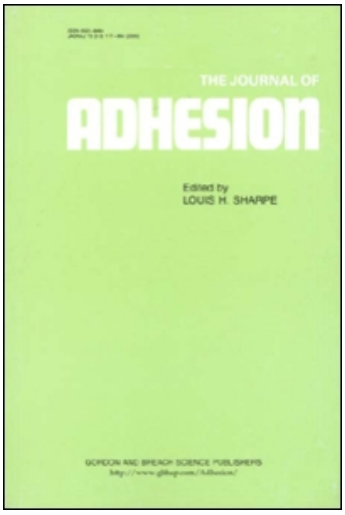

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On the Environmental Durability of Adhesive Bonded Titanium Joints

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On the Environmental Durability of Adhesive Bonded Titanium Joints†

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The durabilities of three pretreatments developed for the structural adhesive bonding of titanium alloys are being investigated. These are alkaline hydrogen peroxide etch (AHP), sodium hydroxide anodise (SHA) and catalytic alkaline hydrogen peroxide etch (CAHP). Natural weathering in several climates and accelerated laboratory aging are being carried out. The AHP etch has proved very durable. To date SHA and CAHP treatments are as good. Comparison of quality control and durability data suggests that wedge test crack growth data may not be suitable for these pretreatments. The use of the accelerated weathering data for predicting natural weathering is discussed.

KEY WORDS Accelerated weathering; environmental durability; natural weathering; structural adhesive bonding; surface pretreatments; titanium alloy.

INTRODUCTION

Many different pretreatments have been suggested over the last twenty years for imparting to titanium and its alloys a surface which would result in durable adhesive bonds.[1–3]

Research into pretreatments and durability has been carried out for the Royal Aircraft Establishment (RAE) since the early 1970s. The first pretreatment developed was the alkaline hydrogen pero-

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xide etch (AHP).[4,5] The durability of this pretreatment in comparison with others current in 1974 is illustrated in Figure 1 which shows the times to failure of joints stressed at 20% ultimate and exposed to 45°C/95–100% RH.[6] Unfortunately, it is not suitable for large scale continuous production and further work has been directed towards modifying it or developing equally durable alternatives.[7–9] RAE are investigating sodium hydroxide anodising (SHA) and a catalytic alkaline hydrogen peroxide etch (CAHP).[8,9]

Durability of adhesive bonded TA10 (Ti6Al4V) pretreated by the AHP, SHA and CAHP methods is being assessed by stressed and unstressed static exposure of double lap joints exposed to hot-wet, hot-dry and temperate natural climates and accelerated laboratory aging at elevated temperature and high humidity.

EXPERIMENTAL

Three separate exposure trials have been started, but only the first has been completed. Outdoor natural weathering has been carried out at a temperate site (RAE, Farnborough) and two tropical sites

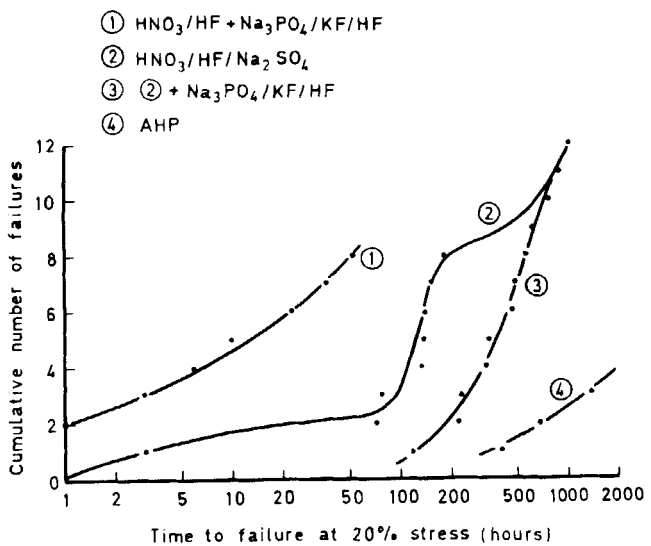

FIGURE 1 Stressed durability of TA10 joints exposed to 45°C/95–100% RH.

TABLE I
Climatic data for outdoor exposure sites

	Temperate (RAE)	Hot-wet (Innisfail)	Hot-dry (Cloncurry)
Average temperature (°C)	10	23	25
Average humidity (%)	78	83	55
Average monthly rainfall (mm)	49	297	39

at the Joint Tropical Test and Research Establishment (JTTRE) in Queensland, Australia. The average annual climates of the three sites are given in Table I. Average monthly data are shown in Figure 2. Table II lists the exposure sites, accelerated laboratory conditions and stress levels used in each trial.

Specimen Preparation

All adherends were TA10 (Ti6Al4V). Pretreatments were carried out as in Ref. 8 except that adherends were wet-blasted with alumina grit between vapour degreasing and alkaline degreasing. Adherends were primed with recommended surface protection solutions and bonded with Redux 312/5 modified epoxy film adhesive cured for 30 minutes at 120°C to give double overlap shear joints (overlap 25.4 × 12.7 mm, nominal total glueline thickness 0.2 mm).

Quality Control

Adherends for the making of shear joints were pretreated in batches, each batch being accompanied by adherends for the preparation of three wedge test specimens,[10] which were also bonded in the same autoclave run as the shear joints.

The preparation of specimens for Trial A was also used to determine the pretreatment bath life of the AHP process.[11] Crack growths on wedge test specimens were measured after 5 hours exposure at 50°C/100% RH. Batches of adherends were put through each pretreatment bath until crack growth had reached ≥25 mm. Bonded joints made from every batch of adherends were included in the trial. Data can therefore be used to determine how good a predictor of long term durability the wedge test is.

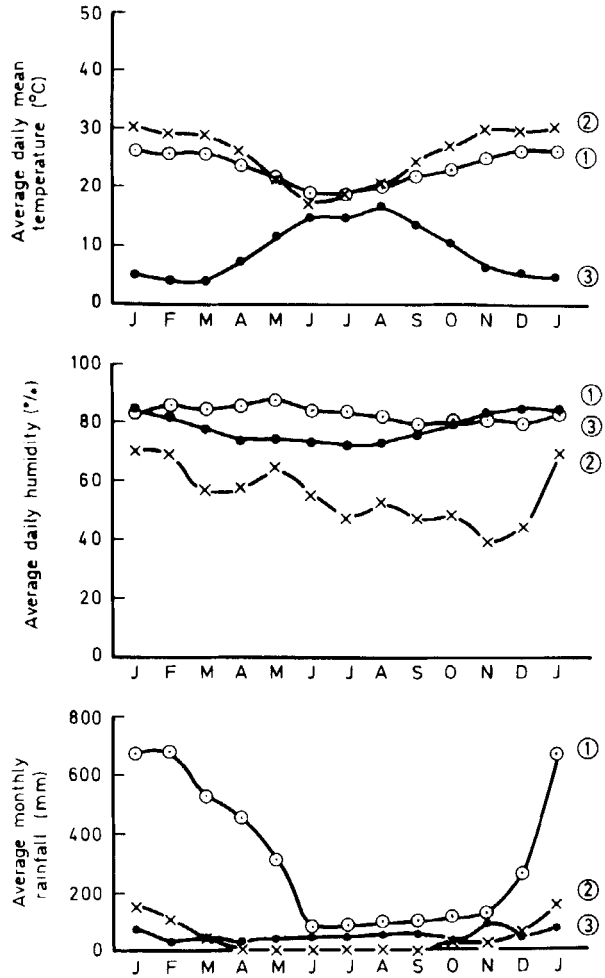

FIGURE 2 Meteorological summary for sites used for exposure trials: (1) hot-wet, Innisfail, (2) hot-dry, Cloncurry, (3) temperate, RAE.

At least two joints from each batch were tested in tension. The average failure load of the control joints over all the batches in each trial were used to set the loads applied to stressed joints in that trial. Test rates for Trials A and B were 2 mm min^{-1} or 8.9 kN min^{-1} and 1 mm min^{-1} or 4.4 kN min^{-1} for Trial C. One of

TABLE II
Trials conditions

Trial	Pretreatment	Exposure sites	Laboratory conditions	Stress levels (%)
A	AHP	Temperate Hot-wet Hot-dry	20°C/65% RH	0, 5, 10, 20
B	AHP	Hot-wet	35°C/85% RH	0, 20
C	SHA and CAHP	Hot-wet	50°C/95% RH	0, 10, 20

the five establishments at which testing was carried out used constant loading rate and the others constant crosshead speed.

Testing After Exposure

After withdrawal from exposure, joints were tested in tension in a laboratory environment of about 20°C/65% RH. Failure loads were recorded. In most of the discussion in this paper, results are expressed in terms of strength retention, which is defined as the measured failure load after exposure expressed as a percentage of the quality control strength for the appropriate batch of joints.

The strongest and weakest joints of each set of specimens were examined under a low-powered microscope (×2.5). Percentage areas of voids in the adhesive, cohesive failure in the adhesive and apparent interfacial failure between adhesive and metal were estimated.

RESULTS AND DISCUSSION

Effect of Different Climates

In Trial A, joints were exposed to four different climates, three natural and the fourth constant 20°C/65% RH. The changes in strength retention measured are shown in Figure 3. No stressed joints failed during outdoor exposure in eight years and there was no statistically significant difference between the residual strengths measured for stressed and unstressed joints.

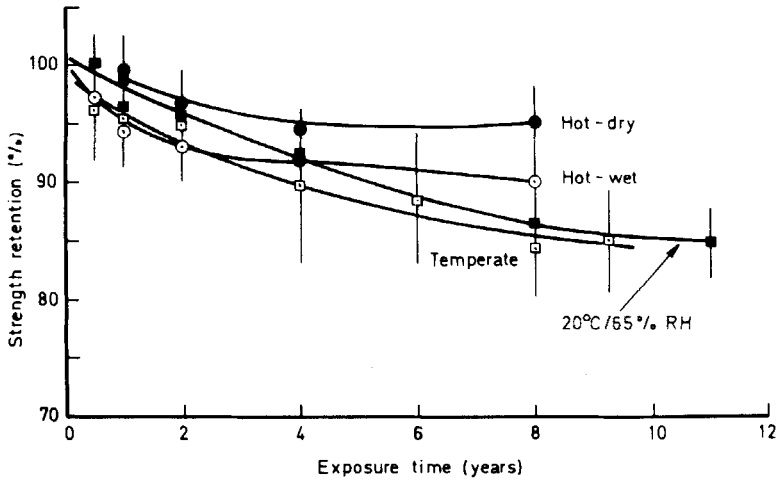

FIGURE 3 Effect of exposure to different climate on joint strength (Trial A).

Even after 8 years exposure to the hot-wet climate only 10% of the initial joint strength had been lost, and only 15% after 11 years at 20°C/65% RH. These results therefore confirm the durability of the alkaline hydrogen peroxide pretreatment.

Comparison of Trials/Pretreatments

The available data for Trials A, B and C for joints exposed at Innisfail is shown in Figure 4. Strength retention is referred to the

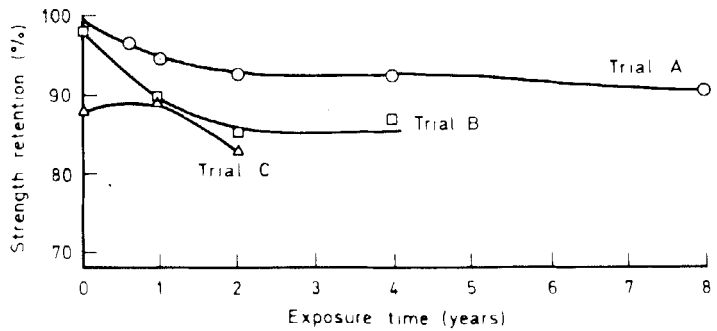

FIGURE 4 Effect of hot-wet natural exposure on retention of joint strength for different surface pretreatments.

control strengths of joints as measures by the manufacturers. The values given are averages over stressed and unstressed joints. Trial C points are, for simplicity, averages over both pretreatments. Zero time points refer to tests carried out at JTTRE when the joints are mounted in the stress frames.

From Figure 4, it can be seen that the durability of joints in Trial B appears to be lower than those in Trial A, although, as in Trial A, loss of strength between 2 and 4 years was nil. The joints for Trials A and B were prepared by different manufacturers, so that the observed differences between the trials might be confirmation of difficulties in using the AHP process for production. However, the trials also employed different recommended primer systems and it may be that this has contributed to the observed differences in strength retention. It is intended to carry out further work to test this theory, since the primers concerned were developed for use on aluminium rather than titanium surfaces.

The zero time strengths measured at JTTRE for joints in Trial C were substantially lower than the manufacturer's control strengths. There is no obvious reason for this, although significant differences have been observed for joints in other trials and it has been suggested that the conditions under which joints are shipped to Australia may be having an effect.

If the zero time strength retention for Trial C is ignored, retentions after exposure are comparable with those measured in Trial B. Results of tests due in 1988 are awaited with interest to see whether the trend of minimal strength loss between 2 and 4 years measured in Trials A and B is also found in Trial C, or whether the new pretreatments have a lower durability than the AHP etch.

No joints from Trials A and B have failed under 20% stress, but three TA10/CAHP joints have failed, one in February 1986 and one each in February and July 1987. All are from a batch which it is suspected were improperly pretreated; this will be discussed in more detail later. It is interesting to look at failure dates in conjunction with climatic data. Figure 5 shows the number of failures recorded in each month of the year over a range of adhesives and adherends. Comparison with the average monthly rainfall and the average monthly temperature suggests that failures tend to take place when the temperature is high and there is substantial rainfall.

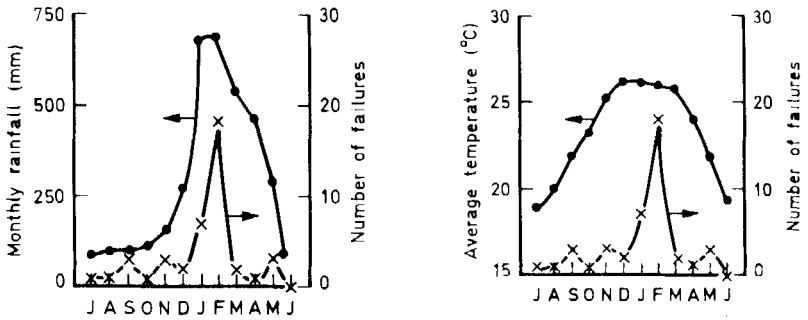

FIGURE 5 Correlation between failures under 20% stress and climate; (a) rainfall, (b) temperature.

Prediction of Durability

Outdoor exposure trials may take many years to yield the desired data. While it is possible to carry out accelerated laboratory tests by increasing test temperature and/or humidity or by using higher stress levels, it is necessary to be able to relate the results to those of natural weathering.

Two methods are considered in this paper: the comparison of quality control data with outdoor weathering and the use of accelerated aging at elevated temperature and humidity.

Quality control data The quality control tests used by the manufacturers of the joints were the Boeing wedge test and static tensile strength. The wedge test is a stressed exposure test and is generally used for the quality control of surface pretreatment, poor or inadequate treatments giving large crack growths. Static joint strength can be affected by incomplete cure of the adhesive and by bondline flaws, and by inadequate surface pretreatment.

During the preparation of joints for Trial A, tests were also carried out to determine the life of the alkaline hydrogen peroxide etch bath. The effect of bath aging on the wedge test crack growth over 5 hours at 45–50°C/95–100% RH is shown in Figure 6. In general, etch rate decreased and crack growth increased with bath age. All joints prepared were included in the trial so that it is possible to determine whether there was any difference in durability between batches of joints with crack growths which varied from 2 to

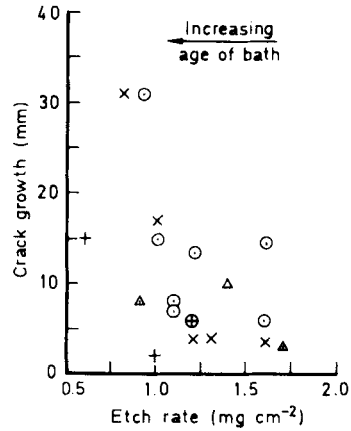

FIGURE 6 Effect of AHP etch rate on wedge test crack growth.

31 mm. Average batch control strengths varied between 29.2 kN and 32.2 kN.

Figure 7 shows how the strength retention of Trial A joints varied with exposure to hot-wet conditions. Separate lines are drawn for batches of joints of a range of wedge test crack growths. The lines for 8 mm crack growth include data for two batches of joints. These were very close in durability and are not differentiated by symbols.

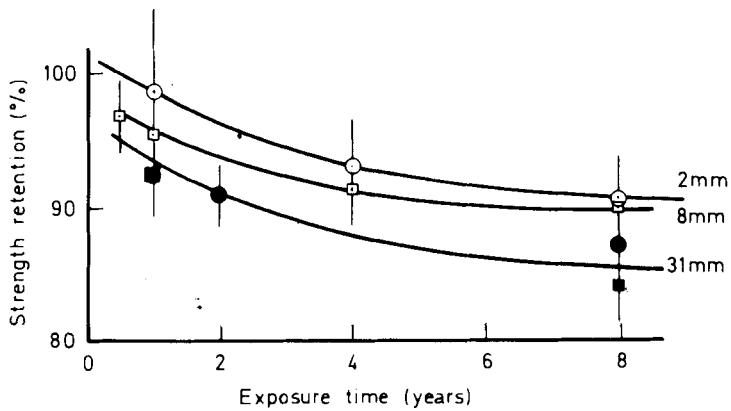

FIGURE 7 Durability on exposure to hot-wet climate of batches of joints of different crack growth (Trial A, AHP).

The lines for 31 mm crack growth also include data for two batches of joints, those which had the highest and lowest control joint strengths. In this case, solid circles denote the batch of higher strength and solid squares that of lower strength. It does appear from the figures that there is some relationship between durability and wedge test crack growth, despite the variability of strength retention within batches of joints.

This relationship is shown in Figure 8, where strength retention (stressed and unstressed) after 8 years at Innisfail is shown as a function of crack growth. While there is a slight decrease in retention with increasing crack growth, the change is not statistically significant. Data for Trial C joints after 2 years at Innisfail are also shown. With the CAHP pretreatment, there was a wide enough range of crack growths available for there to be a possibility that strength retention might depend on crack growth.

However, it is clear that any dependence of durability on wedge test crack growth is very slight for titanium joints pretreated by any of the three methods tested here. The wedge test does not therefore appear to be a good control method for titanium with these pretreatments.

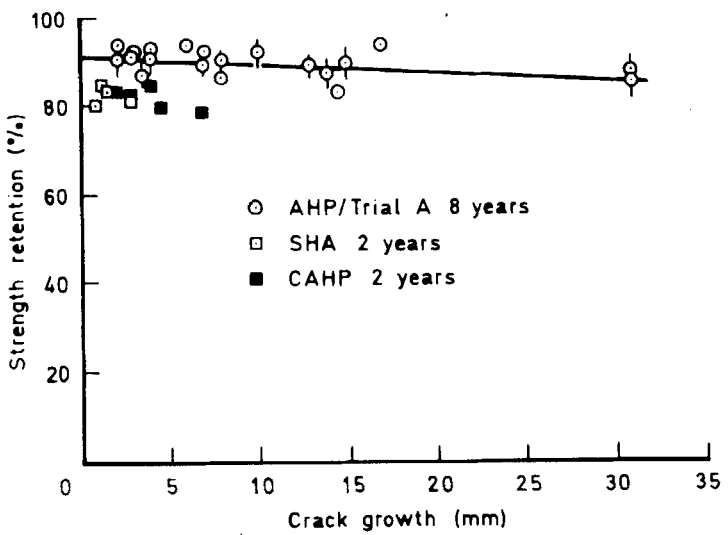

FIGURE 8 Wedge test crack growth and joint durability after hot-wet natural exposure.

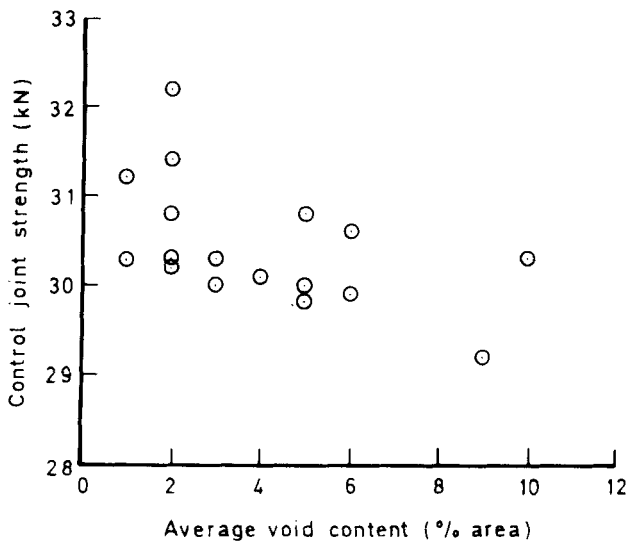

FIGURE 9 Effect of void content on strength of unaged joints (Trial A).

With respect to the use of the control strengths to predict durability, results noted above indicate that control strength was not related to wedge test crack growth. However, it does appear from Figure 9 that control strength is to some extent related to the estimated average void content of the relevant batch of joints. Void contents were estimated from weathered joints because the actual control joints are no longer available for examination.

While within any one set of joints the weaker ones tend to have higher void contents, there is no evidence from this study that residual strengths are lower for void-containing than for void-free joints. Evidence from other work[12] suggests that higher void contents are associated with shorter times to failure under load, as well as lower control strengths. Figure 10 gives data for a different adhesive system and TA10/AHP adherends, exposed at Innisfail and stressed at 20%.

Laboratory aging data In each trial, joints have been exposed to constant conditions of temperature and relative humidity in the laboratory (see Table II). In Trial A, joints were stored under

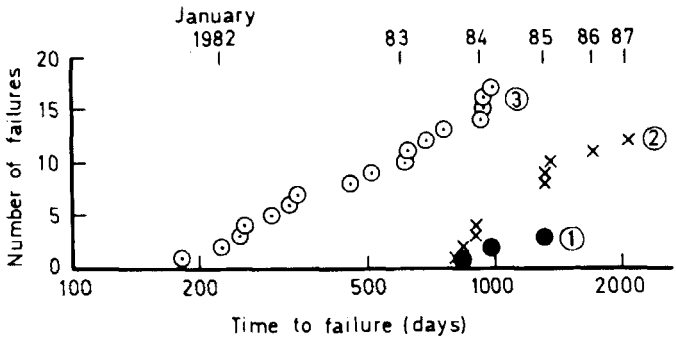

FIGURE 10 Dependence of time to failure on batch void content/control strength: (1) 3 ± 2%/30.1 ± 1.1 kN, (2) 1 ± 1%/32.1 ± 1.6 kN, (3) 29 ± 8%/27.7 ± 0.3 kN.

standard laboratory conditions of 20°C/65% RH. The conditions for Trial B were based on the climate at Innisfail. The relative humidity of 85% used was close to the natural average of 83%, while the temperature of 35°C was the average daily maximum temperature during the hottest three months of the year (December to February). Joints in Trial C were exposed to 50°C/95–100% RH, i.e. the maximum possible humidity and an accelerating temperature.

The strength retentions which were measured are shown in Figure 11. Elevated temperature exposures were terminated at 60 weeks. The last laboratory-stored specimens in Trial A were tested after 11 years: the full results are shown in Figure 3 [solid squares].

Given that the variability about the average strength retention at any test time and exposure condition in Trial A was 3–4%, the retentions measured at 20°C/65% RH were significantly different from those for joints exposed to the temperate climate, even though the average retention tended to be higher. However, in comparison with weathering at Innisfail, strength losses after the first six months were significantly less at 20°C/65% RH. It is interesting to see (Fig. 12) that the average % strength lost at any exposure time generally increased with environmental humidity, despite variability and the different temperatures of the environments.

The laboratory environment of 35°C/85% RH used in Trial B results in a clear acceleration of strength loss. From Figure 11 it can

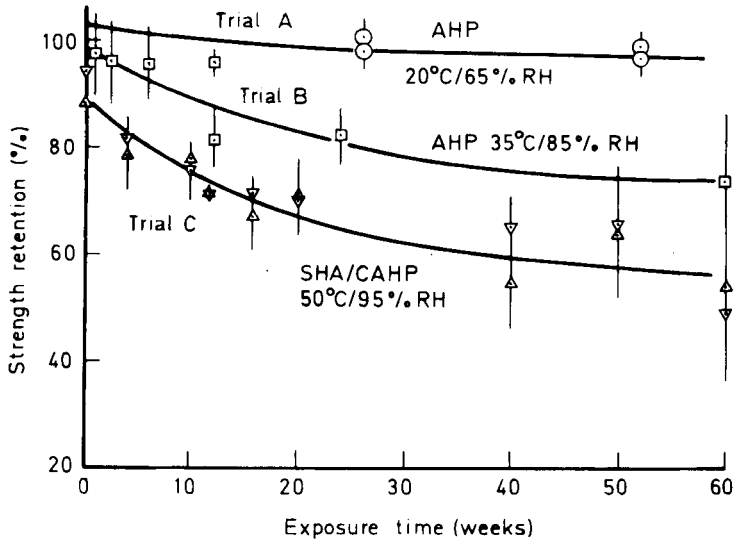

FIGURE 11 Effect of laboratory exposure on strength retention.

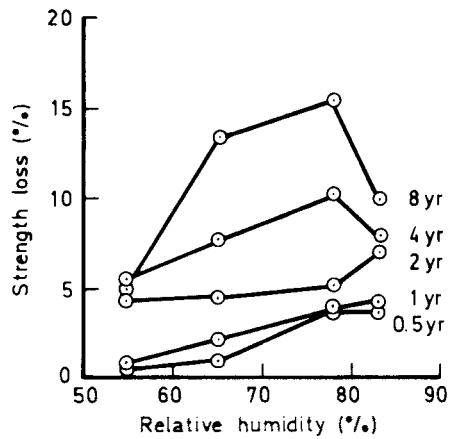

FIGURE 12 Effect of environmental humidity on loss of joint strength with exposure. Trial A: strength loss = 100 − strength retention.

be seen that after 1 year (52 weeks) 26% strength had been lost as against only 10% at Innisfail (Figure 4). After one year, the 50°C/95% RH exposure used in Trial C produced an even greater acceleration of 43% strength loss as against 11% loss at Innisfail. In these trials, increased temperature clearly had an accelerating effect in addition to any effect due to increased humidity—assuming that temperature and humidity effects are approximately the same for the different pretreatments.

Water Diffusion and Joint Strength

With the advent of fibre reinforced composite materials, much data has been collected on the effect of the diffusion of moisture into epoxy resins. Diffusion was found generally to obey Fick's second law. The approximate solution for this at short absorption times is:

$$D^{1/2} = \frac{\pi^{1/2} h}{4M_m} \cdot \frac{dM}{dt^{1/2}} \tag{1}$$

where M is the water content (weight %) at time t, M_m is the saturation moisture content, h the specimen thickness and D the diffusion coefficient. M_m is dependent on the ambient humidity while D is dependent on temperature.

While less work has been done as yet on epoxy adhesives and bonded joints, it has been confirmed that water uptake into joints is Fickian and it has been shown that joint strength is linearly related to the water content of the bonded joint.[13–15] It might be expected that joint strength would obey an equation similar to Eq. (1) with strength, or strength retention, at time t substituted for M, and with a minimum strength retention reached when the joint was saturated at the ambient humidity. Thus, a plot of strength against $t^{1/2}$ would be linear until saturation was reached, after which further exposure would not result in any further loss of joint strength. There is some evidence for this with bonded carbon fibre composite joints.[16]

Figures 13 and 14, for natural and laboratory exposure respectively, show joint strength retention as a function of $t^{1/2}$. Linear regression lines through the data points are shown; all had correlation coefficients better than 0.9. Eight-year results for Trial A hot-dry exposure were not included as joint strength appeared to

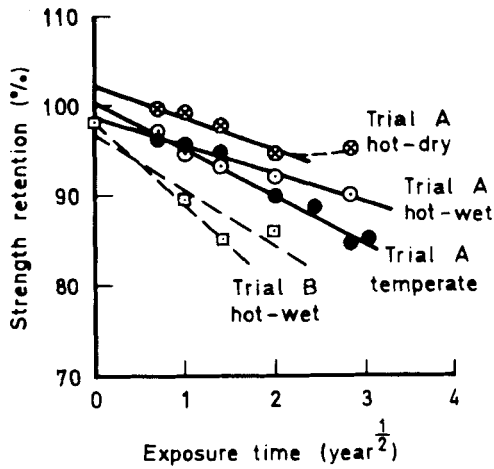

FIGURE 13 Strength retention vs (exposure time)$^{1/2}$ for natural weathering.

have reached a minimum. Two lines are shown through the Trial B hot-wet exposure points, one through all data and the other excluding the four-year value. Calculated gradients of the lines are given in Table III.

Rates of strength loss (i.e. $-1 \times$ rate of change of strength retention) are shown as a function of relative humidity in Figure 15.

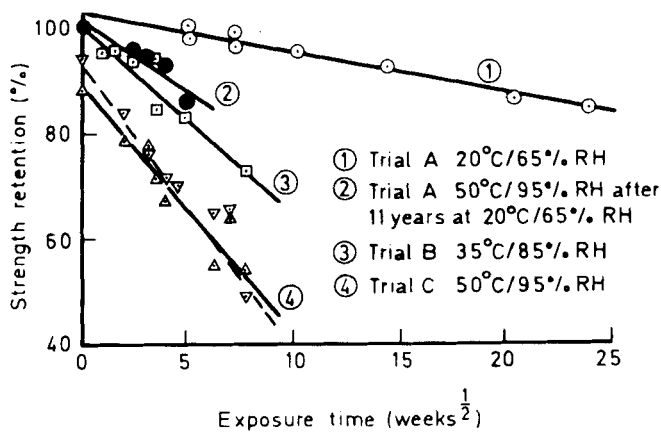

FIGURE 14 Strength retention vs (exposure time)$^{1/2}$ for laboratory exposure.

TABLE III
Rates of change of joint strength during exposure to various environments

Trial	Environment	Rate of change of strength retention ($\%^{-1/2} \times 10^4$)
A	Hot-wet	−5.9
	Hot-dry	−4.5
	Temperate	−9.8
	20°C/65% RH	−10.0
	50°C/95% RH after 11 years at 20°C/65% RH	−33.1
B	Hot-wet (2 years)	−16.3
	(4 years)	−10.9
	35°C/85% RH	−45.6
C/SHA	50°C/95% RH	−60.4
C/CAHP	50°C/95% RH	−61.7

It is not possible to tell from these results whether the rate of strength loss was affected by relative humidity, as no two sets of results in the same trial were obtained at the same temperature. However from the Trial A data (Figures 4 and 11 and Table III) the effect of relative humidity could well be small. As can be seen from Eq. (1), if D is independent of humidity, then at constant

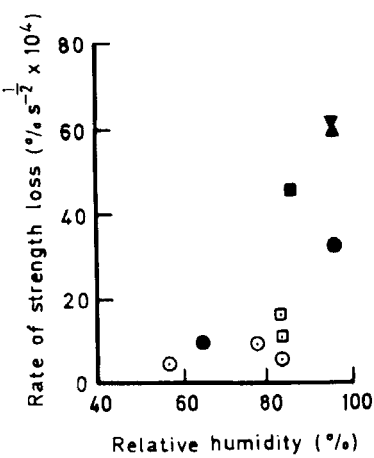

FIGURE 15 Rate of strength loss in different environments (open symbols—natural weathering: closed symbols—laboratory tests).

temperature $dM/dt^{1/2}$ should vary with M_m: hence the rate of strength change should show some dependence on relative humidity and M_m.

At constant relative humidity, D, and hence $dM/dt^{1/2}$ and, by analogy, the rate of strength change, should be dependent on temperature, according to an equation of the Arrhenius form.

$$D = D_0 \exp(-E/RT) \tag{2}$$

where D_0 is a constant for the system, E the activation energy for diffusion, R the universal gas constant and T the absolute temperature.

Using only the results for Trial B, which were obtained at two different temperatures and approximately the same relative humidity, activation energies were calculated using the calculated rates of strength changes. The values obtained were 35 or 76 kJ mole$^{-1/2}$ depending on whether the rate calculated over 2 years or 4 years is used. These values of E are comparable with those that have been measured for cast epoxy resins, which range between 34 kJ mole^{-1} [17] and 74 kJ mole^{-1} [18] for different resins.

If data can be obtained on the effect of relative humidity on the rate of strength change at constant temperature and if an activation energy can be calculated for constant humidity conditions, then it may be possible to predict residual strengths during the period when strength is falling.

Further data are also required on the diffusion of moisture into the adhesive in order to calculate saturation times for joints and to find out what happens to strength after the joint is saturated.

Mode of Failure

Metal-to-adhesive bonds consist of three layers; metal, metal oxide and adhesive (plus primer if used). Joint failure takes place at the weakest layer. Joints are generally designed so that failure does not occur in the metal, but within the adhesive. On exposure to high humidity, water diffuses into the joint. Adhesive properties are reduced by plasticisation, the metal oxide may change due to reaction with the diffused water and displacement of adhesive from the metal oxide surface may take place. All these can have an effect on joint strength.

Rates of change of joint strength as calculated above include all the effects which are present in the set of joints, and these effects generally cannot be separated.

Data from joints exposed to different environments should only be compared if the modes of failure are the same in all cases, or if the relationship between joint strength and mode of failure is the same for each environment.

Figure 16 shows how the estimated average area of apparent interfacial failure varied with exposure to natural weathering for all three trials. Each point is the average of both sides of the two strongest and two weakest joints in each set. Variability within each set was about ±25%: the dashed lines show approximately one standard deviation on either side of the average values. Because of this variability there is no statistical difference between sets or exposure times. However, for all trials except B, there is a general trend of decreasing area of interfacial failure with exposure time.

Figure 17 shows the effect of laboratory exposure on mode of failure. Again the dashed lines represent one standard deviation. In contrast to natural weathering, constant-environment laboratory

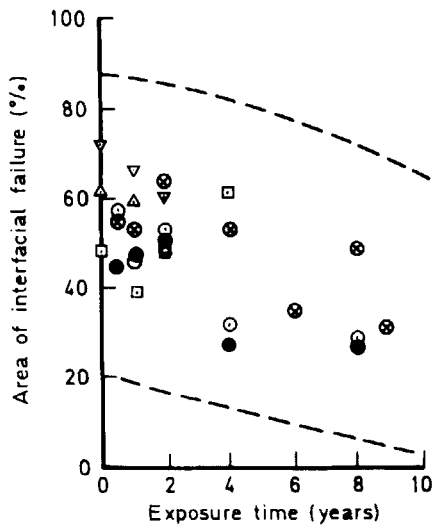

FIGURE 16 Effect of natural weathering on mode of joint failure. Trial A: hot-wet ○, hot-dry ●, temperate ⊗. Trial B: hot-wet □. Trial C: hot-wet, SHA △, CAHP ▽.

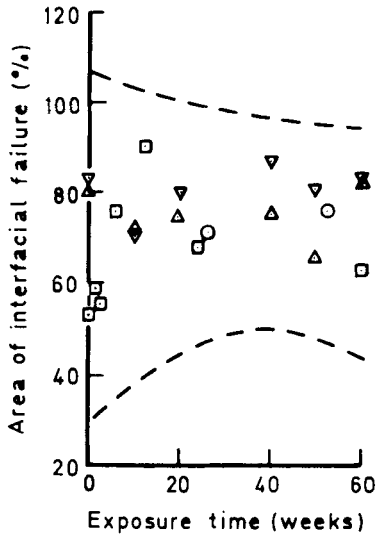

FIGURE 17 Effect of laboratory exposure on mode of joint failure. Trial A, ○; Trial B, □; Trial C, SHA △, CAHP ▽.

exposure did not produce any change in mode of failure with exposure time; the average level was constant at 70–80%, which was higher than any average value for natural weathering.

It may, therefore, be the case that constant-environment accelerated exposure does not have an effect truly comparable with variable-condition natural weathering for titanium adherends pretreated by the methods used in this work.

Only in the case of joints from one batch of CAHP pretreated adherends was there any evidence of an increase in interfacial failure with exposure that might be interpreted as a displacement of adhesive by water during exposure. Figure 18 shows the variation in average % interfacial failure for individual joints, six from each set returned from Australia. Solid symbols are points relating to the faulty batch of joints. It can be seen from the figure that at strength retention greater than about 76%, the area of interfacial failure varies widely between joints, and that there is, on average, a large decrease in area of interfacial failure as strength retention falls from 92 to 76%. Only joints from the faulty batch showed lower strength retention than this and, indeed, three have failed under stress. It also appeared that the area of interfacial failure increased as

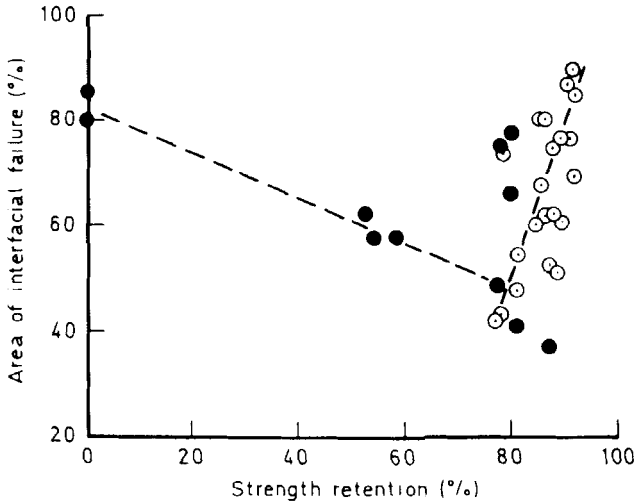

FIGURE 18 Mode of failure vs strength retention. Trial C: CAHP, hot-wet exposure; good joints ○, faulty joints ●.

strength retention fell below 76%. Figure 19 shows photographs of joints (magnification ×2.8) from this batch before and after 4 years exposure in Australia. On the left-hand side of the exposed joint there is apparently complete separation between adhesive and metal. This is associated with a difference in the colour of the metal surface which can be seen in the lower photograph as a change between lighter and darker surface about a third of the joint width from the left-hand edge of the joint. The change in colour is indicative of a difference in structure or thickness of the surface oxide.

The general lack of change in the mode of joint failure suggests that the interfacial region of titanium joints pretreated by the methods used in these trials is not greatly affected by moisture and that changes taking place in the adhesive due to absorbed moisture have more effect on joint strength than to any changes at the interface.

Much work has been done in recent years on the structure and stability of titanium oxides produced by different surface pretreatment methods. Venables and co-workers[19] have shown that surface pretreatments that produce durable adhesive joints are those which

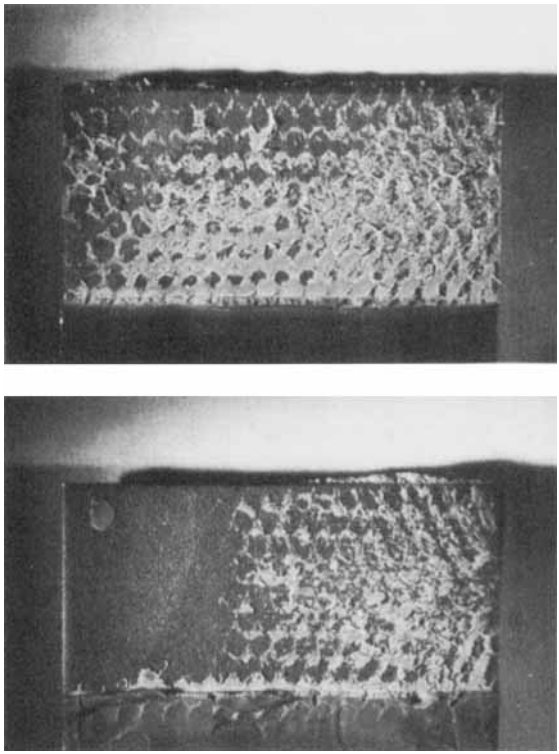

FIGURE 19 Effect of exposure on imperfectly treated titanium joints. Upper picture—before exposure; Lower picture—after 4 years hot-wet exposure.

result in thick, porous oxide films. These include chromic acid anodising and alkaline hydrogen peroxide (AHP) pretreatments. Wightman and Filbey have recently shown[20] that sodium hydroxide anodising (SHA) also produces a porous oxide. This confirms the work of Jones, Pitcher and Poole[9] who showed that the three pretreatments used here, AHP, SHA, and CAHP, all produce porous oxides with the SHA surface having the highest porosity.

It has been shown[21,22,23] that the titanium oxide produced during pretreatments which give good joint durability is relatively stable in the presence of moisture. The initial amorphous oxide changes slowly to crystalline anatase with an increase in oxide mass. The change is much slower than the reaction of Al_2O_3 with water to give boehmite, and it is suggested that any weakening of the joint it

causes will only be a problem at elevated temperatures (>85°C). The changes in mode of failure observed in this work are consistent with these findings.

CONCLUSIONS

TA10 titanium joints made with adherends pretreated by alkaline hydrogen peroxide etching (AHP) and bonded with Redux 312/5 adhesive have proved very resistant to natural weathering in tropical and temperature climates, with and without applied stress. In eight years exposure only 10% of initial strength was lost on average.

Joints of a second exposure trial with AHP-treated TA10, but made by a different manufacturer with a different primer system, have apparently a slightly lower durability, but even so have lost only 15% strength in four years. New pretreatments, sodium hydroxide anodising (SHA) and catalytic alkaline hydrogen peroxide etch (CAHP) have been on trial for two years and are of comparable durability to the second AHP trial.

The possibility of predicting durability has been considered. Two approaches have been investigated. It was found that there was no correlation between control strength data and durability as measured by a Boeing wedge test. While there was some correlation between the wedge test crack growth and strength retention after 8 years exposure (AHP-treated adherends), the difference between batches of joints with 2 mm and 31 mm crack growth was only 5% strength retention, with there being a large variation in strength retention within each batch. Control joint strengths were not related to strength retention but did distinguish between batches of different void contents, which was related to time to failure under stress. The alternative approach to durability prediction was to measure strength changes during accelerated, constant-condition, exposure to elevated temperature and/or humidity. It was found that % strength loss was a linear function of (exposure time)$^{1/2}$: that is, strength changed in a way analogous to water uptake by Fickian diffusion. It may, therefore, be possible to treat durability mathematically as a diffusion process where the rate of strength loss is dependent on exposure temperature, adhesive and metal surface

pretreatment (i.e., rate of reaction of surface oxide with water) and where the minimum strength after exposure is related to relative humidity during exposure, adhesive and surface pretreatment. The data thus obtained from accelerated weathering might be used to predict natural weathering by extrapolation, *provided that* natural and accelerated exposure result in the same mode of joint failure.

Examination of broken joints indicated that naturally weathered joints showed less interfacial failure at the same strength retention than those artifically weathered. However, there was wide variation (±25% of area) between joints with the same strength retention. The percentage of apparent interfacial failure was generally unaffected by exposure or decreased with increasing exposure time.

The results in general confirm the stability of the titanium oxide produced on the metal surface by all three pretreatments.

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