 mins in 1% aqueous solution of epoxy-silane, pre-hydrolysed 60 minutes

g. oven dry 1 hour at 110^0C

2.1.4 Scotchbrite + Silane (SB+Silane)

The following steps were used in the scotchbrite and silane abrasion of the metallic adherend surfaces:

a. solvent degrease (MEK)

b. scotchbrite abrade (one direction only) with distilled water

c. debris removal using lint free tissues wet with distilled water

d. dip 15 mins in 1% aqueous solution of epoxy-silane

e. oven dry 1 hour at 110^0C

2.1.5 Abrasion with Grit Paper (PXXX)

The following steps were used in the grit paper abrasion of the metallic adherend surfaces:

a. solvent degrease (MEK)

b. grit paper abrade (one direction only) dry

c. debris removal using lint free tissues wet with distilled water

e. oven dry 15 mins at $110^{0}C$

2.1.6 Abrasion with Grit Paper + Silane (PXXX+Silane)

The following steps were used in the grit paper + silane abrasion of the metallic adherend surfaces:

a. solvent degrease (MEK)

b. grit paper abrade (one direction only) dry

c. debris removal using lint free tissues wet with distilled water

d. dip 15 mins in 1% aqueous solution of epoxy-silane

e. oven dry 1 hour at $110^{0}C$

2.1.7 Grit-blast + Hot water solution (GB + Dist $100^{0}C$)

The following steps were used in the grit-blasting and hot water solution treatment of the metallic adherend surfaces:

a. solvent degrease (MEK)

b. scotchbrite abrade (one direction only) with distilled water

c. debris removal using lint free tissues wet with distilled water

d. oven dry 15 mins at $110^{0}C$

e. grit-blast at 450 kPa

f. distilled water dip 15 mins at $100^{0}C$

g. oven dry 1 hour at $110^{0}C$

2.1.8 Grit-blast + Hot water solution + Silane (GB + Dist $100^{0}C$ + Silane)

The following steps were used in the grit-blasting, hot water solution and silane treatment of the metallic adherend surfaces:

a. solvent degrease (MEK)

b. scotchbrite abrade (one direction only) with distilled water

c. debris removal using lint free tissues wet with distilled water

d. oven dry 15 mins at 110^{0}C

e. grit-blast at 450 kPa

f. distilled water dip 15 mins at 100^{0}C

g. dip 15 mins in 1% aqueous solution of epoxy-silane

h. oven dry 1 hour at 110^{0}C

2.1.9 Pasajell® (PRC Desoto 105) (PJ)

The following steps were used in the Pasajell treatment of the metallic adherend surfaces:

a. solvent degrease (MEK)

b. P220 grit paper abrade (one direction only) dry

c. debris removal using lint free tissues wet with distilled water

d. Pasajell® applied with brush to adherend for 15 mins

e. excess removed with cheesecloth soaked with tap water and water break check performed

f. steps d. & e. repeated

g. oven dried 15 mins at 80^{0}C

2.1.10 Grit-blast + Primer (GB + Primer)

The following steps were used in the grit-blasting and priming of the metallic adherend surfaces:

a. solvent degrease (MEK)

b. scotchbrite abrade (one direction only) with distilled water

c. debris removal using lint free tissues wet with distilled water

e. oven dry 15 mins at 110^{0}C

f. grit-blast at 450 kPa

g. primer lightly brushed on surface. Primers used were EA9203 (Hysol), EC1945 and EC3901 (3M)

h. Dried 30 mins at room temperature followed by 30 mins at 80^{0}C

The abbreviations used throughout the report to designate a particular pre-treatment are detailed in Table 1.

Descriptor	Adherend Processing Steps
GB	Grit-blast at 450kPa
GB+Silane	Grit-blast at 450kpa + Silane (1% A187 epoxy) dip 15 minutes
SB	Scotchbrite abrade (one direction) with distilled water
SB+Silane	Scotchbrite abrade (one direction) with distilled water + Silane (1% A187 epoxy) dip 15 minutes
PXXX	Grit paper (eg P80, P220, P320 grit) abrade one direction - dry
GB+Dist 100C	Grit-blast at 450kPa + Distilled water dip 15 mins @ 100C
GB+Dist 100C+ Silane	Grit-blast at 450kPa + Distilled water dip 15 mins @ 100C + Silane (1% A187 epoxy) dip 15 mins
PJ	Pasajell (PRC Desoto 105) applied by brush to adherend for 15 minutes
GB+Pri	Grit-blast at 450kPa + primer lightly brushed onto surface

Table 1 *The descriptor and details of the surface pre-treatment procedures applied to the adherends prior to bonding with paste adhesives*

2.2 Adhesives and Cure Conditions

2.2.1 EA9309.3 NA

EA9309.3 NA from Hysol-Dexter was applied to both sides of the metallic adherends with a wooden spatula and cured at 25^0C for 18 hours using 100μm thick shims and a pressure of 20 psi, followed by a post cure for 1 hour at 50^0C.

2.2.2 EA934.NA

EA934.NA from Hysol-Dexter was applied to both sides of the metallic adherends with a wooden spatula and cured at 25^0C for 24 hours using 100μm thick shims and a pressure of 12 psi, followed by a post cure for 1 week at room temperature.

2.2.3 EC2216 B/A

Scotch-weld EC2216 B/A from 3M was applied to both sides of the metallic adherends with a wooden spatula and cured at 25^0C for 24 hours using 100μm thick shims and a pressure of 12 psi, followed by a post cure for 1 week at room temperature.

2.2.4 Scotch Weld EC3549 B/A

Scotch-weld EC3549 B/A from 3M was applied to both sides of the metallic adherends with a wooden spatula and cured at 25^0C for 24 hours using 100μm thick shims and a pressure of 12 psi, followed by a post cure for 1 week at room temperature.

2.2.5 EA9320NA

EA9320NA from Hysol-Dexter was applied to both sides of the metallic adherends with a wooden spatula and cured at 25^0C for 18 hours using 100μm thick shims and a pressure of 20 psi, followed by a post cure for 1 hour at 50^0C.

2.2.6 EA9321

EA9321 from Hysol-Dexter was applied to both sides of the metallic adherends with a wooden spatula and cured at 25^0C for 18 hours using 100μm thick shims and a pressure of 20 psi, followed by a post cure for 1 hour at 50^0C.

2.2.7 EA9317

EA9317 from Hysol-Dexter was applied to both sides of the metallic adherends with a wooden spatula and cured at 25^0C for 18 hours using 100μm thick shims and a pressure of 20 psi, followed by a post cure for 1 hour at 50^0C.

2.2.8 EA9396

EA9396 from Hysol-Dexter was applied to both sides of the metallic adherends with a wooden spatula and cured at 25^0C for 18 hours using 100μm thick shims and a pressure of 20 psi, followed by a post cure for 1 hour at 50^0C.

2.2.9 Araldite K138

Araldite K138 (AV138+HV998) from Ciba-Vantico was applied to both sides of the metallic adherends with a wooden spatula and cured at 25^0C for 18 hours using 100μm thick shims and a pressure of 20 psi, followed by a post cure for 2 hours at 50^0C.

2.3 Adherends

2.3.1 Aluminium Alloys

Table 2 indicates the composition of the aluminium alloys used in the Wedge durability tests.

Alloy	Composition By Weight (%)							
	Si	Fe	Cu	Mn	Mg	Cr	Zn	Zr/Ti	Aluminium
2024	0.5	0.5	3.8-4.9	0.3-0.9	1.2-1.8	0.1	0.25	0.2	Remainder
7075	0.4	0.5	1.2-2.0	0.3	2.1-2.9	0.18-0.28	5.1-6.1	0.25	Remainder

Table 2 Compositions of the aluminium alloys used for preparation of bonded joints [4]

2.3.2 Titanium and Stainless Steel

Titanium 6Al-4V alloy was used i.e. titanium with 6 weight percent of Aluminium, 4 weight percent of Vanadium and a remainder of Titanium.

304 Stainless Steel was used with a composition of 18-20% Chromium, 8-12% Nickel and approximately 70% Iron.

2.4 Durability Testing

Wedge style double cantilever beam specimens were prepared in accordance with ASTM D3762-79 [3]. This involves bonding two 1/8" thick plates of 6" X 6" dimension and milling the plates to produce 5 duplicate samples for each adhesive, adherend and surface pre-treatment combination examined. The test provides a qualitative assessment of the relative durability of particular surface pre-treatments applied to the adherend prior to adhesive application. All samples were tested in a 50°C/100% relative humidity (R.H.) environment. Crack-growth measurements were performed an hour after wedge insertion and at 1, 2, 4, 6, 25, 50, 100, 500 and 1000 hours, once the specimens were exposed to the humid environment. The testing temperature of 50°C and 100% R.H. was chosen as these are the conditions prescribed in the RAAF Engineering Standard [2]. Clearly, with the paste adhesives being used there is some concern that the test environment will alter the mechanical properties of the adhesive system being used and influence the durability results reported. Table 3 indicates the effect of temperature and moisture on the mechanical properties for a range of adhesives used in the durability studies. The data suggests that at 50°C the tensile strength of the EC2216 and 3549B/A adhesives is likely to be affected with the peel strength of the EC2216 adhesive being dramatically affected. In terms of the wedge test, this would suggest deterioration in the physical properties of the EC2216 adhesive would prevent significant conclusions regarding the durability of the surface pre-treatment being made. The poor peel strength of the EA934 and K138 adhesives may also mean that the wedge test results for these adhesives would be relatively insensitive to the influence of surface pretreatment procedures on bond durability. The remaining adhesives, however, suggest that they can be tested at 50°C without significant alteration to their mechanical properties influencing the durability performance measured from the wedge tests.

Adhesive	Service Temp. (°C)	Tg-dry (°C)	Tg-wet (°C)	Tensile Strength (psi)			Peel Strength(lbf/in)	
				25°C	80°C	30 days at 50°C/100% R.H.	25°C	80°C
EA9309.3	80	59	53	4800	1000	5000	35	---
EA9396	177	---	---	4600	3300	---	25	20
EA9320	80	80	---	4600	1500	---	20	---
EA9321	121	110	88	4000	1700	3700	6	42
EA934	150	88		3100	2200	2900	nil	nil
EC2216B/A	---	---	---	2500	400	2650	25	3.5
3549B/A	---	---	---	2000	300	---	---	---
K138	100	---	---	3000	2700	---	15.1	---

Table 3 Selected paste adhesives used in this study indicating the effect of temperature and moisture on mechanical strength properties[5].

2.5 Fracture Analysis

X-ray Photoelectron Spectroscopy (XPS) was used to analyse the surfaces of failed wedge samples to determine the true locus of fracture. XPS analysis was performed on the surfaces of the failed specimens as close as possible to the crack tip region using 30W AlK_α X-rays and a Fixed Retard Ratio (FRR) of 53 in high magnification mode, where the area of analysis was approximately 2mm in diameter. The sensitivity factors provided by the manufacturer were used to quantify the data.

2.6 Surface Roughness Measurements

The surface roughness caused by abrasion of Ti-6V-4Al and Al-2024 clad aluminium was assessed to determine the depth of scratches or indentations resulting from abrasion or grit-blasting. These parameters are of particular concern when dealing with fatigue critical components made from titanium alloys.

The roughness measurements employed an automated Laser Depth Measuring Device called a Perthometer. The instrument scans a laser beam across the surface. Measurement requires that the laser maintains focus as it traverses the surface. A rapid feed-back adjustment alters the height of the laser to maintain focus. The height adjustment is recorded and plotted as a function of the beam's horizontal translation, providing a surface profile of the roughened surface. The Perthometer provides an *average roughness*, R_A, which corresponds to the mean peak to valley height over the entire profile as well as the *maximum roughness*, R_{MAX}, which corresponds to the greatest peak to valley depth over the entire profile. Profiles were also analysed statistically to determine the average height of surface features, after correction for background slope, as well as the average angle of the surface features, with respect to the surface normal.

3. Results

3.1 Al-2024 T3 Clad Aluminium Alloy

3.1.1 EA9309.3 NA

Figure 1 and Figure 2 indicate the crack-growth as a function of exposure time to a humid environment for Al-2024 T3 Clad aluminium alloy adherends bonded with EA9309.3 NA. The surface pre-treatments used are indicated in the graph legend.

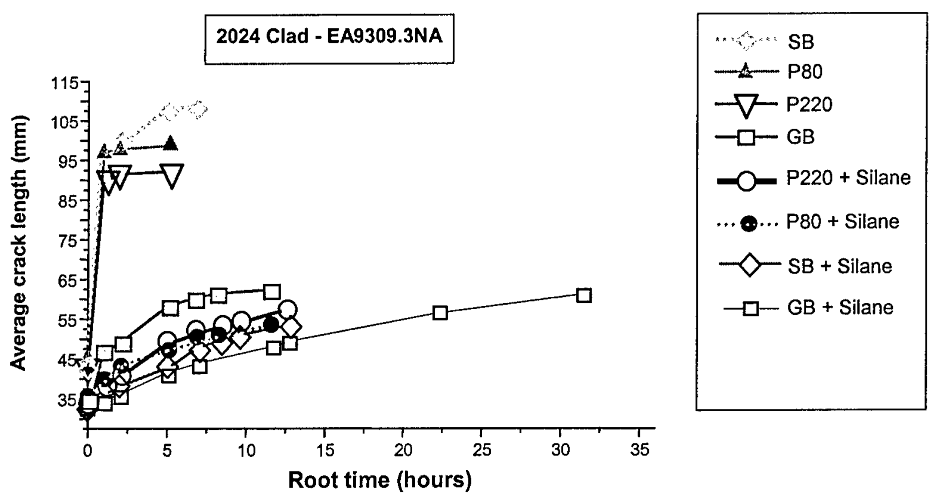


Figure 1 *Bond durability data for Al-2024 T3 clad aluminium bonded to EA9309.3NA paste adhesive as a function of the surface pre-treatment.*

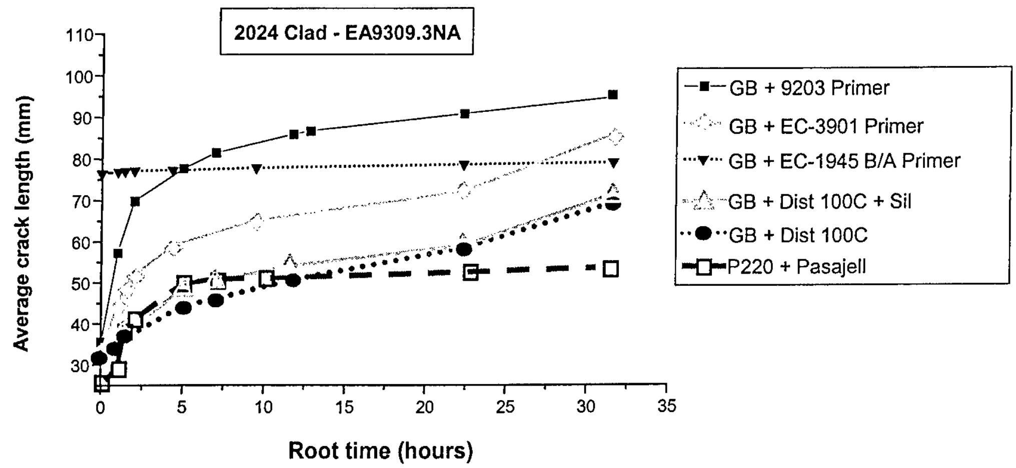


Figure 2 *Bond durability data for Al-2024 T3 clad aluminium bonded to EA9309.3NA paste adhesive as a function of the surface pre-treatment.*

3.1.2 EA9317

Figure 3 indicates the crack-growth as a function of exposure time to a humid environment for Al-2024 T3 Clad aluminium alloy adherends bonded with EA9317. The surface pre-treatments used are indicated in the graph legend.

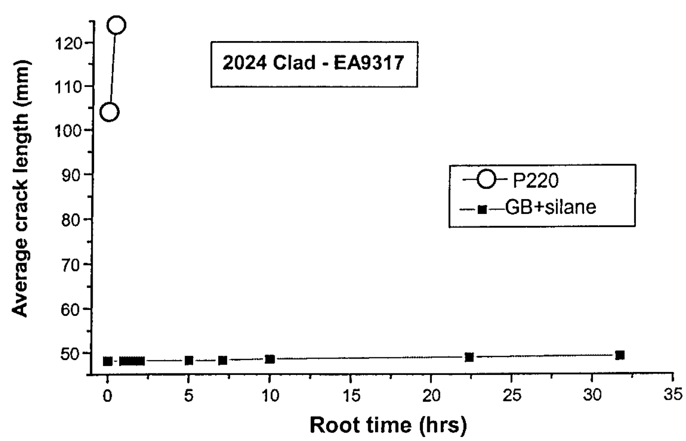


Figure 3 *Bond durability data for Al-2024 T3 clad aluminium bonded to EA9317 paste adhesive as a function of the surface pre-treatment.*

3.1.3 EA9320 and EA9321

Figure 4 indicates the crack-growth as a function of exposure time to a humid environment for Al-2024 T3 Clad aluminium alloy adherends bonded with EA9320 and EA9321. The surface pre-treatments used are indicated in the graph legend.

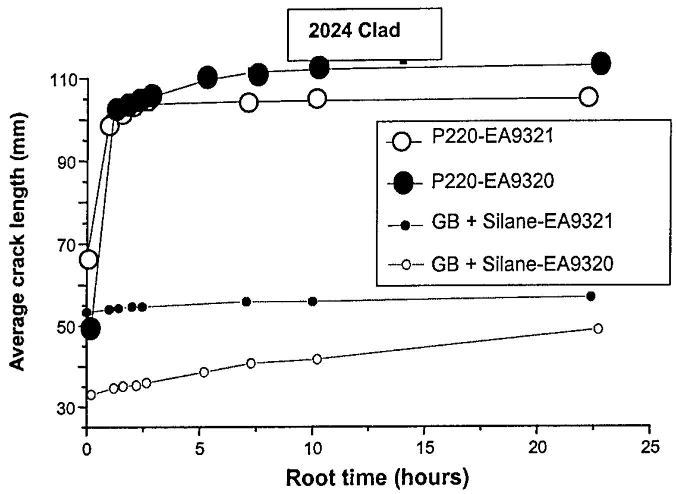


Figure 4 *Bond durability data for Al-2024 T3 clad aluminium bonded to EA9321 paste adhesive as a function of the surface pre-treatment.*

3.1.4 EA934.NA and EA9396

Figure 5 indicates the crack-growth as a function of exposure time to a humid environment for Al-2024 T3 Clad aluminium alloy adherends bonded with EA934.NA and EA9396. The surface pre-treatments used are indicated in the graph legend.

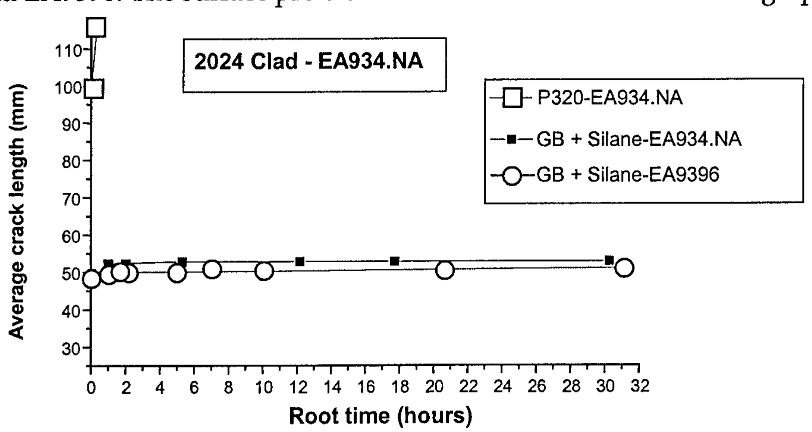


Figure 5 *Bond durability data for Al-2024 T3 clad aluminium bonded to EA934.NA and EA9396 paste adhesive as a function of the surface pre-treatment.*

3.1.5 EC2216 and EC3549

Figure 6 indicates the crack-growth as a function of exposure time to a humid environment for Al-2024 T3 Clad aluminium alloy adherends bonded with EC2216. The surface pre-treatments used are indicated in the graph legend.

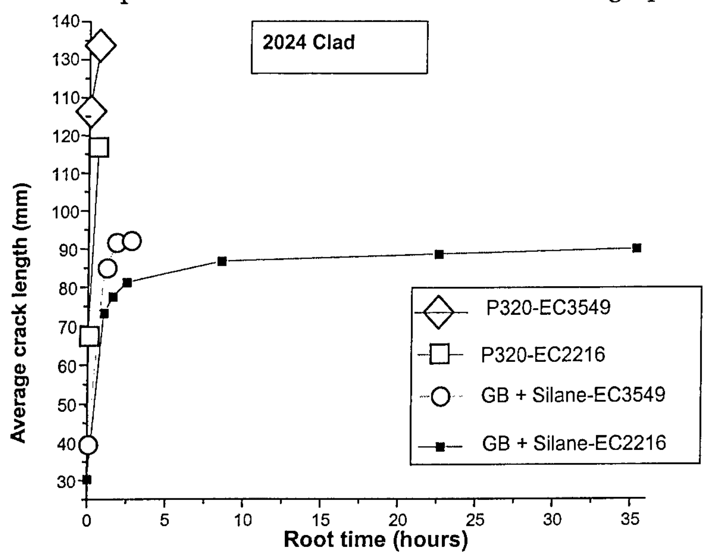


Figure 6 *Bond durability data for Al-2024 T3 clad aluminium bonded to EC2216 and EC3549 paste adhesive as a function of the surface pre-treatment.*

3.1.6 K138

Figure 7 indicates the crack-growth as a function of exposure time to a humid environment for Al-2024 T3 Clad aluminium alloy adherends bonded with K138. The surface pre-treatments used are indicated in the graph legend.

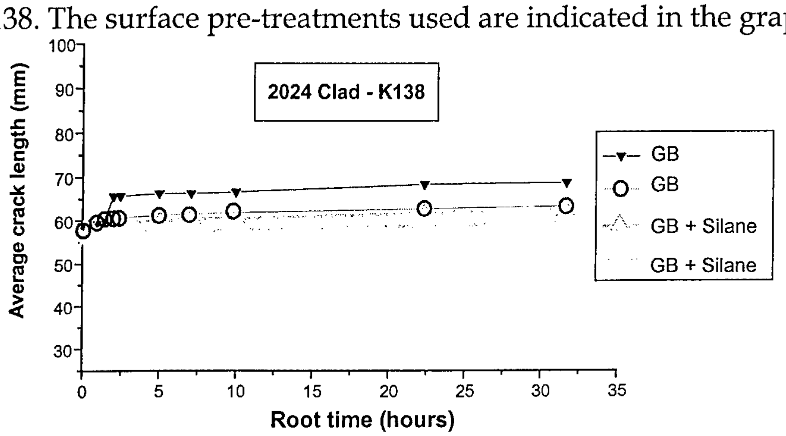


Figure 7 *Bond durability data for Al-2024 T3 clad aluminium bonded to K138 paste adhesive as a function of the surface pre-treatment*

3.2 Al-2024 T3 Unclad Aluminium Alloy

3.2.1 EA9309.3NA

Figure 8 indicates the crack-growth as a function of exposure time to a humid environment for Al-2024 T3 Unclad aluminium alloy adherends bonded with EA9309.3 NA. The surface pre-treatments used are indicated in the graph legend.

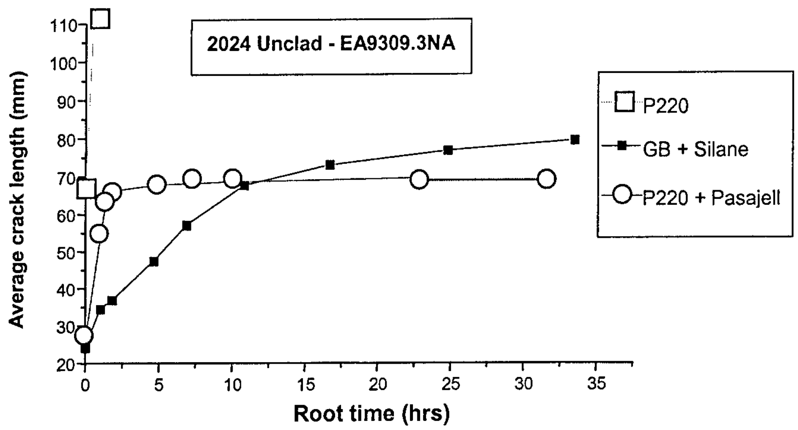


Figure 8 *Bond durability data for Al-2024 T3 unclad aluminium bonded to EA9309.3NA paste adhesive as a function of the surface pre-treatment*

3.2.2 EA9317

Figure 9 indicates the crack-growth as a function of exposure time to a humid environment for Al-2024 T3 Unclad aluminium alloy adherends bonded with EA9317. The surface pre-treatments used are indicated in the graph legend.

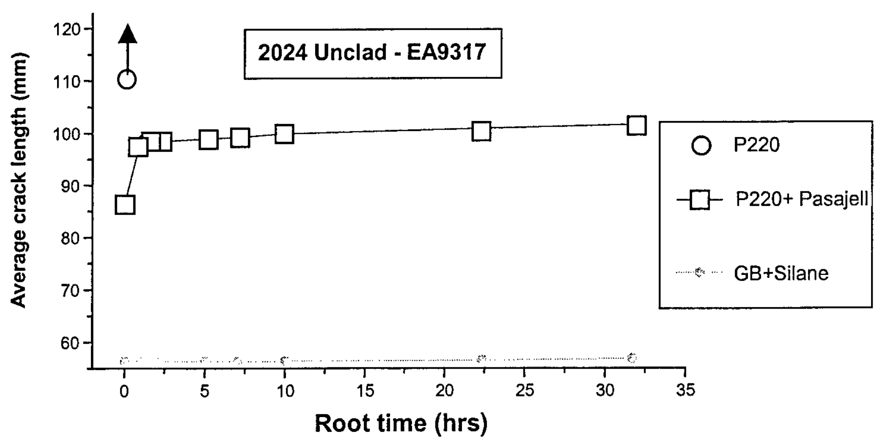


Figure 9 *Bond durability data for Al-2024 T3 unclad aluminium bonded to EA9317 paste adhesive as a function of the surface pre-treatment*

3.2.3 EA9320.NA

Figure 10 indicates the crack-growth as a function of exposure time to a humid environment for Al-2024 T3 Unclad aluminium alloy adherends bonded with EA9320.NA. The surface pre-treatments used are indicated in the graph legend.

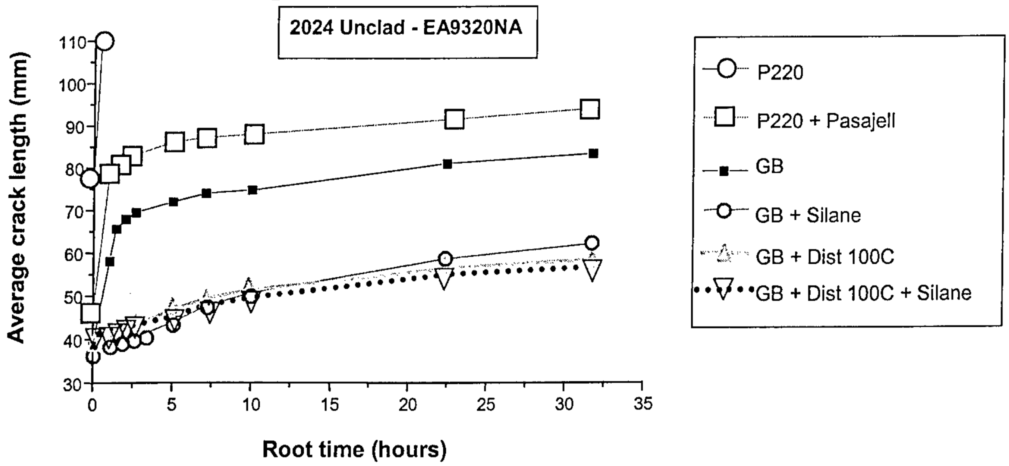


Figure 10 *Bond durability data for Al-2024 T3 unclad aluminium bonded to EA9320.NA paste adhesive as a function of the surface pre-treatment.*

3.2.4 EA9321

Figure 11 indicates the crack-growth as a function of exposure time to a humid environment for Al-2024 T3 Unclad aluminium alloy adherends bonded with EA9321. The surface pre-treatments used are indicated in the graph legend.

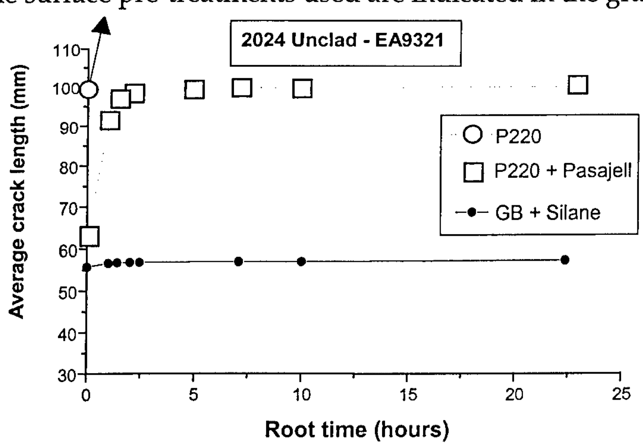


Figure 11 *Bond durability data for Al-2024 T3 unclad aluminium bonded to EA9321 paste adhesive as a function of the surface pre-treatment.*

3.2.5 EA934.NA and EA9396

Figure 12 indicates the crack-growth as a function of exposure time to a humid environment for Al-2024 T3 Unclad aluminium alloy adherends bonded with EA9396 and EA934.NA. The surface pre-treatments used are indicated in the graph legend.

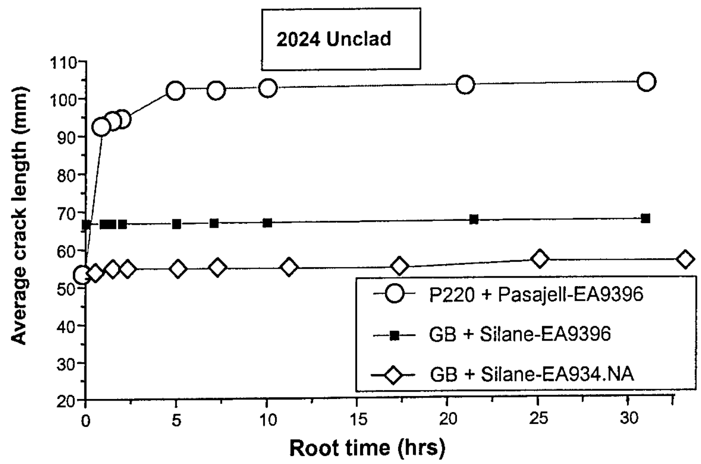


Figure 12 *Bond durability data for Al-2024 T3 unclad aluminium bonded to EA9396 and EA934.NA paste adhesive as a function of the surface pre-treatment.*

3.2.6 EC3549 and EC2216

Figure 13 indicates the crack-growth as a function of exposure time to a humid environment for Al-2024 T3 Unclad aluminium alloy adherends bonded pre-treated with grit-blast and silane prior to bonding with EC3549 and EC2216.

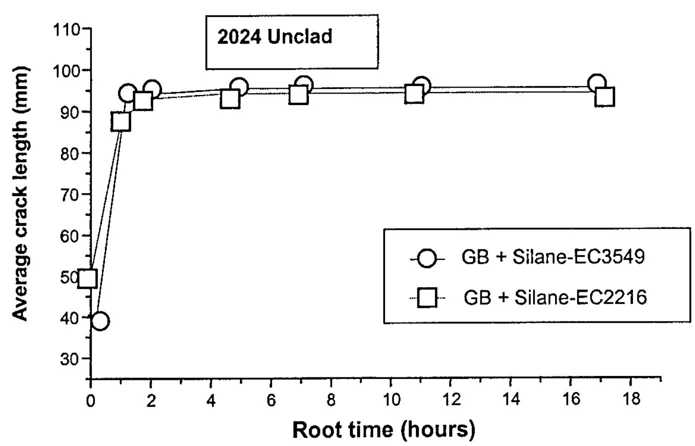


Figure 13 *Bond durability data for grit-blast and silane treated Al-2024 T3 unclad aluminium bonded to EC3549 and EC2216 paste adhesive.*

3.2.7 K138

Figure 14 indicates the crack-growth as a function of exposure time to a humid environment for Al-2024 T3 Unclad aluminium alloy adherends bonded with K138. The surface pre-treatments used are indicated in the graph legend.

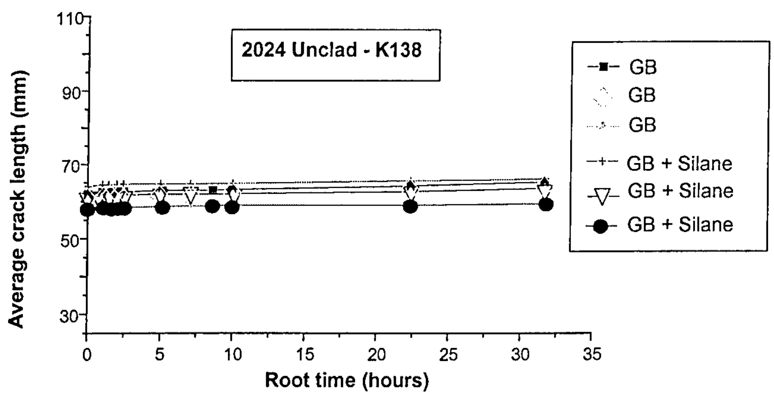


Figure 14 *Bond durability data for Al-2024 T3 unclad aluminium bonded to K138 paste adhesive as a function of the surface pre-treatment.*

3.3 Al-7075 T6 Unclad Aluminium Alloy

3.3.1 EA9309.3NA

Figure 15 indicates the crack-growth as a function of exposure time to a humid environment for Al-7075 T6 Unclad aluminium alloy adherends bonded with EA9309.3 NA. The surface pre-treatments used are indicated in the graph legend.

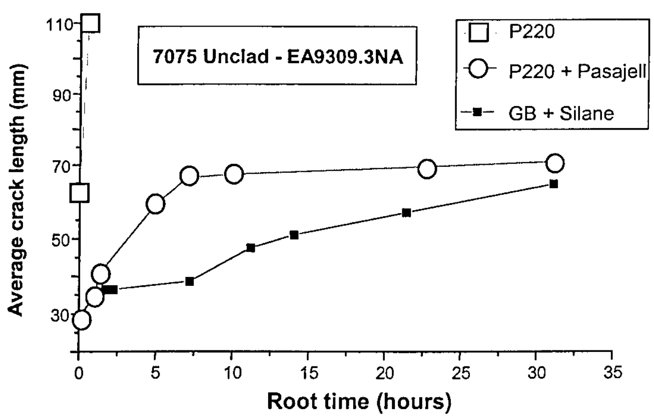


Figure 15 *Bond durability data for Al-7075 T6 unclad aluminium bonded to EA9309.3NA paste adhesive as a function of the surface pre-treatment.*

3.3.2 EA9320.NA and EA9317

Figure 16 indicates the crack-growth as a function of exposure time to a humid environment for Al-7075 T6 Unclad aluminium alloy adherends bonded with EA9320.NA. The surface pre-treatments used are indicated in the graph legend.

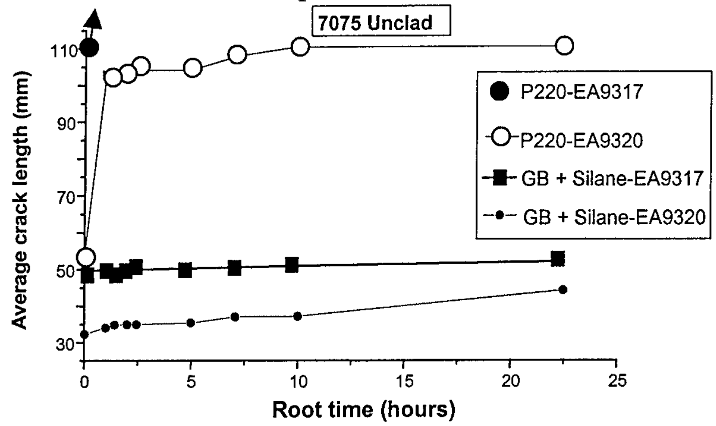


Figure 16 *Bond durability data for Al-7075 T6 unclad aluminium bonded to EA9320.NA paste adhesive as a function of the surface pre-treatment.*

3.3.3 EC3549, EC2216, EA9396, EA9321, EA934.NA

Figure 17 indicates the crack-growth as a function of exposure time to a humid environment for Al-7075 T6 Unclad aluminium alloy adherends pre-treated with grit-blast and silane prior to bonding with EC3549 B/A, EC2216, EA9396, EA9321, EA934.NA, .

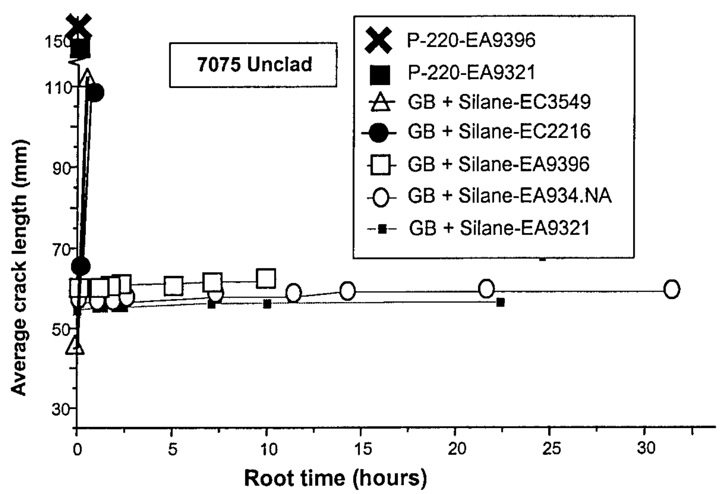


Figure 17 *Bond durability data for Al-7075 T6 unclad aluminium pre-treated with grit-blast and silane prior to bonding with EC3549, EC2216, EA9396, EA9321, EA934.NA paste adhesive*

3.3.4 K138

Figure 18 indicates the crack-growth as a function of exposure time to a humid environment for Al-7075 T6 Unclad aluminium alloy adherends bonded with K138. The surface pre-treatments used are indicated in the graph legend.

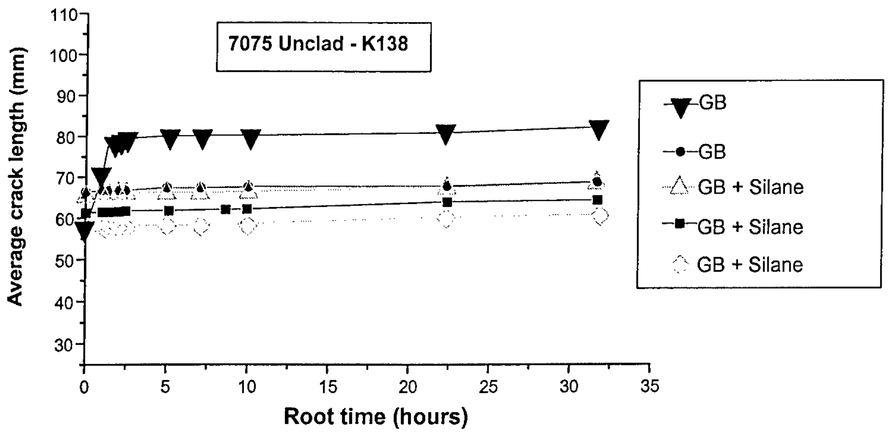


Figure 18 *Bond durability data for Al-7075 T6 unclad aluminium bonded to K138 paste adhesive as a function of the surface pre-treatment.*

3.4 Titanium 6Al-4V

3.4.1 EA9309.3NA

Figure 19 indicates the crack-growth as a function of exposure time to a humid environment for Titanium 6A1-4V adherends bonded with EA9309.3 NA. The surface pre-treatments used are indicated in the graph legend.

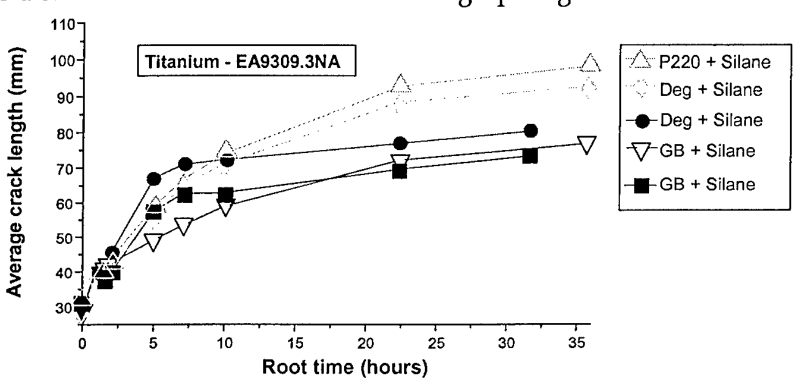


Figure 19 *Bond durability data for Titanium 6A1-4V adherends bonded to EA9309.3NA paste adhesive as a function of the surface pre-treatment.*

3.5 Titanium 6Al-4V/ 304 Stainless Steel

3.5.1 EA9309.3NA

Figure *20* indicates the crack-growth as a function of exposure time to a humid environment for Titanium 6A1-4V/ 304 Stainless Steel adherends bonded with EA9309.3 NA. The surface pre-treatments used are indicated in the graph legend.

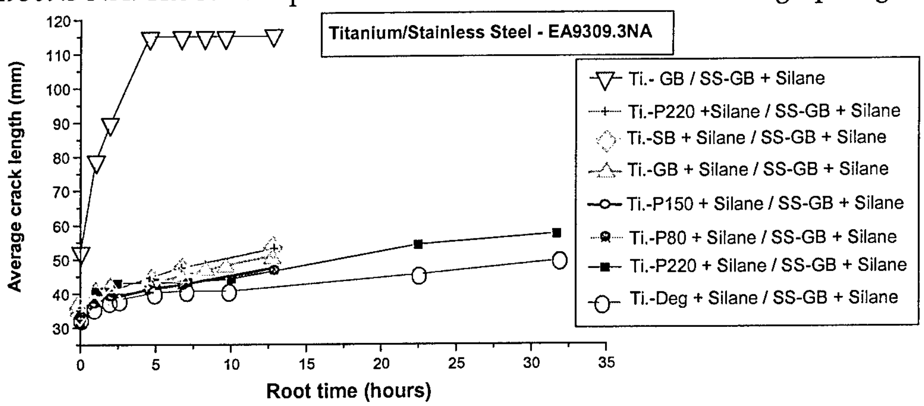


Figure 20 *Bond durability data for Titanium 6A1-4V/Stainless Steel adherends bonded to EA9309.3NA paste adhesive as a function of the surface pre-treatment.*

3.6 Fracture Analysis

Table 4 indicates the fracture surface compositions from the failed wedge test samples indicated in Figure 1. The data indicates that failure occurs predominantly between the adhesive and aluminium interface for the abraded or grit-blasted surfaces and within the silane layer for the abraded surfaces treated with epoxy-silane. Evidence for this failure is provided by the high carbon concentration present on the adhesive face that is indicative of the epoxy adhesive and the low levels of aluminium. All abraded fracture surfaces indicated silicon that may come from grit embedded in the adhesive present on the abraded aluminium surface and/or from the silica spheres present in the EA9309.3NA adhesive, which are used to control bondline thickness. The epoxy-silane treated samples indicated an increase in the silicon levels on the complementary fracture surfaces, indicating the presence of the coupling agent.

Treatment	Fracture Face	Atomic concentration (%)				
		O	N	C	Si	Al
Scotchbrite Abrade	Adhesive	19.2	3.7	71.7	4.6	0.8
	Metal	41.0	0.6	26.1	0.4	31.9
P-80 Abrade	Adhesive	17.6	4.6	72.4	2.7	2.7
	Metal	37.9	2.1	31.2	1.7	27.0
P-220 Abrade	Adhesive	18.5	5.1	70.6	3.0	2.8
	Metal	40.9	1.3	28.2	1.2	28.4
Grit-blast	Adhesive	11.0	4.4	78.0	3.3	3.3
	Metal	27.8	1.0	34.2	1.1	35.9
Scotchbrite Abrade + Silane	Adhesive	16.7	1.8	73.4	6.0	2.1
	Metal	39.9	0.8	30.0	4.5	24.8
P-80 Abrade + Silane	Adhesive	17.7	1.8	66.5	11.9	2.1
	Metal	26.3	1.8	47.4	10.4	14.2
P-220 Abrade + Silane	Adhesive	19.4	2.2	65.8	10.1	2.5
	Metal	32.1	0.8	30.0	6.2	30.9
Grit-blast + Silane	Adhesive	11.4	2.8	75.7	6.3	3.9
	Metal	22.8	1.7	43.7	5.2	26.6

Table 4 *Atomic concentrations of the elements detected on the fracture surfaces resulting from wedge tests manufactured from Al-2024T3 clad aluminium and EA9309.3NA, refer Figure 1*

The fracture surfaces from these failed samples are displayed in Appendix 1 in Figure A23. The images indicate that the abrasion procedures lead to large areas of adhesive failure. The addition of the silane to the abraded surfaces reduces the area of adhesion failure, however, the shiny appearance of the metallic adherend is still evident. In contrast, the grit-blast and grit-blast + silane treatments significantly reduce the area of adhesion failure. The failure surface from the grit-blast + silane treatment also shows markedly reduced crack propagation infront of the region of cohesive failure of the EA9309 adhesive, caused by the wedge insertion in the dry environment.

Table 5 indicates the fracture surface compositions for the failed wedge samples indicated in Figure 2. The abraded surfaces that have been treated with commercially available primers, and that are recommended by the adhesive manufacturer (9203 primer), all indicated failure occurred within the primer layer, suggesting the primer is not hydrolytically stable in the humid environment used to conduct the wedge test. Evidence for this failure is provided by the high carbon and silicon levels on the metal and adhesive surfaces and the low aluminium signal on the metal failure surface.

Table 5 also indicates the failure surface compositions for the Pasajell and Boiling Water treatments. The data indicates that the boiling water treatments have similar failure surfaces. The similar levels of silicon on both fracture surfaces is unexpected if interfacial failure was occurring between the adhesive and aluminium, given the silane treated surface may be expected to show an increased silicon concentration. If the silicon is due primarily to the silica present in the adhesive, then the failure surfaces of both samples may suggest large regions of cohesive fracture in the adhesive. However, contrary to this conclusion is the presence of a large aluminium signal on the metal fracture surface, more consistent with interfacial fracture. Possibly, fracture surface investigation with SEM may be required to resolve the true fracture path for the boiling water treatment. The Pasajell treatment indicates high levels of aluminium on the adhesive fracture surface, together with small amounts of silicon on both fracture surfaces than was seen for the other treatments. These fracture surface compositions suggest that the failure is different from the abrasion and grit-blast silane treatments in that some failure occurs as a result of moisture ingress to the aluminium-adhesive interface producing a cohesively weak hydrated oxide layer.

Figure A24 in Appendix 1 displays the fracture surfaces from the wedge test samples shown in Figure 2. The sample treated with EC1945B primer indicates a green tinge on the surface that has a metallic appearance, confirming the XPS analysis that indicated cohesive failure of the primer layer resulted in crack propagation. Another feature of Figure A24 is the adhesive failure surface of the Pasajell treatment. The metallic appearance, consistent with adhesion failure identified with XPS analysis, indicates an area larger than the adhesion failure area observed for the grit-blast and silane treatment, refer Figure A23. This suggests that the silane treatment provides a more durable surface treatment than the Pasajell, despite the similar final crack-length values measured for the respective treatments, Figures 1 and 2.

Treatment	Fracture Face	Atomic concentration (%)				
		O	N	C	Si	Al
Grit-blast + 9203 Primer	Adhesive	12.4	11.3	63.8	9.5	3.1
	Metal	13.5	9.9	61.6	8.2	6.9
Grit-blast + EC-3901 Primer	Adhesive	6.6	3.4	76.6	9.4	4.0
	Metal	30.5	3.0	39.2	8.4	18.9
Grit-blast + EC1945 Primer	Adhesive	14.5	1.4	75.6	7.3	1.3
	Metal	20.9	2.0	67.2	7.7	2.2
Grit-blast + Dist 100C	Adhesive	21.0	3.3	63.6	8.0	4.1
	Metal	34.9	1.5	32.2	6.8	24.5
Grit-blast +Dist 100C+ Silane	Adhesive	17.7	1.8	68.3	8.4	3.9
	Metal	33.6	1.1	35.9	7.7	21.7
P-220 Abrade + Pasajell	Adhesive	35.4	2.7	42.0	3.0	17.0
	Metal	39.5	1.6	32.9	0.5	25.5

Table 5 *Atomic concentrations of the elements detected on the fracture surfaces resulting from wedge tests manufactured from Al-2024T3 clad aluminium and EA9309.3NA, refer Figure 2*

Table 6 indicates the fracture surface compositions from the failed titanium wedge samples indicated in Figure 20.The fracture surfaces show similar results to the aluminium wedge samples in Table 4. The fracture appears to propagate at the titanium-adhesive interface and particularly within the silane layer. Evidence for this mode of fracture is provided by the high carbon and low titanium levels on the metal surface and the presence of silicon on both the metal and adhesive surfaces.

Figure A38 in Appendix 1 shows the failure surfaces resulting from the wedge tests carried out in Figure 20. The surfaces all display similar features with the titanium metallic surface indicating similar areas where adhesion failure has occurred post exposure of the wedge specimen to the hydro-thermal environment.

Treatment	Fracture Face	Atomic concentration (%)				
		O	N	C	Si	Ti
P-80 Abrade + Silane	Adhesive	27.1	4.1	61.6	6.6	0.6
	Metal	32.9	5.3	52.3	4.9	4.6
P-150 Abrade + Silane	Adhesive	29.6	5.0	57.0	8.4	0.0
	Metal	31.1	5.3	51.9	7.1	4.6
P-220 Abrade + Silane	Adhesive	22.0	3.7	65.1	8.8	0.4
	Metal	35.3	4.6	46.3	5.0	8.7
Scotchbrite Abrade + Silane	Adhesive	30.7	5.7	57.7	5.2	0.7
	Metal	30.8	6.3	55.7	3.5	3.8

Table 6 *Atomic concentrations of the elements detected on the fracture surfaces resulting from wedge tests manufactured from Titanium 6Al-4V/Stainless Steel and EA9309.3NA, refer* Figure 20.

3.7 Surface Roughness Measurements

Figure 21 indicates the surface roughness profiles of abraded or grit-blasted Al-2024 T3 clad aluminium alloy. Statistical averages of a number of line profiles measured for each sample were used to establish surface roughness values and the height and angle of surface features. These values are provided in Table 7. The data indicates that, apart from the P-80 abrasion, all surfaces have similar roughness of between 1 and 2μm. The maximum roughness is between 15 and 25μm, suggesting all surfaces have some deeper scratches. The P-80 abrasion increases the average roughness and maximum roughness values, indicative of the larger grit size used for the abrasion. Grit-blasting shows similar roughness values to the finer grit papers, but surface features suggest slightly larger heights and angles.

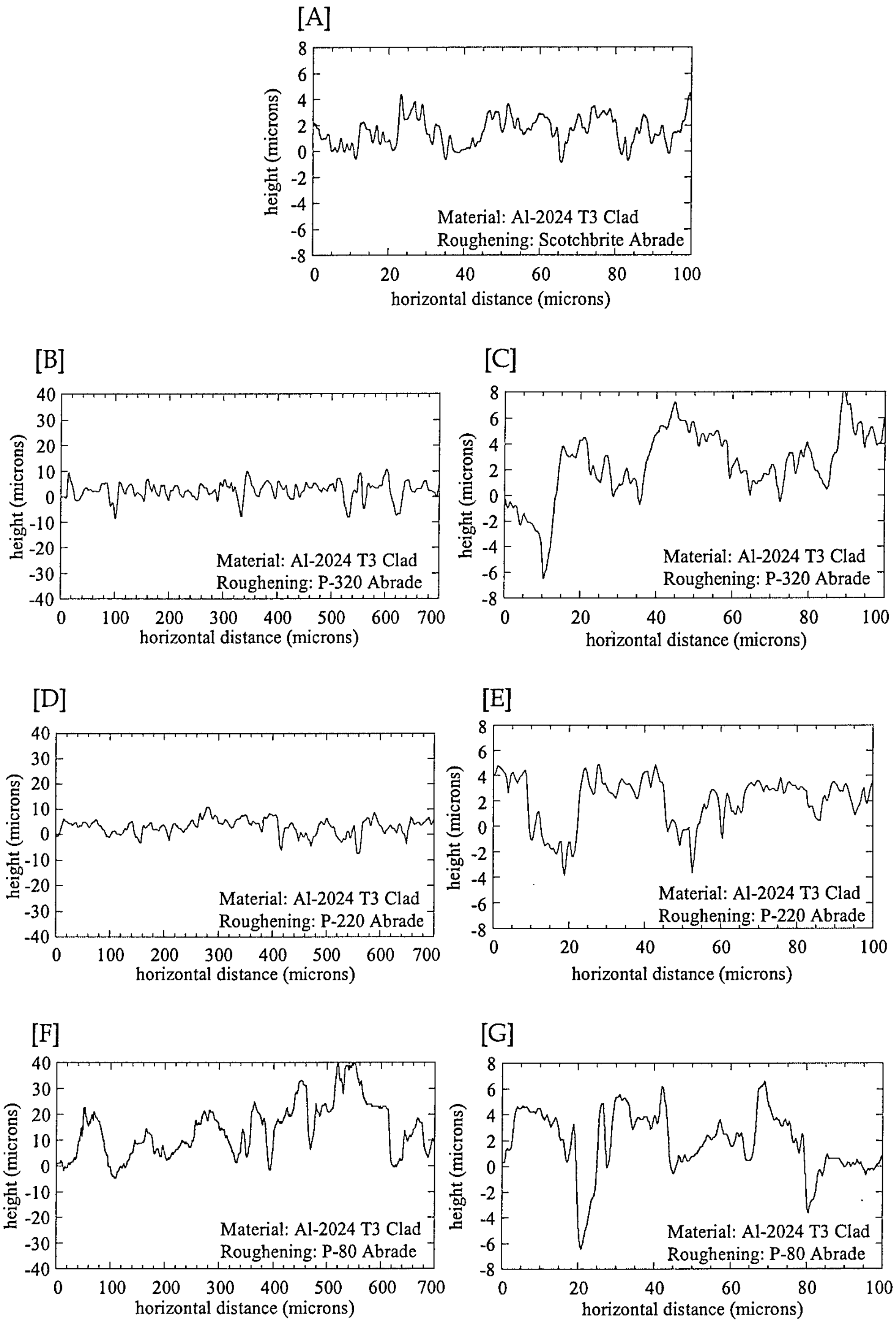
Figure 22 indicates the surface roughness profiles of abraded or grit-blasted Titanium 6Al-4V alloy. Statistical averages of a number of line profiles measured for each sample were used to establish surface roughness values and the height and angle of surface features. These values are provided in Table 8. In comparison with the aluminium surface, the Titanium surfaces show reduced surface roughness values, as would be expected on the basis of the surface hardness of the two materials. Whilst the average roughness doesn't appear to change substantially as a function of grit size, the P-80 abrasion does increase the depth of the biggest scratches. The hardness of the titanium surface is illustrated by the similarity in the roughness values measured for the finer grit abrasion and the 1μm polished surface. The average angle for the polished surface features are notably lower, indicating the polishing smooths the edges of the surface scratches introduced by the abrasion. The grit-blasted titanium surface actually produces similar surface roughness to that observed for the aluminium surface and is similar to the P-80 abraded titanium surface. However, the grit-blasted titanium surface indicates that the angle of the surface features are notably greater than those observed for the abraded surfaces.

Al-2024T3 Clad Treatment	Average Roughness (μm)/S.D.	Maximum Roughness (μm)/S.D.	Average Height (μm)/S.D.	Average Angle (Degrees)
P-80 Abrade	6.4/0.8	50.9/6.3	12/12	32/23
P-220 Abrade	1.6/0.1	24.4/1.8	2.8/2.1	36/23
P-320 Abrade	1.7/0.2	24.9/5.8	2.9/3.4	37/26
Scotchbrite Abrade	1.1/0.2	17.6/2.6	2.0/1.6	21/18
Grit-blast	1.6/0.1	18.5/5.2	3.7/2.5	43/25

Table 7 *Roughness, average height and angle of Al-2024T3 clad aluminium surfaces abraded and grit-blasted.*

Titanium 6Al-4V Treatment	Average Roughness (μm)/S.D.	Maximum Roughness (μm)/S.D.	Average Height (μm)/S.D.	Average Angle (Degrees)
P-80 Abrade	0.97/0.07	14.6/2.8	1.5/1.4	21/18
P-150 Abrade	0.69/0.09	7.6/1.3	0.9/0.9	18/15
P-220 Abrade	0.54/0.05	7.8/1.6	0.49/0.7	16/14
Scotchbrite Abrade	0.56/0.04	6.7/0.4	0.62/0.7	22/19
1μm Polish	0.37/0.02	2.8/0.04	0.77/0.5	3/5
Grit-blast	1.3/0.1	13.7/2.2	2.5/1.8	43/25

Table 8 *Roughness, average height and angle of Titanium 6Al-4V alloy surfaces abraded and grit-blasted.*


[A]
height (microns)
horizontal distance (microns)
Material: Al-2024 T3 Clad
Roughening: Scotchbrite Abrade
[B]
height (microns)
horizontal distance (microns)
Material: Al-2024 T3 Clad
Roughening: P-320 Abrade
[C]
height (microns)
horizontal distance (microns)
Material: Al-2024 T3 Clad
Roughening: P-320 Abrade
[D]
height (microns)
horizontal distance (microns)
Material: Al-2024 T3 Clad
Roughening: P-220 Abrade
[E]
height (microns)
horizontal distance (microns)
Material: Al-2024 T3 Clad
Roughening: P-220 Abrade
[F]
height (microns)
horizontal distance (microns)
Material: Al-2024 T3 Clad
Roughening: P-80 Abrade
[G]
height (microns)
horizontal distance (microns)
Material: Al-2024 T3 Clad
Roughening: P-80 Abrade

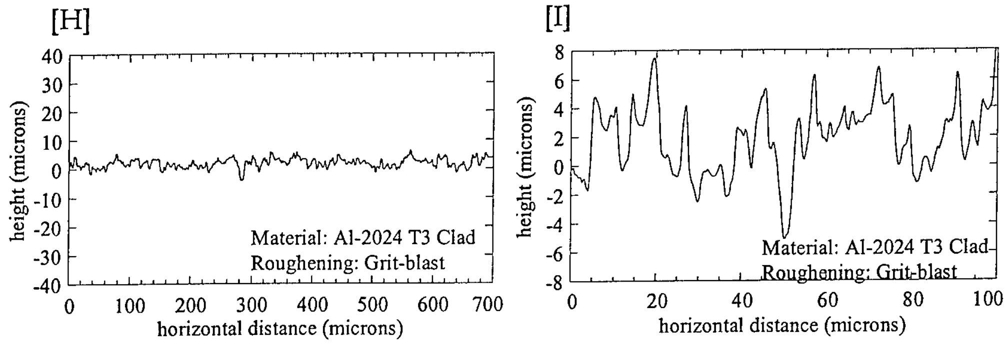
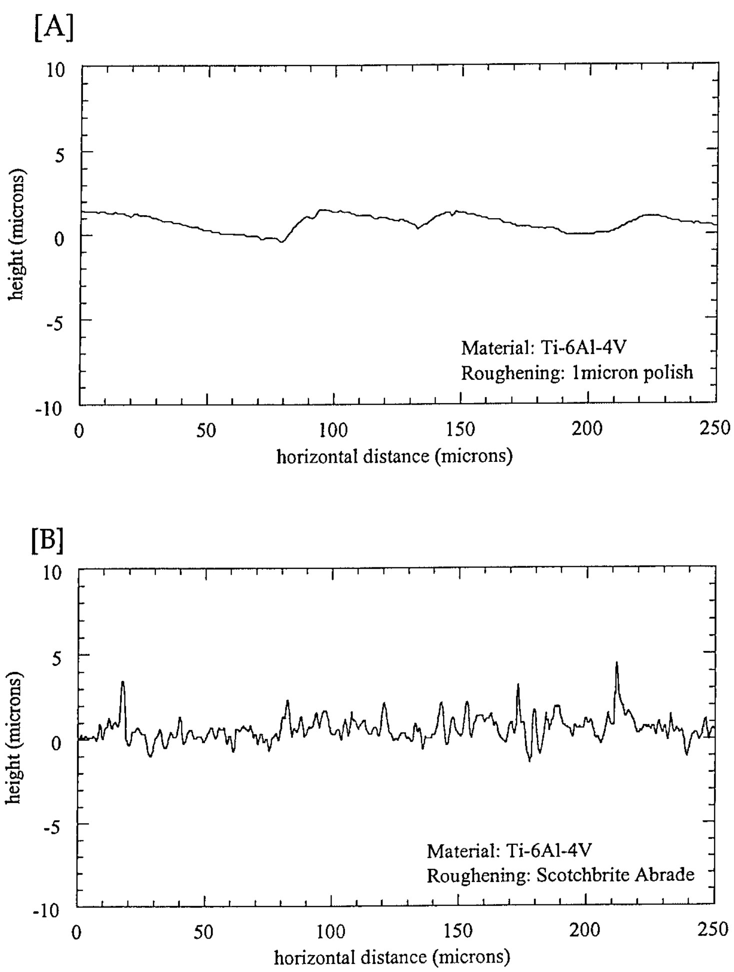
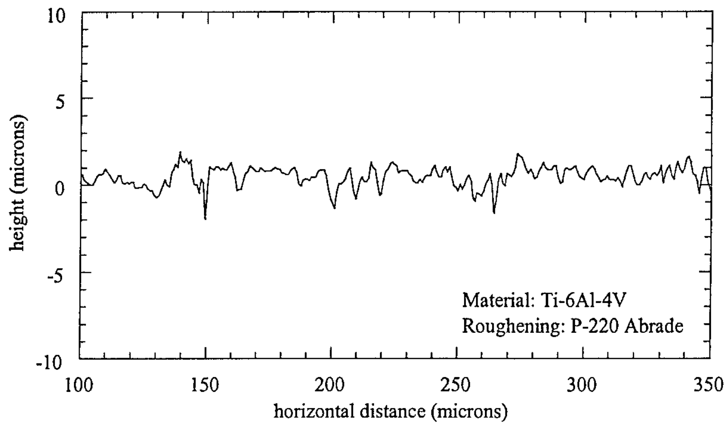


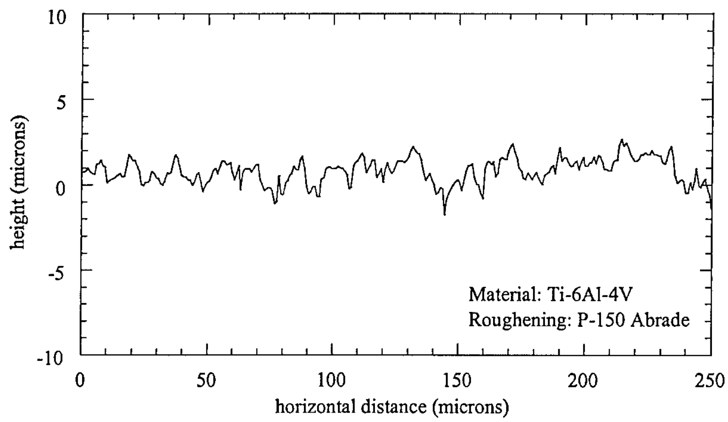
Figure 21 *[A] to [I] indicate line profiles of Al-2024T3 clad aluminium abraded and grit-blasted, measured using the Perthometer.*



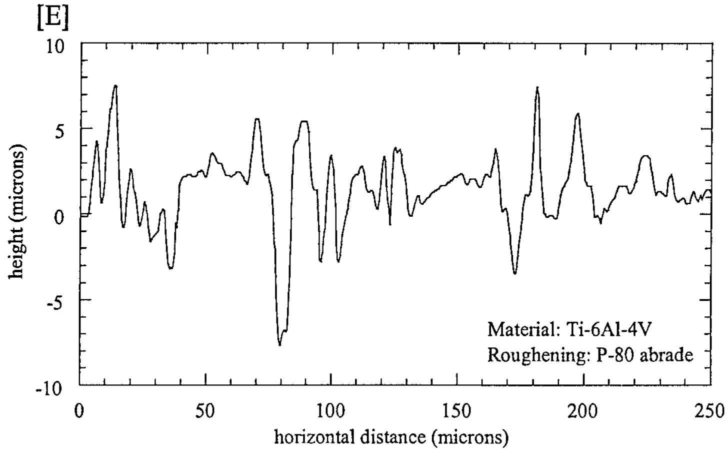
[C]


10
5
0
-5
-10
height (microns)
100
150
200
250
300
350
horizontal distance (microns)
Material: Ti-6Al-4V
Roughening: P-220 Abrade

[D]


10
5
0
-5
-10
height (microns)
0
50
100
150
200
250
horizontal distance (microns)
Material: Ti-6Al-4V
Roughening: P-150 Abrade

[E]


10
5
0
-5
-10
height (microns)
0
50
100
150
200
250
horizontal distance (microns)
Material: Ti-6Al-4V
Roughening: P-80 abrade

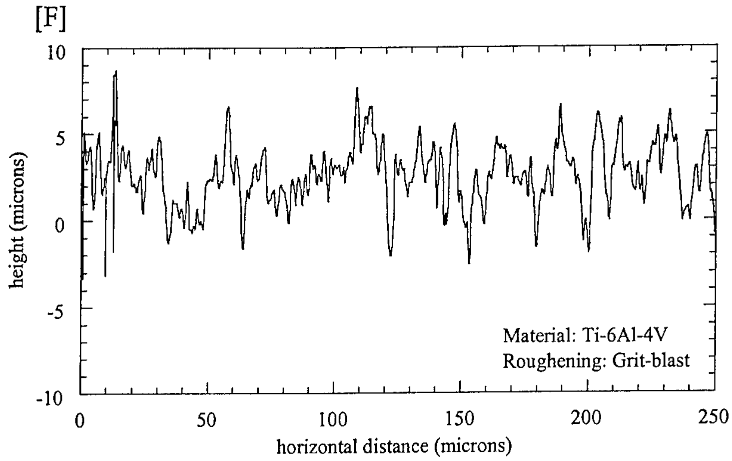


Figure 22 *Figures [A] to [F] indicate line profiles of Titanium 6Al-4V abraded and grit-blasted, measured using the Perthometer.*

4. Discusion

4.1 Al-2024T3 Clad Aluminium Alloy

4.1.1 EA9309.3 NA Paste Adhesive

The data in Figure 1 and Figure 2 suggest that both the grit-blast and silane and Pasajell treatments offer the best durability for bonds formed between EA9309.3NA adhesive and Al-2024T3 clad aluminium alloy. Grit-blasting as a pre-treatment alone appears to offer significant improvements relative to the abrasion with grit paper or scotchbrite pad. Addition of silane to all the abraded surfaces improves the durability to a level that is better than the grit-blast alone, but not as good as the grit-blast silane treatment. The surface roughness of the abrasion and grit-blasting procedures, refer Figure 21 and Table 7, suggest that the scotchbrite provides the smoothest surface and this may explain the poor durability result for this abrasion method. The surface roughness differences between the P-80 abrade and the grit-blast surface is not as obvious. The two surfaces appear to have slightly different heights and angles. Potentially, the increase in surface angle of the surface features resulting from grit-blasting are responsible for the improved performance, although further examination of surface roughness parameters and factors such as residual stress induced by the grit-blasting procedure should be examined.

The addition of a range of commercially available primers in place of the silane treatment, refer Figure 2, to the grit-blasted surface suggests that they are all inferior to the silane treatment. Fracture analysis of these primed surfaces, refer Table 5, indicates that the primer layers are hydrolytically unstable and cohesively weak when exposed to stress and high levels of environmental moisture.

The abrasion and silane treatments indicated that failure occurred predominantly at the adhesive to aluminium interface, refer Table 4. These failure modes suggest that the addition of the silane improves the hydrolytic stability of the interfacial region and retards the diffusion of moisture and the displacement of adhesive bonds, which leads to bond degradation. In contrast the failure mode of the Pasajell treatment is within a weakened hydrated oxide layer. The reason for the change in failure mode with respect to the grit-blast and silane treatment is unclear. Possibly, the Pasajell surface alters the surface chemistry and roughness of the aluminium in a beneficial way for the production of durable adhesive bonds. Pasajell is an inorganically-thickened blend of acids, activators and inhibitors and the effect of individual components may improve the hydrolytic stability of the interface. Pasajell is a on-aircraft treatment based on a acid etch treatment which uses sulphuric acid and chromic acid[6], and is known to improve bond strength of untreated surfaces by cleaning and producing a surface micro-roughness.

An alternative surface treatment that was employed involved immersing the aluminium in boiling water prior to silane treatment and bonding. These treatments, refer Figure 2, did not appear to improve the grit-blast and silane treatment. Previous work with FM-73 film adhesive suggested that this treatment may improve bond durability for aluminium-epoxy bonding[7]. The fine network structure of the boiling water film may prevent wetting by the viscous paste adhesive used here. The EA9309.3NA paste adhesive contrasts with the FM-73 adhesive which has a reduced viscosity during cure and enables penetration and wetting of the oxide network structure produced by the boiling water treatment.

4.1.2 EA934, EA9317, EA9320, EA9321, EA9396, EC2216 and EC3549

Figure 3 to Figure 6 indicate similar general trends in durability as a function of surface treatment. Grit-blast abrasion followed by silane treatment provides a marked improvement in durability of bonds formed between the paste adhesive and the clad Al-2024T3 surface. In all cases the grit-blast and silane treatment prevents significant crack-growth once the wedge is exposed to a high humidity environment. In contrast the abrasion procedures exhibit very high crack-growth rates and often fail within the first few hours of testing. Images of the failure surfaces in Appendix 1 suggest that the failure modes are similar to those observed for the EA9309.3NA adhesive, with the silane improving the hydrolytic stability of the interfacial region. The performance of the EC2216 and EC3549 adhesives is obviously inferior to the other paste adhesives despite their satisfactory initial crack-length values and the reported high peel strength values of 25piw. The reason for the poor performance of the EC2216 and EC3549 adhesives is presumably due to the degradation in mechanical properties which occurs at 50^{0}C, refer Table 3. It should be noted, however, that the silane in both cases significantly improves the relative durability and initial crack-length in comparison with the abraded surface.

4.1.3 K-138

Figure 7 indicates that the durability of the grit-blast treatment is not significantly improved by the addition of silane after the grit-blast treatment. Figure A32 in Appendix 1, indicates that the samples fail as a result of fracture within the adhesive layer. This provides an explanation why there does not appear to be any obvious improvement resulting from the silane treatment. The good result for grit-blasting alone, also seen for the EA9309.3NA adhesive, refer Figure 1, suggests that this procedure provides interfacial bonds that are stronger than the K138 bonds in a humid environment under load. The grit-blast treatment has been used for a previous bonded repair performed in the field using the K-138 adhesive [8]. The recent removal of these repairs after 20 years of service[9] indicated failure within the adhesive layer, suggesting that the interfacial bonds were still intact after an extended period.

4.2 Al-2024T3 Unclad Aluminium Alloy

4.2.1 EA9309.3 NA

Figure 8 indicates similar trends observed in Figure 1, for the clad Al-2024T3 surface. The Pasajell and grit-blast and silane treatments produce similar durability performance and this is markedly improved relative to the abraded surface treatment. The grit-blast and silane treatment, whilst having a similar final crack-length value actually performs better than the Pasajell treatment in the early stages of crack-growth, which may be important in terms of the ability to identify disbonds on the aircraft before the problem becomes significant. In comparison with the clad surface, Figure 1, the unclad surface shows slightly larger final crack-length values, suggesting bonds formed with the EA9309.3NA adhesive are less durable than the clad aluminium case.

4.2.2 EA934, EA9320NA, EA9321, EA9396, EC2216 and EC3549

Figure 9 to Figure 13 indicate that the grit-blast and silane treatment significantly improves the bond durability of bonds formed between the paste adhesives and unclad Al-2024T3 aluminium. However, unlike the EA9309.3NA adhesive, the Pasajell treatment is notably inferior to the grit-blast and silane treatment. However, the Pasajell treatment does improve the bond durability of the abraded surface. The boiling water treatment, refer Figure 10, does not improve the grit-blast treatment, as was the case with the EA9309.3NA adhesive and clad Al-2024T3 sample. Generally, the bond durability performance is similar to the clad aluminium samples, refer section 4.2.2, or slightly worse.

4.2.3 K138

Figure 14 indicates wedge data for the K138 adhesive bonded to unclad Al-2024T3 aluminium is similar to the clad aluminium results, refer Figure 7. The grit-blast and grit-blast followed by silane treatments show similar durability. The final crack-length values are also similar for the clad and unclad materials. Figure A10 indicates that, as with the clad aluminium samples, failure for both surface pre-treatments resulted from cohesive failure of the adhesive. This result is important in terms of assessing the influence that the presence of the clad layer on aluminium will have on long term bond durability in the service environment. The presence of a clad layer cannot always be guaranteed given maintenance procedures such as surface abrasion can lead to removal. The results indicate that removal of the clad layer would not influence the long term bond durability for the K138 and Al-2024T3 bond system.

4.3 Al-7075T6 Unclad Aluminium Alloy

4.3.1 EA9309.3NA

Figure 15 indicates that the Al-7075T6 aluminium alloy to EA9309.3NA adhesive bond durability is similar to that observed for the clad and unclad Al-2024T3 cases, refer Figure 1 and Figure 8. Abrasion provides very poor bond durability and the Pasajell and grit-blast silane procedure improves overall performance significantly. The final crack-length values are similar to the Al-2024T3 unclad aluminium results and are slightly inferior to the clad Al-2024T3 results. The initial crack-growth rate of the grit-blast silane treatment is superior to the Pasajell treatment and slightly better at extended exposure time.

4.3.2 EA9317 and EA9320

Figure 16 indicates the trend in bond durability for the EA9320 and EA9317 paste adhesives bonded to Al-7075T6 alloy is similar to the results with the Al-2024T3 alloy. The grit-blast and silane procedure significantly improves bond durability relative to the P-220 abrasion procedure, with the EA9317 showing inferior durability to the EA9320 adhesive.

4.3.3 EA934, EA9321, EA9396, EC2216 and EC3549.

Figure 17 indicates that the bond durability for the EA9321 and EA9396 adhesives bonded to Al-7075T6 alloy treated with the grit-blast and silane method are significantly improved relative to the abrasion treatment. The relative durability of the grit-blast and silane treated samples are slightly poorer than those observed for the clad Al-2024 alloy, but similar to the unclad Al-2024 alloy. The EA934 adhesive bonded to the grit-blast and silane treated Al-7075 alloy shows similar durability to that observed for the Al-2024 unclad alloy. Both the EC3549 and EC2216 adhesives show poor durability for the grit-blast and silane treatment, although this is still a significant improvement on the P-220 abraded samples, which failed almost immediately in the dry environment after wedge insertion. The poor performance of the EC3549 and EC2216 adhesives was also observed for the Al-2024T3 alloys, refer Figure 6 and Figure 13.

4.3.4 K138

Figure 18 indicates the relative durability performance for the grit blasted and grit-blast followed by silane treated Al-7075T6 alloy bonded to K138 adhesive. Some inconsistent results were observed for the grit-blasted treatment as shown in Figure 18. Observation of the fracture surfaces for the poor grit-blast samples and the grit-blast and silane samples, refer Figure A36 in Appendix 1, revealed that the grit-blast sample had failed at the adhesive-aluminium interface, whereas the grit-blast and silane treated surface had failed cohesively, as was observed for the Al-2024T3 alloy samples. This result provides evidence that the silane treatment improves the hydrolytic stability of the interfacial region for aluminium to K138 adhesive bonds, and suggests that the excellent durability observed for the infield repair, refer 4.1.3, would be further enhanced by the addition of silane to the grit-blasted surface. The result also provides further indication that the adhesive bonds formed with Al-7075T6 unclad aluminium alloy are more sensitive to environmental exposure than the Al-2024T3 alloy.

4.4 Titanium 6Al-4V

4.4.1 EA9309.3NA adhesive

Figure 19 indicates the relative performance of Ti-6Al-4V titanium alloy bonded to EA9309.3NA paste adhesive. The surface pre-treatments all indicate the relative performance of the silane treatment after abrasion, grit-blasting or a simple degrease. These results provide an interesting trend that suggests the roughening procedures prior to silane application are not significant. Surface roughness profiles provided in Table 8 suggest that the abrasion with P-220 grit paper does not significantly alter the surface roughness of the titanium surface, which may explain the similarity in results between the degreased and silane treated wedge specimen. The lack of improvement created by the grit-blasting prior to silane treatment, however is more difficult to explain. The data in Table 8 indicates that the grit-blasting increases the surface roughness of the titanium to levels just below that observed for the AL-2024T3 alloy surface.

4.5 Titanium 6Al-4V/ 304 Stainless Steel

4.5.1 EA9309.3NA adhesive

Figure 20 indicates the bond durability performance for titanium and stainless steel adherends bonded with EA9309.3NA. These specimens were manufactured in response to a request from HS816 SQN concerning poor performance of adhesively bonded Seahawk Centering Socket Liners on the Main Rotor Hub[10]. The results indicate that addition of silane to an abraded or grit-blasted surface significantly improves bond durability. The results are also consistent with those for the titanium samples shown in Figure 19 and indicate that there is little difference in bond durability for the titanium adherends that are simply degreased or degreased and abraded or grit-blasted prior to silane application. The data in Table 8 indicates that the P-80 abrasion and grit-blasting increased the surface roughness of the titanium surface to the greatest extent. However, the minimal effect of abrasion or grit-blasting on the silane performance may suggest that due to the titanium surface hardness, these procedures do not increase surface roughness to a level that affects bond durability. The comparison of the data in Table 7 and Table 8 for the aluminium and titanium alloys, shows that the aluminium surface roughness is significantly greater than the titanium surface roughness. An improved surface pre-treatment method for bonded repairs of the Main Rotor Hub Socket Liners may simply require degreasing and water wiping the titanium surface to insure a water-break free surface prior to silane application. The current procedure involves an abrade and solvent method followed by application of EA9203 primer. This procedure has been tested at AMRL and shown to be particularly ineffective. The results in Table 5 and Figure 2 indicate that this primer produces a hydrolytically unstable and mechanically weak interfacial region.

Failure surface analysis of the titanium/stainless steel wedge samples, refer Table 6, indicates that all fractures occur near the titanium-adhesive interface, within the silane layer. The improvement in durability, relative to the grit-blast only surface, presumably indicates the increase in the hydrolytic stability of the adhesive bonds resulting from the silane treatment. Figure A38 in Appendix 1 also shows the failure surfaces of the titanium/stainless steel wedge specimens. In all cases failure propagated at the interface between the adhesive and the titanium adherend. The stainless steel surfaces were all treated with the grit-blast and silane method and clearly exhibited greater durability than the titanium surfaces treated with the same procedure.

The results in Figure 20 indicate the stainless steel and titanium adherends have significantly improved durability relative to the titanium adherends in Figure 19. Mechanical tests carried out on the titanium and stainless steel were used to determine the yield stress for these samples in order to determine if plastic deformation of the adherends was likely to occur for the wedge tests. Equation (1) and (2) were used to determine the critical adherend thickness, h_{crit}, and fracture toughness of the EA9309.3NA adhesive.

$$G_I = \frac{h_{crit} . \in^2}{3.E} \quad (1)$$

$$G_I = \frac{3.h^3 E.w^2}{16.a^4} \quad (2)$$

where G_1 (J/m^2) is the fracture toughness, h_{crit} (m) is the adherend thickness, $\in$ (Pa)is the yield strain, E (Pa), Young's modulus, w (m) is crack opening displacement and a (m) is cracklnegth.

Material	Al-2024T3	Ti-6Al-4V	Stainless 304
$\in$ (MPa)	345	661	372
E(GPa)	72.4	114	200
h(mm)	3.15	2.3	3.15
G_1(J/m^2) (eqn1)	1726	2811	724
Initial crack length(mm) (from wedge test)	33	30	---
G_1(J/m^2) (eqn2)	3607	3233	---

Table 9 Critical parameters from wedge tests carried out using EA9309.3 NA paste adhesive indicating aluminium and stainless steel adherends would be expected to deform plastically during initial wedge test insertion.

Table 9 results indicate that all adherends would be expected to deform after wedge insertion. However, the stainless indicates the lowest G_1 value for the adherends used and would be expected to deform to a much larger extent than the titanium adherend. This may explain why the titanium/stainless steel samples, refer Figure 20, were superior to the titanium samples in Figure 19.

5. Conclusions

The following conclusions can be made about the durability of bonds formed between paste adhesive and aluminium alloy and titanium alloy surfaces as assessed by the wedge test carried out at 50^0C and 100% R.H.:

1) Grit-blast and silane treatment of clad and unclad Al-2024T3 and Al-7075T6 alloy significantly improves the durability performance for a range of paste adhesives currently used in bonded repairs of Defence Force Aircraft.

2) The paste adhesives examined indicated that the grit-blast and silane treatment performed at a similar or superior level to a standard treatment using Pasajell. The grit-

blast silane method would be used in preference to the Pasajell treatment due to the toxicity of the chemicals present in the Pasajell paste.

3) Abrasion of aluminium surfaces provides a very poor surface treatment method for bonding with aluminium alloys. The use of the grit-blast and silane treatment significantly improves the bond durability and strength for a range of paste adhesives.

4) Unclad Al-2024 and Al-7075T6 alloys generally produced bonds with paste adhesives that exhibited poorer durability than the clad Al-2024T3 alloy.

5) Fracture analysis indicated that the wedge specimens failed at the adhesive to metal interface and that the presence of silane in this region improved the hydrolytic stability of the bonds and thereby retarded the bond degradation process.

6) The application of silane to titanium Ti-6Al-4V surfaces dramatically improved bond durability when the opposite adherend was stainless steel. Plastic deformation of the steel adherend may have contributed to the bond durability results. Unlike the aluminium wedge samples, however, abrasion or grit-blasting of the titanium prior to silane application did not appear to significantly affect the durability of the wedge test samples.

7) Measurements of abraded and grit-blasted clad Al-204T3 aluminium and titanium Ti-6Al-4V indicated the aluminium layer had significantly increased surface roughness relative to the titanium. The hard titanium surface may not have been roughened sufficiently for improvements in bond durability performance with the silane treatment to have occurred.

8) Due to problems with scratches present on the Seahawk Main Rotor Hub, a viable surface pre-treatment for the socket liner replacement may simply involve a degreasing step to achieve a water-break free surface followed by silane application. This method would provide significant durability improvement over the current field repair method.

9) The bond durability performance of 3M Scotchweld EC2216 B/A and EC3549 B/A, an epoxy and urethane paste adhesive, were markedly poorer than the other paste adhesives examined. The epoxy silane and grit-blast treatment offered improved strength and durability over an abrasion procedure, however, the overall performance of these adhesives were very poor. The test temperature is known to dramatically influence the mechanical properties of these adhesives and prevents definitive conclusions regarding the surface pre-treatment performance being made.

6. Recommendations

The following recommendations can be made about the use of the grit-blast and silane procedure for adhesively bonded repairs with aluminium alloys using room temperature curing paste adhesives, on the basis of wedge tests performed at 50^0C and 100%R.H. :

1) The grit-blast and silane surface pre-treatment of Al-2024 and Al-7075 alloys should be used for bonded repairs using epoxy based paste adhesives in preference to current procedures that either involve abrasion and solvent wiping or Pasajell® (PRC Desoto 105)

2) Further studies examining the effect of the grit-blast and silane treatment for bonding paste adhesives to titanium and stainless steel adherends should be undertaken

3) Further adhesive bond durability and strength testing should be undertaken for aluminium alloys and other metallic adherends not examined in this report that are commonly encountered in bonded repairs using paste adhesives

4) Further adhesive bond durability and strength testing should be undertaken for paste adhesives not examined in this report that are commonly encountered in bonded repairs with metallic components.

5) Further adhesive bond durability and strength testing should be undertaken for current Structural Repair Manual surface pre-treatment procedures not examined in this report that are commonly used in bonded repairs of metallic components with paste adhesives.

7. References

1 A. A. Baker, R. J. Chester, International Journal of Adhesion and Adhesives, 12, 73-78, 1992

2 Royal Australian Air Force Engineering Standard C5033, "Composite Materials and Adhesive bonded Repairs", September 1995, RAAF Headquarters Logistics Command, Melbourne, Victoria, Australia.

3 ASTMD3762-79, ASTM, Annual Book of ASTM Standards Section 15, vol 15.06, Adhesives. Philadelphia: ASTM, 1992.

4 N.E. Woldman In: "Woldman's Engineering Alloys", J.P. Frick (ed.), 7th Edition, ASM International, Ohio, 1990.

5 (a) Loctite Product Selector Guide and Data Sheets, Loctite Aerospace, 2850 Willow Pass Road, Bay Point, CA, 2001

(b) 3M Data Sheets, 3M Adhesive Systems Industrial Tape and Specialist Division, St Paul, MN, 1995

6 Marceau, JA. In: Thrall EW, Shannon RW (editors), Adhesive Bonding of Aluminium Alloys , Chap. 4. New York: Marcell-Dekker, 1985.

7 A. N. Rider and D. R. Arnott, International Journal of Adhesion and Adhesives, 20, 209-220 (2000)

8 A.A.Baker, Composite Structures 2(1984), 153-181.

9 Minute BM2/53 addressed to RAAF Support Command, "Repair of Lightning Burns on Orion A9-753", 1981.

10 Requests for Alternative Bonding Procedures for MRH Socket Liners on Seahawk Helicopters:

[A] 75/153480 HS816 561/98 dated 28 Sep 98

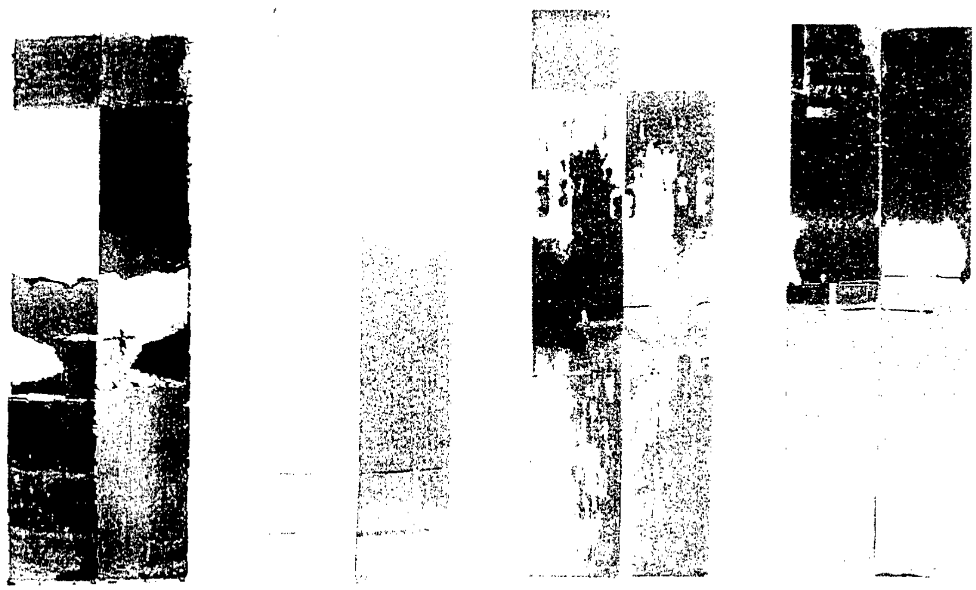
[B] AIR97/121 dated Jan99 File Reference BM2/157/Pt7 F407

[C] ASI/4027/2/6 Pt 1 (10) dated 21 Jan 99

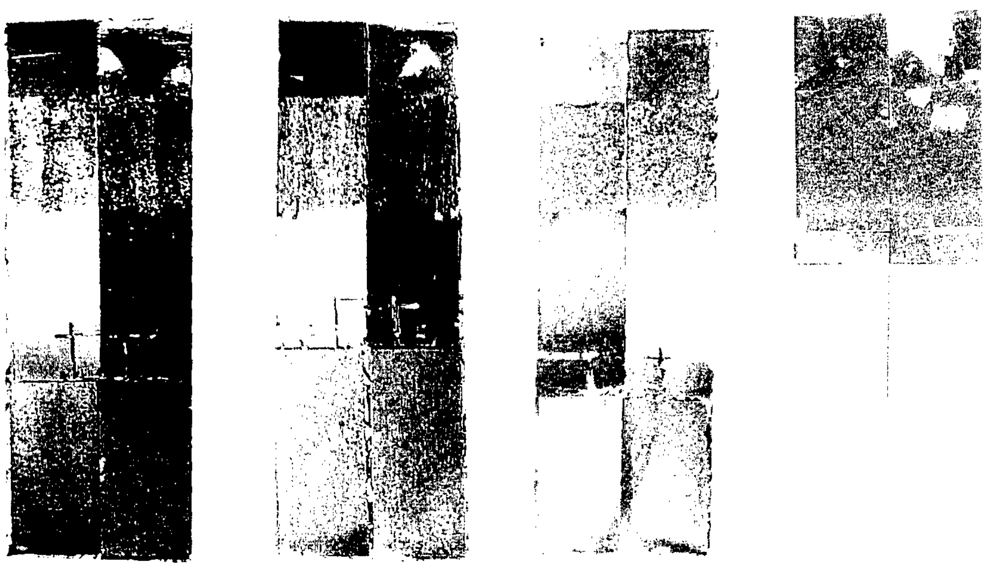
[D] ASI/COM99002 Pt 1 (13) dated 27 Jan 99

[E] ASI/COM99002 Pt 1 (14) dated Jan 99

Appendix A: Failed Wedge Test Images



Scotchbrite abrade | P-80 abrade | P-220 abrade | Grit-blast



P-220 Abrade + Silane | P-80 Abrade + Silane | Scotchbrite abrade + Silane | Grit-blast+ Silane

Figure A23 *Images of failed wedge test specimens corresponding to Figure 1. Al-2024 T3 clad aluminium bonded with EA9309.3NA paste adhesive.*

Grit-blast + 9203 primer

Grit-blast + EC-3901 primer

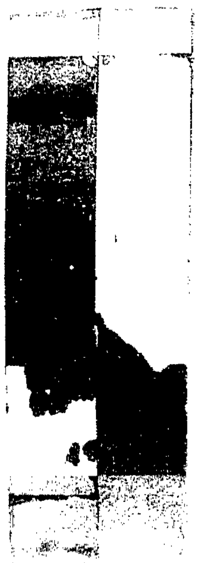
Grit-blast + EC-1945B/A primer

Grit-blast + Dist 100^{0}C

Grit-blast + Dist 100^{0}C + Silane

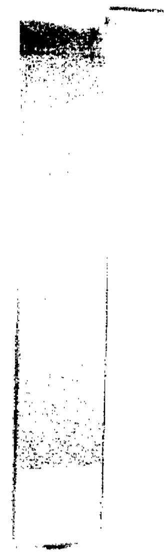
P220+Pasajell

Figure A24 *Images of failed wedge test specimens corresponding to Figure 2. Al-2024 T3 clad aluminium bonded with EA9309.3NA paste adhesive.*

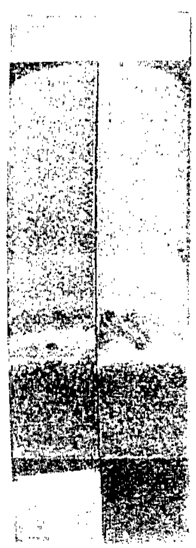


P-220 Abrade:
EA9317

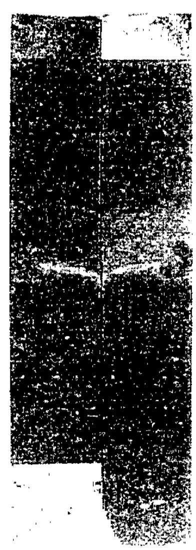
Grit-blast + Silane
EA9317



P-220 Abrade:
EA9321



P-220 Abrade:
EA9320



Grit-blast + Silane
EA9321

Grit-blast + Silane
EA9320

Figure A25 *Images of failed wedge test specimens corresponding to Figures 3 and 4. Al-2024 T3 clad aluminium bonded with EA9317, EA9321 and EA9320 paste adhesive.*

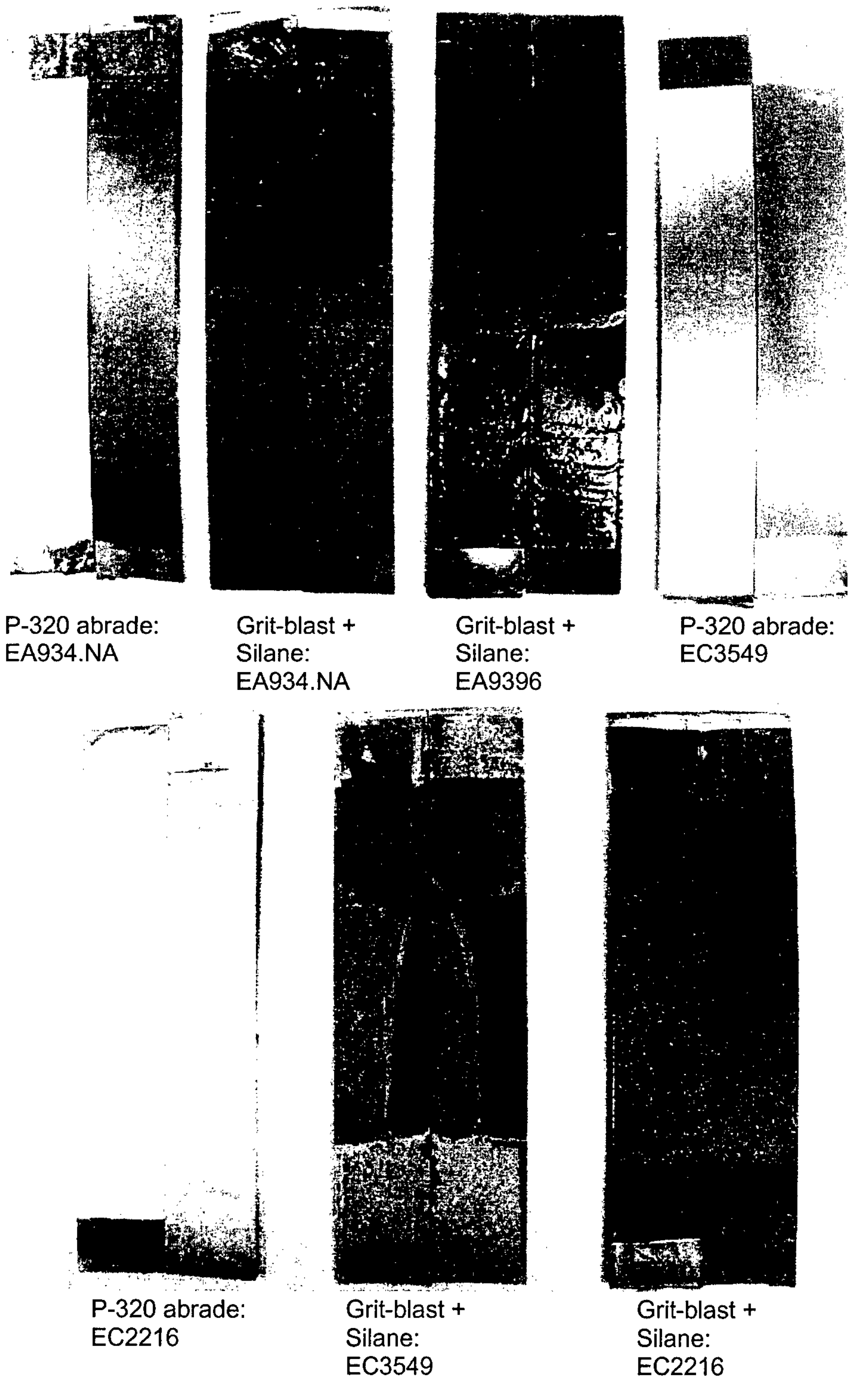
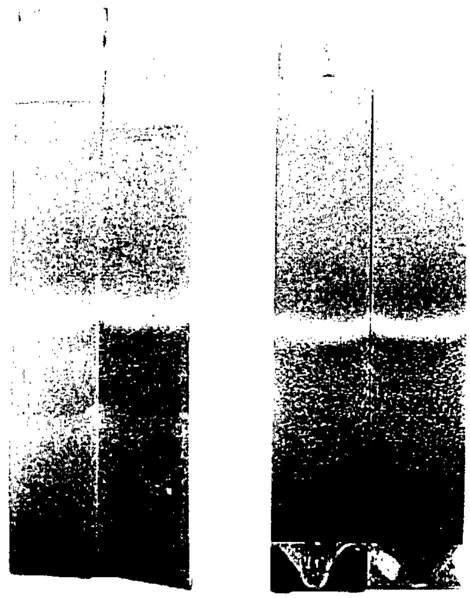


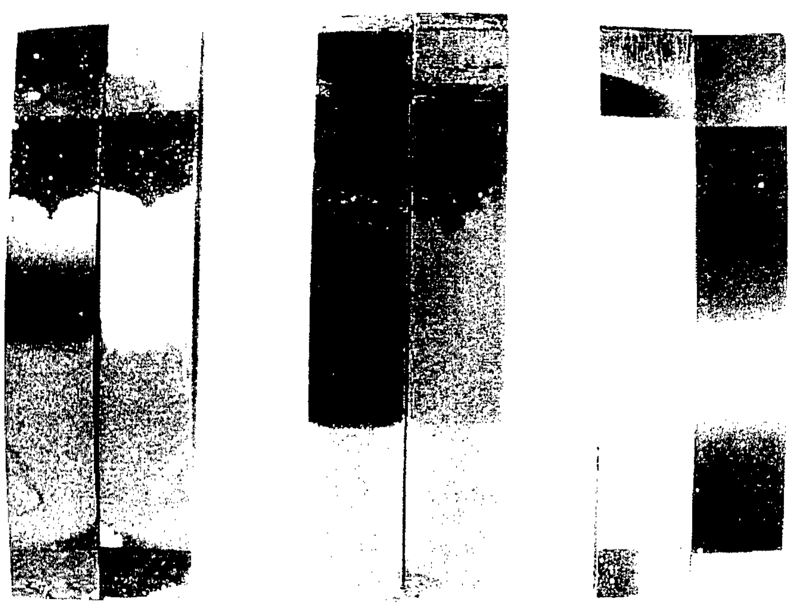
Figure A26 *Images of failed wedge test specimens corresponding to Figures 5 and 6. Al-2024 T3 clad aluminium bonded with EA934.NA, EA9396, EC3549 and EC2216 paste adhesives.*



Grit-blast

Grit-blast + Silane

Figure A27 *Images of failed wedge test specimens corresponding to Figure 7. Al-2024 T3 clad aluminium bonded with K138 paste adhesive.*



P-220 Abrade

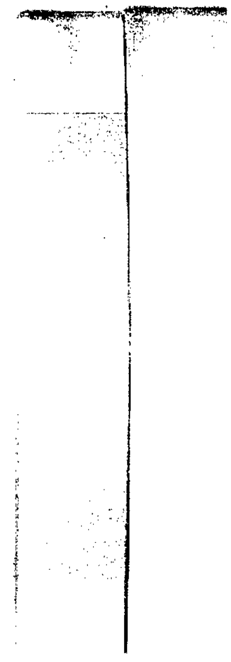
Grit-blast + Silane

P-220 Abrade + Pasajell

Figure A28 *Images of failed wedge test specimens corresponding to Figure 8. Al-2024 T3 Unclad aluminium bonded with EA9309.3NA paste adhesive.*

P-220 Abrade

P-220 Abrade + Pasajell



Grit-blast + Silane

Figure A29 *Images of failed wedge test specimens corresponding to Figure 9. Al-2024 T3 Unclad aluminium bonded with EA9317 paste adhesive.*

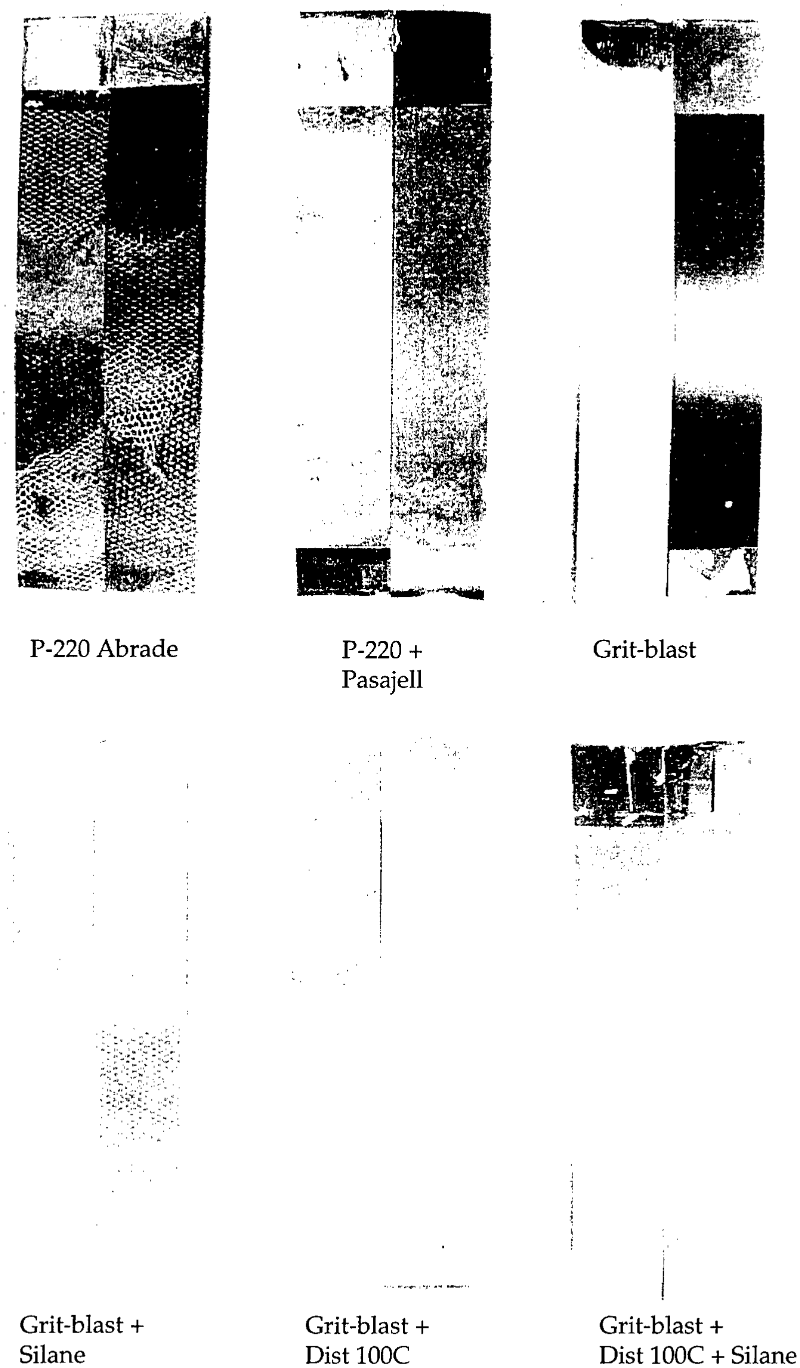


Figure A30 *Images of failed wedge test specimens corresponding to Figure 10. Al-2024 T3 Unclad aluminium bonded with EA9320NA paste adhesive.*

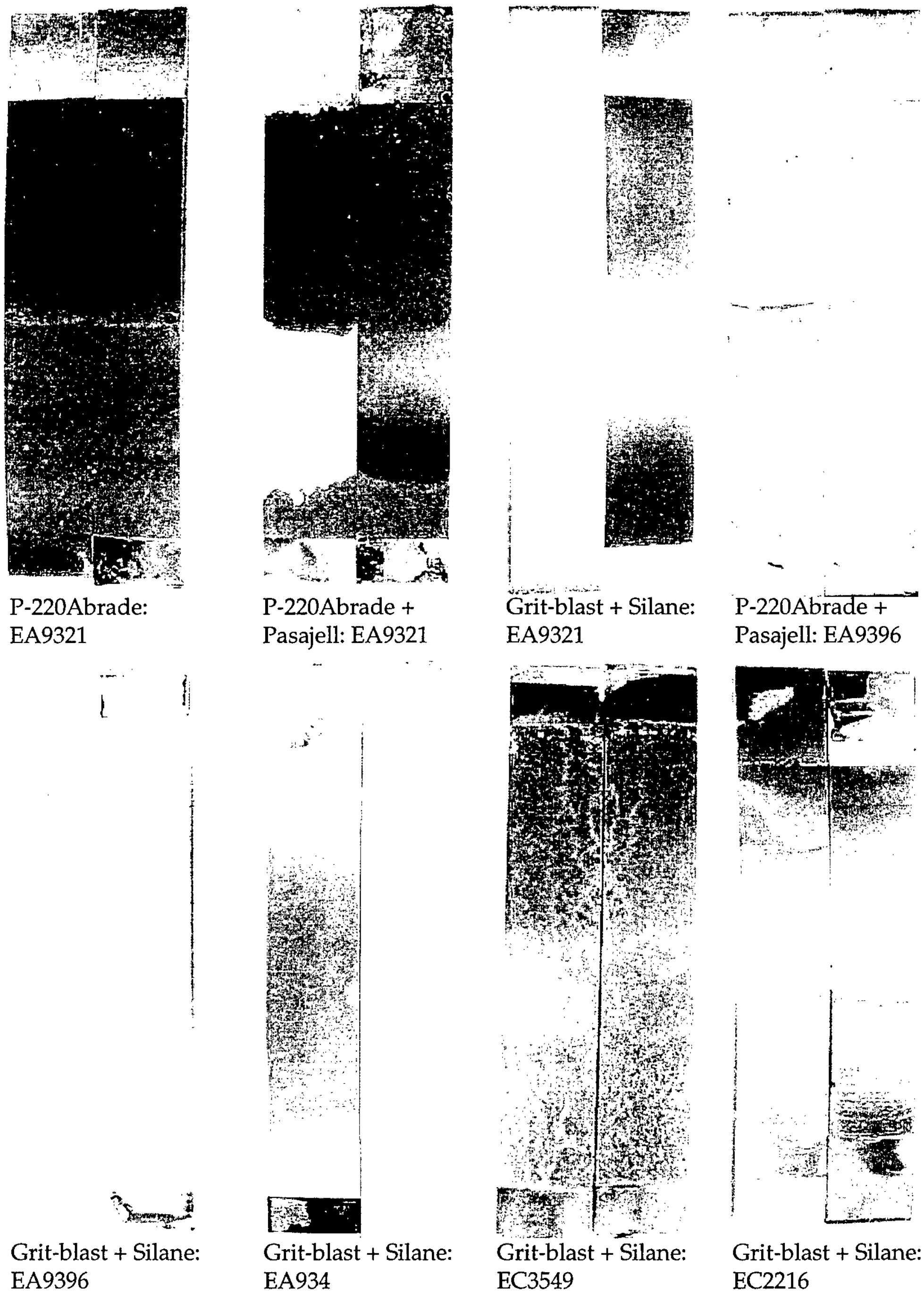
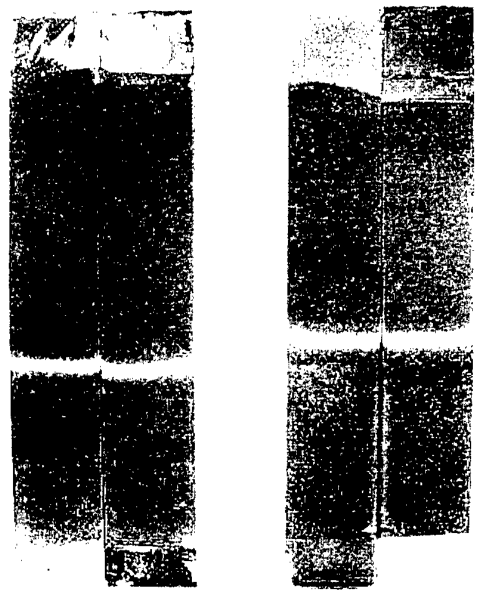


Figure A31 *Images of failed wedge test specimens corresponding to Figures 11, 12 and 13. Al-2024 T3 Unclad aluminium bonded with EA9321,EA9396, EA934,EC3549 and EC2216 paste adhesives.*

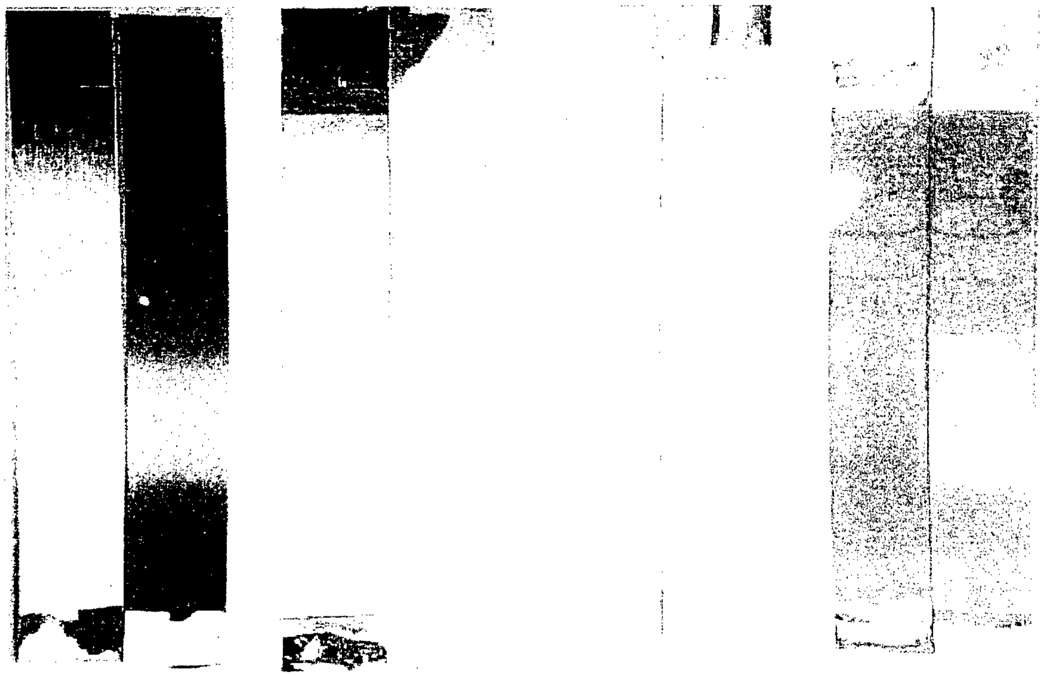


Grit-blast Grit-blast + Silane

Figure A32 *Images of failed wedge test specimens corresponding to Figure 14. Al-2024 T3 Unclad aluminium bonded with K138 paste adhesive.*

P-220 Abrade P-220 Abrade + Pasajell Grit-blast + Silane

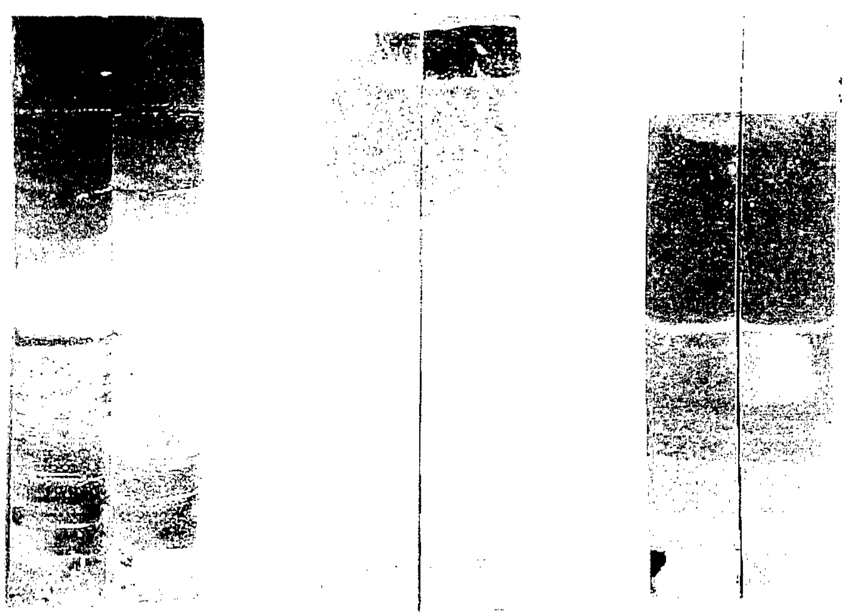
Figure A33 *Images of failed wedge test specimens corresponding to Figure 15. Al7075 T6 Unclad aluminium bonded with EA9309.3NA paste adhesive.*



P-220 Abrade: EA9317 | P-220 Abrade: EA9320 | Grit-blast + Silane:EA9320 | Grit-blast + Silane:EA9317

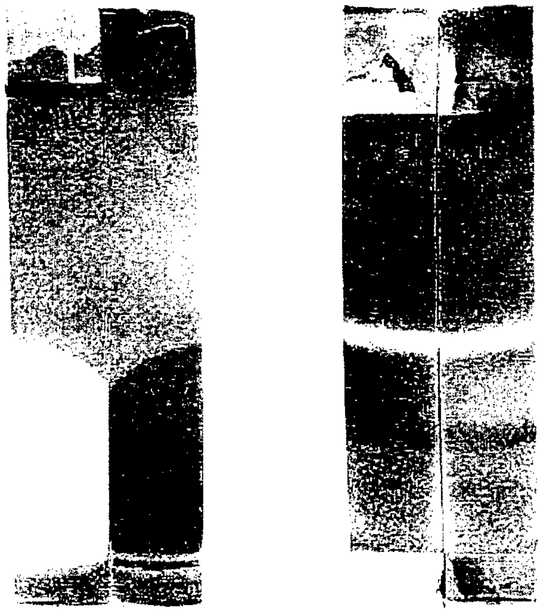
Figure A34 *Images of failed wedge test specimens corresponding to Figure 16. Al7075 T6 Unclad aluminium bonded with EA9320NA and EA9317 paste adhesives.*

P-220 Abrade: EA9396 | P-220 Abrade: EA9321 | Grit-blast + Silane: EC3549 | Grit-blast + Silane: EC2216



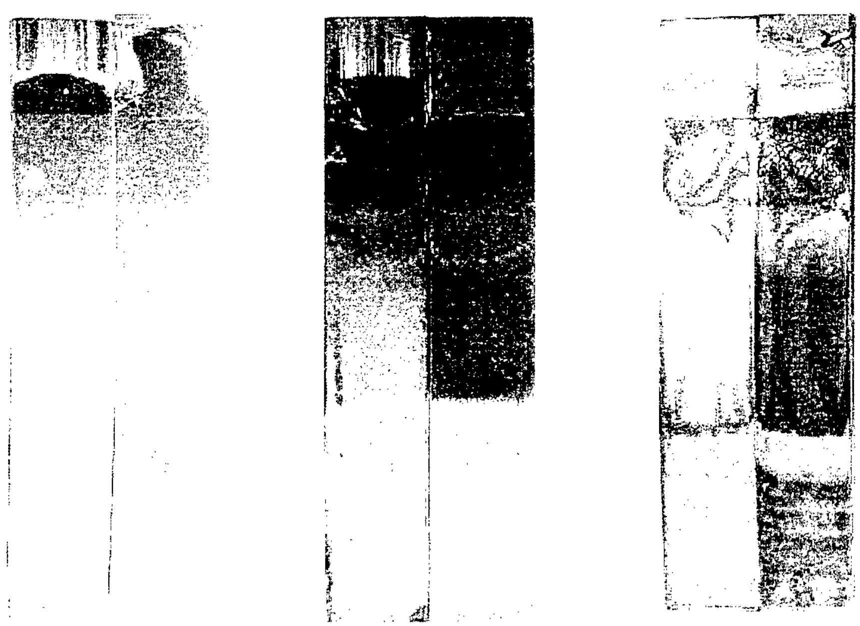
Grit-blast + Silane: EA9396 | Grit-blast + Silane: EA934NA | Grit-blast + Silane: EA9321

Figure A35 *Images of failed wedge test specimens corresponding to Figure 17. Al7075 T6 Unclad aluminium bonded with EA9396, EA9321, EC3549, EC2216, and EA934NA paste adhesives.*



Grit-blast | Grit-blast + Silane

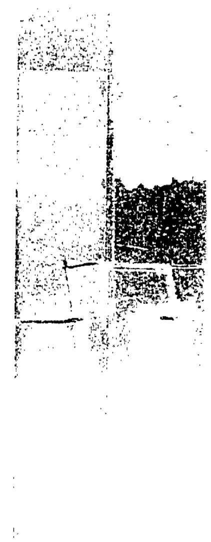
Figure A36 *Images of failed wedge test specimens corresponding to Figure 18. Al-7075 T6 Unclad aluminium bonded with K138 paste adhesive.*



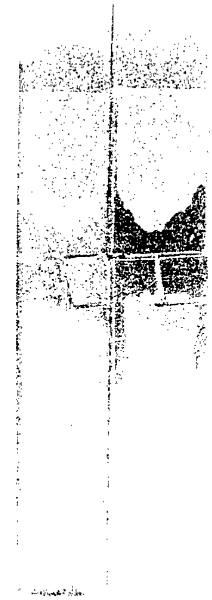
Degrease + Silane | Grit-blast + Silane | P-220 Abrade + Silane

Figure A37 *Images of failed wedge test specimens corresponding to Figure 19. Titanium 6Al-4V bonded with EA9309.3NA paste adhesive.*

Titanium:
Scotchbrite Abrade + Silane



Titanium:
P-150 Abrade + Silane



Titanium:
P-80 Abrade + Silane

Titanium:
P-220 Abrade + Silane

Titanium:
Degrease + Silane

Figure A38 *Images of failed wedge test specimens corresponding to Figure 20. Titanium 6Al-4Vand Stainless Steel bonded with EA9309.3NA paste adhesive. Failure occurred on the Titanium adherend. The Stainless Steel adherend was treated with grit-blast and silane.-*

DISTRIBUTION LIST

Bond Durability of Grit-blast and Silane-treated Metallic Adherends Bonded with Room Temperature Curing Adhesives

A.N. Rider

AUSTRALIA

DEFENCE ORGANISATION

Task Sponsor

ASI4A
DGTA

S&T Program

Chief Defence Scientist
FAS Science Policy
AS Science Corporate Management
Director General Science Policy Development
shared copy
Counsellor Defence Science, London (Doc Data Sheet)
Counsellor Defence Science, Washington (Doc Data Sheet)
Scientific Adviser to MRDC Thailand (Doc Data Sheet)
Scientific Adviser Policy and Command (Doc Data Sheet)
Navy Scientific Adviser (Doc Data Sheet and distribution list only)
Scientific Adviser - Army (Doc Data Sheet and distribution list only)
Air Force Scientific Adviser
Director Trials (Doc Data Sheet and distribution list only)

Aeronautical and Maritime Research Laboratory

Director
Chief Airframes and Engines Division
Alan Baker
Andrew Rider
Richard Bartholomuesz
Roger Vodicka

DSTO Library and Archives

Library Fishermans Bend (Doc Data Sheet)
Library Maribyrnong (Doc Data Sheet)
Library Salisbury
Australian Archives
Library, MOD, Pyrmont (Doc Data sheet only)
US Defense Technical Information Center, 2 copies
UK Defence Research Information Centre, 2 copies
Canada Defence Scientific Information Service, 1 copy
NZ Defence Information Centre, 1 copy
National Library of Australia, 1 copy

Capability Systems Staff

Director General Maritime Development (Doc Data Sheet only)
Director General Aerospace Development (Doc Data Sheet only)

Army

Stuart Schnaars, ABCA Standardisation Officer, Tobruck Barracks, Puckapunyal, 3662 (4 copies)
SO (Science), Deployable Joint Force Headquarters (DJFHQ) (L), MILPO Gallipoli Barracks, Enoggera QLD 4052 (Doc Data Sheet only)

Air Force

ASI-SRS

Intelligence Program

DGSTA Defence Intelligence Organisation
Manager, Information Centre, Defence Intelligence Organisation

Corporate Support Program

Library Manager, DLS-Canberra(Doc Data Sheet only)

UNIVERSITIES AND COLLEGES

Australian Defence Force Academy
Library
Head of Aerospace and Mechanical Engineering
Serials Section (M list), Deakin University Library, Geelong, 3217
Hargrave Library, Monash University (Doc Data Sheet only)
Librarian, Flinders University

OTHER ORGANISATIONS

NASA (Canberra)
AusInfo

OUTSIDE AUSTRALIA

ABSTRACTING AND INFORMATION ORGANISATIONS

Library, Chemical Abstracts Reference Service
Engineering Societies Library, US
Materials Information, Cambridge Scientific Abstracts, US
Documents Librarian, The Center for Research Libraries, US

INFORMATION EXCHANGE AGREEMENT PARTNERS

Acquisitions Unit, Science Reference and Information Service, UK
Library - Exchange Desk, National Institute of Standards and Technology, US
National Aerospace Laboratory, Japan
National Aerospace Laboratory, Netherlands

SPARES (5 copies)

Total number of copies: 44

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION
DOCUMENT CONTROL DATA

	1. PRIVACY MARKING/CAVEAT (OF DOCUMENT)
2. TITLE Bond Durability of Grit-blast and Silane treated Metallic Adherends Bonded with Room Temperature Curing Adhesives	3. SECURITY CLASSIFICATION (FOR UNCLASSIFIED REPORTS THAT ARE LIMITED RELEASE USE (L) NEXT TO DOCUMENT CLASSIFICATION) Document (U) Title (U) Abstract (U)
4. AUTHOR(S) Andrew Rider	5. CORPORATE AUTHOR Aeronautical and Maritime Research Laboratory 506 Lorimer St Fishermans Bend Victoria 3207 Australia

6a. DSTO NUMBER DSTO-TR-1187	6b. AR NUMBER AR-011-949	6c. TYPE OF REPORT Technical Report	7. DOCUMENT DATE July, 2001

8. FILE NUMBER M1/9/967	9. TASK NUMBER AIR 01/123	10. TASK SPONSOR DGTA	11. NO. OF PAGES 50	12. NO. OF REFERENCES 9

13. URL on the World Wide Web http://www.dsto.defence.gov.au/corporate/reports/DSTO-TR-1187.pdf	14. RELEASE AUTHORITY Chief, Airframes and Engines Division

15. SECONDARY RELEASE STATEMENT OF THIS DOCUMENT

Approved for public release

OVERSEAS ENQUIRIES OUTSIDE STATED LIMITATIONS SHOULD BE REFERRED THROUGH DOCUMENT EXCHANGE, PO BOX 1500, SALISBURY, SA 5108

16. DELIBERATE ANNOUNCEMENT

No Limitations

17. CASUAL ANNOUNCEMENT Yes

18. DEFTEST DESCRIPTORS

Adhesive Bonding, Organo-silane coupling agent

19. ABSTRACT

The "Australian Silane Treatment" has been successfully used for bonded repairs carried out at RAAF Airbases for a number of years. This surface treatment has provided a reliable and non-toxic alternative to surface pre-treatments recommended in Structural Repair Manuals (SRM) for metallic adhesive bonded repairs. Generally, however, the silane treatment has only been applied in bonded repairs involving the use of high temperature curing structural adhesives. The purpose of the study detailed in this report was to examine the feasibility of extending the application of the silane pre-treatment to metallic repairs involving the use of room temperature or paste adhesive systems employed in a range of airbase repairs. Wedge style durability tests were conducted for a range of metallic adherends and room temperature curing adhesives. The durability performance of the grit-blast and epoxy silane metallic adherend pre-treatment was compared with standard pre-treatments recommended in a range of SRMs. Generally, the data indicated that the grit-blast and silane pre-treatment offered either improved or similar performance to the SRM alternative pre-treatments on the basis of results from wedge style durability tests conducted at $50^{0}C$ and 100% relative humidity.