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Long-term durability in water of aluminium alloy adhesive joints bonded with epoxy adhesives

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This paper begins with a review of some of the previous literature on the topic of durability of adhesive bonds to aluminium alloys. A number of papers published during the period 1977 to 1991 are discussed. The paper then details the current test programme using the wedge test to ASTM D-3762 and the adhesives and surface preparations chosen. A number of cold-setting epoxies were tested and a smaller number of hot-setting epoxy film adhesives. All testing was done on 2024-T3 clad aluminium alloy; specimens were immersed in distilled water at room temperature and readings of crack length taken at intervals. Readings were taken frequently for the first month and then at longer intervals. Fracture energy values were calculated after each set of readings. In the last 3years of the programme readings were taken at intervals of 2 or 3months. After 5.5years of total immersion the specimens were handed over to AEA Harwell for further testing and surface analysis of failures by scanning electron microscopy. Four surface preparation methods were compared. These were: (1) tank-type chromic acid anodise; (2) portable chromic acid anodise (Selectrons); (3) Deoxidine 202, a phosphoric acid paste etch; and (4) abrasion with 100grit glass paper. From the literature a number of factors affecting durability are listed.

A number of conclusions are drawn from the test programme and a further set from subsequent work on these specimens at AEA Harwell. Some relate to observations on electron microscope photographs of the surfaces of specimens after joint failure. Others show that, for a given type of surface preparation and a given type of adhesive chemistry, the durability of adhesive bonds depends on the permeability of the adhesive towards water. © 1997 Elsevier Science Ltd.

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INTRODUCTION

This programme and review was started with the aim of elucidating the most important factors governing the durability of epoxy resin bonds to aluminium alloys. In addition to the major part of the work, which used chromic acid anodising as the surface preparation, some tests were done with Redux 410 and Hysol EA 9330 after surface preparation by means of Selectrons portable chromic acid anodising, Deoxidine 202 paste etch and glass paper abrasion. These results were compared with those obtained for both hot- and cold-setting adhesives used with chromic acid tank anodising. The results certainly showed the importance of the choice of surface preparation if long-term durability is required. Armstrong[1] details work on the durability of adhesive bonds to carbon-fibre composites and compares peel ply on abraded and dry surfaces with that of water-immersed and dried surfaces.

LITERATURE SURVEY

The literature in the period 1976 to 1991 has been reviewed; this was not exhaustive. Some of the points to emerge are given in chronological order.

Patrick[2] found that, in a region of corrosion, the pH of the electrolyte may be affected by amine curing agents. He also found that nitrile epoxies have high peel strength and reasonably good bond durability. As a comment on this, it is suggested that toughness may assist durability by spreading the load so that some benefits may come from mechanical properties and others from the chemistry.

Cotter[3] reported good durability performance with epoxy/novolacs.

De Lollis[4] found that nitrile phenolic bonds were the most durable.

Stern and Albericci[5] considered wet debonding to be quite different from corrosion.

Albericci[6] found distilled water to be a more damaging environment than salt water for epoxy, acrylic and polyurethane paint coatings. Coatings were found to absorb less water as the strength of the salt solution increased. Redux 775 specimens were more affected by salt solutions than by distilled water, a reversal of the result for epoxy.

Garnish[7] tested a one-part, hot-curing epoxy (AV1566GB) on two stainless steels, a steel and an aluminium alloy (Alclad L.73). He concluded that: (1) etched stainless steel (EN58J) is a stable interface in water-immersion tests; (2) aluminium surfaces are less stable than ferrous surfaces in corresponding prebond

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*Presented at Oxford Brookes Conference 1996 processes; and (3) immersion changes are largely reversible on an etched surface provided that the dehydration stage is not too severe. Drying of specimens after immersion and before testing indicated that irreversible damage is done with stainless steel and aluminium alloy joints if drying is at 80°C. At 40°C and 23°C, drying showed that damage was reversible for stainless steel but irreversible for aluminium alloy joints even at the lower drying temperatures. These findings could be significant for adhesively bonded metal aircraft structures, which can reach high temperatures (above 100°C) on upper surfaces when parked in hot sunny areas. The results obtained indicate that a durable surface preparation must produce a hydration-resistant oxide on the metal surface, or bond that cannot be displaced by water, or both. With the same adhesive the durability is better on stainless steel than on aluminium alloy, indicating an effect of the surface.

Reinhart[8] studied the effect of primers. He found that, after chemical treatments that produced a hydrated oxide, aluminium and titanium surfaces without primer exhibited a gradual decline in their ability to form strong, durable bonds. He showed that the application of suitable primers, to freshly treated surfaces, could maintain the bondability for 1 year or more if the surfaces were protected from gross contamination.

Bijlmer[9] studied surface potential difference (SPD) for aluminium surfaces. He considers that SPDs only indicate the condition of a surface after a given treatment. Optimum values of SPD exist for each treatment, above and below which values bondability drops off sharply. Hot rinsing was found to cause hydration of the oxide if high-purity water was used, resulting in a weaker oxide and a weaker bond. All contact with and contamination of surfaces should be avoided between rinsing and bonding. Bijlmer found that brittle adhesives are more likely to show interfacial failure. Armstrong[10] obtained a similar result with wedge tests.

Bijlmer found that, with FM 123-5 adhesive and BR 127 primer, the effect of primer thickness is critical. The difference he found between Redux 775 and EC 2216 is most likely a consequence of the great difference in their elastic moduli. Most manufacturers point out that primer thickness is critical. The easiest way to get it right is by comparison with a colour chart from the manufacturer showing three sections: too thin, correct and too thick.

Kinloch[11] found that, while the locus of failure of well-prepared joints is invariably by cohesive fracture in the adhesive layer, after environmental exposure it is via apparent adhesive failure between the adhesive (or primer) and the substrate. He found the following parameters to affect durability:

(1) environment—the presence of a hostile environment, with water being one of the most harmful;
(2) adhesive type—phenolics are more durable than epoxies;
(3) substrates—metallic substrates are the main problem. Plastics, glass and carbon fibre are much less susceptible to water;
(4) substrate surface pretreatment—this factor is extremely important. It is necessary to form stable oxides; primers are often helpful;
(5) temperature—increasing the temperature increases the rate of strength loss;
(6) applied stress—this increases the rate of environmental attack; and
(7) joint design—stress concentrations at, or near, the interface will tend to reveal durability effects more readily; e.g. the peel test is more severe than the lap-shear test.

Corrosion of the substrate occurred after debonding. This finding is confirmed by DRA (RAE) Farnborough and by Boeing. The cause of debonding needs to be explained. Water must be prevented from reaching the interface in sufficient concentration to cause damage, or the intrinsic durability of the interface must be increased.

Kinloch[12] also studied silane-based primers, which improved durability on aluminium alloys and mild steel substrates. Secondary-ion mass spectrometry (SIMS) revealed the presence of $\mathrm{Fe{-}Si{-}O^+}$ radicals from the primer-coated surface. This was considered strong evidence for the production of chemical bonds, probably Fe–O–Si, between the metal oxide and the siloxane primer. No such radicals were found for several other silane-coated surfaces where there was no improvement in joint durability. The presence of interfacial covalent bonds may also explain why phenolic-based adhesives generally impart very good durability characteristics.

Stevenson and Andrews[13] studied epoxy/titanium bonds and found that the pH of the rinse water was important. They found that water with a low pH (acid) weakened the bond whereas a high pH (alkaline) retarded the process.

Comyn *et al.*[14] measured rates of absorption of water, and equilibrium absorption (solubility) of water in epoxides. The resins tested were formulated from the diglycidyl ether of bisphenol-A and a range of hardeners. Among their conclusions, they found that total water uptake is an important factor in determining the strength of a lap joint and that the strength of wet joints cannot be accounted for by plasticisation of the adhesive.

Armstrong[10] has found that water uptake sometimes produces embrittlement.

Cotter and Kohler[15], who studied the influence of pretreatment on the durability of adhesively bonded aluminium alloys, found that (1) spray rinsing with cold deionised water was better than rinsing in hot tap water; (2) autoclave curing was better than press curing; (3) thin primer layers (10^{-3}mm) were better than thick layers (10^{-2}mm); and (4) corrosion-inhibiting primers were useful.

Minford[16] quotes Laird[17], who showed that water diffusion along the interface can be as much as 450 times faster than water permeation through the adhesive. This work suggests that this may well be true for poor surface preparations but not for the better ones. He also quotes Kerr *et al.*, who compared the effect of dry ethanol and water on epoxy/aluminium bonds and found that water seriously reduced bond strength and ethanol did not.

Further, Minford mentions Black and Blomquist, who studied probable causes and mechanisms for the deterioration of metal/adhesive bonds at temperatures up to 260°C (500°F). These authors showed the significant effect of metal surface conditions on the permanence of joints made with phenolic/epoxy-type adhesives. Stainless steel joints deteriorated rapidly at 260°C, while aluminium joints bonded with the same adhesive were very stable. This bond durability of the aluminium joint was lost rapidly if iron or copper was deposited on the aluminium surface as a pretreatment. In earlier investigations the same authors had been attempting to develop more heat-resistant adhesives by using phenolic and epoxy resins, with significant results. It was found that bond permanence and strength at 316°C (600°F) was significantly affected by varying the ratio of the resins, the acid accelerators present and surface stabilisers, i.e. chelating agents used to pretreat the aluminium surface.

Minford also quotes Mostovoy and Ripling as finding that only a nitrile phenolic adhesive showed good flaw tolerance in water-immersed double cantilever beam tests.

Lewis and Gounder[18], quoting Kreiger and Politi, state that at high temperature the metal surface catalyses degradation of the adhesive. They showed that atmospheric oxygen was detrimental when compared with a nitrogen atmosphere. That oxygen may also contribute to disbond at room temperature was indicated by Minford[19], who found that joints tested with periods out of water showed greater loss of strength than joints subjected to total immersion tests. Tensile stresses at the interface, as a consequence of the adhesive drying faster at the surface than in the bulk, could also contribute to this.

Comyn[20] presented evidence that water enters a joint by diffusion through the adhesive. He states that 10mm×10mm joints bonded with epoxy adhesives take about 1year to reach a high level of water uptake.

Moloney[21] reports that phosphoric acid anodising was found to provide a more hydration-resistant surface than other anodising solutions, i.e. chromic, sulfuric and oxalic acids. Heat treatment of aluminium causes segregation of magnesium to the surface. Copper and magnesium can assist the electrochemical dissolution of aluminium. Solvent degreasing does not remove the magnesium-rich layer but etching, grit blasting and anodising do remove it. However, it has also been found that heating at 175°C to cure an adhesive causes a dramatic increase in magnesium concentration owing to the diffusion of Mg^{2+} ions. This is contrary to the role of magnesium mentioned above because many 175°C-curing adhesives produce exceptionally durable bonds even on poorly prepared surfaces, e.g. nitrile phenolic adhesives. Further work is needed to clarify whether there is a relationship between magnesium concentration and joint durability.

Kinloch[11, 12] speaks of a critical water content affecting the strength of steel joints and, by implication, the strength of joints with aluminium alloys and other metal adherends. Comyn *et al.*[14] found the same effect. It was, therefore, considered that the saturation water uptake of an adhesive might be one of these factors. Later, Armstrong[10] suspected that the pH of the adhesive itself, or of leached extracts from it, might be one of the key factors for long-term durability.

Pocius *et al.*[22] found the following:

(1) phenolic adhesives have many OH groups, good wetting and good strength;
(2) epoxies have far less OH groups;
(3) EC 2216 (3M) shows much greater durability when used with a corrosion-resistant primer;
(4) hot-curing adhesives show less adhesion failure;
(5) phosphoric acid anodising was shown to be better than FPL etch;
(6) phenolic adhesives seem to be especially good with respect to durability.

Phenolics are known to bond very strongly to aluminium oxide. Weinberg and co-workers[23] have shown that phenol will dissociate on aluminium oxide to form aluminium phenoxide. Aliphatic alcohols such as those in epoxy resins are not acidic enough to react with aluminium oxide. Brockmann *et al.*[24] have also studied this aspect. There seemed to be some confirmation of this possibility when it was found that the phenolic film adhesive Redux 775, known for its durability in service, had an approximately neutral pH and a saturation water uptake of 44%. Epoxies vary from about 2.5% to 15% water uptake at saturation. They also have pH values well into the alkaline range because of their amine hardeners.

Minford[19] also found, in common with Albericci[6], that continuous immersion in a 3.5% sodium chloride solution was less aggressive than immersion in distilled or deionised water. He also tested in a 5% continuous salt fog to ASTM B-117 and two variations of this. In these, joints were exposed to air for 10min every hour for one series of tests and exposed to air for 8h every day in the other. Joints that had been under continuous immersion showed no loss of strength whereas joints exposed to both variations showed a severe loss of strength, the exposure to air for 10min every hour being the worst. Clearly, exposure to atmospheric oxygen makes a big difference to the results.

Hagemeier *et al.*[25] state that heat treatment of an alloy is a vital factor in establishing resistance to corrosion and that heat treatments are very carefully controlled. They do not mention the possible effects of repeated adhesive curing cycles on the previous heat treatment with regard to either strength or corrosion resistance. They also state that, 'Contact between a metal and an hygroscopic material such as asbestos, wood, sponge cork or certain plastics can cause pitting corrosion'. Adhesives come in the last category.

Jurf[26] studied Cyanamid FM73 and FM 300M film adhesives, both dry and wet. Graphs of percentage adhesive failure against temperature showed an increasing amount of adhesive failure for dry and wet specimens as the temperature increases. These results suggest that interfacial bonds are reduced in strength with increasing temperature.

Cognard[27] worked with stainless steel adherends and also carried out long-term water-immersion tests. His results suggest that it could be helpful to evaluate the same adhesives used in this test programme on wedge specimens made from titanium, steel and stainless steel to establish whether the characteristics observed are most likely to be related to the adhesives themselves or to interfacial effects.

Cognard raises the interesting point that methylene chloride is more aggressive than water. Methylene chloride forms the major part of most chemical paint strippers used on aircraft. It is very damaging indeed to acrylic aircraft windows, and epoxy resins have a similar solubility parameter to acrylics. Methylene chloride would therefore be expected to dissolve epoxy resins and in fact has been shown to do so on some fibreglass/epoxy panels that had a large amount of paint stripper left on them for several days. Chemical paint strippers are banned on aircraft parts of composite construction. Simulated atmospheric pollution was also shown to have a dramatic effect.

Charbonnier *et al.*[28] reported new methods of characterising aluminium and titanium alloy surfaces at various pre-bond stages.

De Luccia[29] has patented a modified 7075-type aluminium alloy containing 0.2% by volume (0.6% by weight) of elemental molybdenum, which is produced by using rapid-solidification powder-metallurgy techniques. This alloy is said to have better stress corrosion and corrosion fatigue resistance. He also says, 'Anodised surfaces provide more corrosion protection, abrasion resistance and long term durability than chromated surfaces. Sealing in tap water resulted in inferior corrosion resistance and paint adhesion as compared to that of sealing in distilled water. Since chromate conversion coatings also act to provide a good surface for paint adhesion on aluminium alloys, they are a mainstay in providing a ready pre-treatment of aircraft parts prior to painting. With the coming of restrictions on chromates, surface pretreatments for aluminium alloys that do not contain chromates need to be developed'.

Heat treatment is very important with regard to corrosion resistance and the correct treatment needs to be clearly specified and observed. De Luccia states, 'The advent of heat treatable 7000 series aluminium alloys provided a boon to aircraft designers. The high modulus, high strength and low weight of these alloys made them ideal for the high performance of advanced aircraft. Their susceptibilities to intergranular corrosion, exfoliation and stress corrosion cracking made them less than desirable in corrosive environments. It was discovered that if these alloys were systematically overaged, their susceptibilities to this form of attack would be materially lessened if not totally eliminated. Thus the T73 temper was born. There is an approximately 10% loss in strength accompanying the T73 overaging treatment. This and other work show that both alloy content and heat treatment have an effect on corrosion resistance'. De Luccia also speaks of metals in contact with composite materials and says, 'It has been well known that when graphite/epoxy composite materials are coupled to aluminium, steel or titanium, the metal corrodes, in preference to the strong graphite cathode'. This type of corrosion is called galvanic corrosion and is shown under the left arrow of Figure 1 (in his paper) as one of the forms of time-dependent corrosion. This applies to all graphite-reinforced composites. It should be emphasised that epoxy matrices are susceptible to water accumulation and hence degradation. Epoxies are considered hygroscopic (attracts and accumulates water). Even in the absence of galvanic corrosion water absorption by the epoxy matrix can cause composite strength loss as well as act as a source of electrolyte for the galvanic corrosion of metals to which it is attached. Therefore, graphite/epoxy composites that have undergone matrix degradation by water can be more damaging to metal couples since the galvanic effect is augmented by the material carrying its own corrosive electrolyte.

In-service experience

The Boeing Aircraft Company has long complained about the failure of cold-bonded fuselage lap joints. These were made with room-temperature-curing film adhesives that may not have been allowed to warm to room temperature before use. It has since been reported[30], 'that Boeing 737 pressurised fuselage lap joints, which were hot bonded during manufacture, following the cold glued joints which contributed to the Aloha decompression, may be suspect in aircraft 465–519, and the FAA is proposing additional inspections covering these aircraft'.

By contrast, Schliekelmann[31] reported no problems at all during 60 000 flight hours with similar lap joints on the F.27. These were chromic acid anodised, primed with hot-curing phenolic primer (Redux 101) and bonded with 3M's EC 2216. EC 2216 has a low modulus and a saturation water uptake of 5.7%. The important factor may well be the treatment of the lap joints before bonding, or more likely the possibility that the bonded faces were handled or somehow contaminated before the adhesive was applied. At this point in time the precise cause is unlikely to be found.

Thorough training and tightly controlled procedures are required to avoid contamination between the anodising process and the application of the adhesive.

In the series of tests to be reported here, one test-piece sufferred an adhesive failure on initial application of the wedge and an initial crack length longer than that found on the other two test-pieces of the same set after water immersion for 3years! After collection from the anodising shop these parts were all wrapped in clean tissues and handled only by the edges during adhesive application. All 12 samples in this set were anodised and bonded on the same day. It can only be assumed that one was dropped or otherwise contaminated before collection, or that some contamination on the metal was not fully removed before the anodising step. It must be concluded that it is impossible to be too careful with treated surfaces.

Preliminary conclusions

A preliminary conclusion from this work is that one should not talk of the durability of adhesives so much as the durability of surface preparation methods. Certainly it would seem that the surface preparation and quality are paramount. Results can also be affected in the long term by adhesive chemistry and, of course, by stress level, especially if that is too high. The long-term degradation of the adhesive itself is possible but it seems likely to be preceded by degradation of the bonding surface if stress levels are low and a corrosive environment is involved.

There seem to be a number of advantages of anodising over other methods, these being:

(1) the porosity of the oxide provides for mechanical interlocking and phosphoric acid anodising produces larger pores than chromic acid anodising, see Albericci in Kinloch[12];
(2) the oxide is not electrically conductive and therefore cuts off the flow of electrons necessary to produce corrosion; and
(3) chemical bonding to the oxide layer is possible, see Pocius *et al.*[23]

From the fact that none of the aluminium alloy test-pieces given the tank chromic acid anodising treatment has fallen apart in just under 7years of total immersion (without the use of primers), it may be concluded that, in general, cold-setting adhesives can be as good as hot-setting adhesives from a durability standpoint if bonded to a well-anodised surface and testing takes place at room temperature. In great contrast, when two of the same adhesives were used to bond the same alloy that had been treated by abrasion with glass paper, the joints failed completely after 1day (9330) and 8days (410NA) of water immersion. This shows with great clarity the vital role of a good surface preparation. Other workers have found a large effect of temperature on durability[12]. This work shows that this could be related to increased diffusion coefficients at higher temperatures in addition to faster chemical reactions. Clearly, the glass transition temperature (T_g) is important and must be high enough for the service temperature actually experienced by a bonded part.

It now seems that total immersion is not as aggressive an environment as actual airline service because the amount of oxygen available in the crack is less in the former case[20,32]. Unfortunately, apparatus for cyclic immersion was not available for this series of tests. These tests are, therefore, not as representative of service conditions as could be desired. Any technique that can reduce the amount of oxygen penetrating into a bondline must be helpful. If a form of sealing could be found that could prevent oxygen penetration in the bondline, this would almost certainly be very effective. In a television programme on the Isle of Lewis on 8 October 1993, it was stated that peat bogs contain no oxygen and that this enables them to preserve many things that fall into them. An explanation as to why peat bogs contain no oxygen could be both interesting and helpful to the discovery of a solution to this problem.

The test programme is described below together with the results obtained after just over 2000days (5.5years) for those samples with the longest immersion time. Some tests were started later and have shorter immersion times, but even these are in excess of 3years of immersion.

It was hoped to relate the sequence of failure to one or some of the following factors:

(1) saturation water uptake of the adhesive;
(2) pH of the adhesive or leached extract;
(3) chemistry of the adhesive or curing agent, including the use of corrosion inhibitors;
(4) cure temperature; and
(5) possible effects of additives.

It can now be said that some success has been achieved in that regard; item 1 has been shown to be important together with the diffusion coefficient. Item 2 is probably worth more study and item 3 is definitely important because phenolics seem to be more durable than epoxies. Item 5 can be significant because corrosion inhibitors have been shown to be helpful to durability. It can also be said, having used Deoxidine 202 and glass paper abrasion for comparison with anodising, that anodising is by far the best surface preparation for aluminium alloys and that surface preparation seems to be by far the most significant factor for the achievement of durable bonds (see *Figures 2* and *3*, below).

TEST PROGRAMME

In this programme a small number of cold-setting two-part paste adhesives and hot-setting film adhesives were used. They are listed in *Table 1*. The only test method employed was the Boeing wedge test to ASTM D-3762, with 2024-T3 clad aluminium alloy as the adherends. The wedges were driven in at 10mmmin^{-1} by an RDP/Howden EU500BS testing machine.

Table 1 Adhesives used in this programme

Adhesive	Chemical type	Physical type	Supplier
AF 163	Epoxy/polyether DICY cure	Film	3M
Redux 308A	Polymerically modified epoxy, modified DICY	Film	Hexcel (Ciba)
Redux 408	Epoxy/novolac aliphatic amine	2-part paste	Hexcel (Ciba)
Redux 410NA	Epoxy/aliphatic amine	2-part paste	Hexcel (Ciba)
EA 9330	Epoxy/aliphatic amine	2-part paste	Hysol
EA 9309.3NA	Epoxy/aliphatic amine	2-part paste	Hysol
EC 2216	Epoxy/modified amine	2-part paste	3M
FM 1000	Nylon/epoxy	Film	Cytec
UW 45	Epoxy	2-part paste	Wessex Resins

It is worthy of note in *Figure 1* that the longest time to the first steep drop was found with the blend of Redux 410NA and Redux 408 Redux 408 is an epoxy/novolac (phenolic) and is a room-temperature-curing system

Although the force required to drive the wedge was recorded it was very variable and no useful relation with crack length could be obtained. However, it was clear that tougher resins did require much higher driving forces.

Specimens were immersed in distilled water after measuring the initial crack length and dry crack length after 24h. The susceptibility to corrosion of aluminium alloys varies considerably with the alloy content and heat treatment and therefore the results only have specific applicability to the alloy used. It should be noted that the alloy used was a clad alloy.

The main series of tests, listed in *Table 2*, all used chromic acid anodise (unsealed) to British Airways Standard Practices Manual SPM 20-23-15 as the surface preparation. This series of tests used a range of adhesives with the surface preparation as the constant factor. The second series of tests, in *Table 3*, used two adhesives (Redux 410NA, corrosion inhibited and Hysol EA 9330 with no inhibitor) as the constant factor and three different surface preparations. These were: (1) Selectrons portable chromic acid anodise (denoted in tables as portable anodise); (2) Deoxidine 202 phosphoric acid paste etch (De-ox202); and (3) abrasion with 100grit glass paper (abraded). Redux 410NA and Hysol EA 9330 were also used in the first series, so a total of four surface preparations could be

Table 2 Fracture energy values at various times for the main series of tests using chromic acid anodising (unsealed) as the surface preparation technique

Adhesive	Specimen number	Glueline thickness (mm)	Initial fracture energy (kJm^{-2})	Fracture energy, 24 h dry (kJm^{-2})	Final fracture energy (kJm^{-2})
Redux 410NA	1	0.40	13	11.8	1.8 2197days
EC 2216	25	0.35	4.6	1.7	0.26 157days[a]
1 part Redux 408, 3 parts Redux 410	41	0.32	2.0	2.0	0.75 2197days
	42	0.40	2.4	1.75	1.75 157days[a]
Hysol EA 9330	47	0.35	6.2	5.4	0.95 157days[a]
	48	0.35	5.8	5.8	0.85 319days[a]
Redux 308A, 150°C cure	51	0.25	2.0	2.0	0.3 143days[a]
	52	0.45	5.4	5.4	0.65 143days[a]
Redux 308A, 170°C cure	54	0.17	2.8	2.05	0.34 305days[a]
	55	0.45	4.1	4.1	0.23 2093days
AF 163-2K	72	0.26	5.0	3.7	0.25 1949days
	73	0.50	7.4	7.4	0.8 1949days
	74	0.54	6.4	6.4	1.0 1949days
Hysol EA 9309.3NA	75	0.30	4.0	3.0	1.3 1949days
	77	0.35	6.4	4.6	1.8 1949days
Cyanamid FM 123-2, time exp.	81	0.20	1.4	0.66	0.65 1787days
	83	0.47	0.52	0.42	0.075 1787days

[a] Wedges removed at the times given. These specimens remained immersed until re-tested at Harwell. There were no failures at these times

Table 3 Fracture energy values at various times for the second series of tests using several surface preparations

Adhesive	Specimen number	Glueline thickness (mm)	Initial fracture energy (kJm^{-2})	Fracture energy, 24h dry (kJm^{-2})	Final fracture energy (kJm^{-2})
Redux 410NA, portable anodise	100	0.30	5.0	5.0	0.18 1632days
	101	0.55	2.8	2.8	0.85 1632days
Hysol EA 9330, portable anodise	102	0.37	0.11	0.11	0.065 1632days
	103	0.45	0.145	0.145	0.14 1632days
Redux 410NA, De-ox202	105	0.40	1.7	1.5	Split 8days
	106	0.30	3.5	3.5	Split 8days
Hysol EA 9330, De-ox202	107	0.30	0.97	0.42	Split 474days
	108	0.60	0.64	0.36	Split 541days
Redux 410NA, abraded	109	0.27	4.0	3.5	Split 8days
	110	0.30	3.5	3.5	Split 8days
Hysol EA 9330, abraded	111	0.25	0.35	0.16	Split 1day
	112	0.62	0.3	0.22	Split 1day

compared. The results are shown in *Figure 1* for a range of adhesives on chromic acid anodise and in *Figures 2* and *3* for Redux 410NA and Hysol EA 9330 on the various surface preparations. All samples were immersed in distilled water. This was changed periodically as algae developed (mainly in the summer months) and a certain amount of corrosion occurred on the outer faces of the aluminium alloy specimens. It is recommended that crack length readings, after water immersion, should be taken daily for the first week, weekly for the first month, monthly for the first 2years and eventually at intervals of about 2months. Actual readings were taken approximately on these lines but not as frequently as might have been desirable. These recommendations are made to improve the precision of any future work of this type.

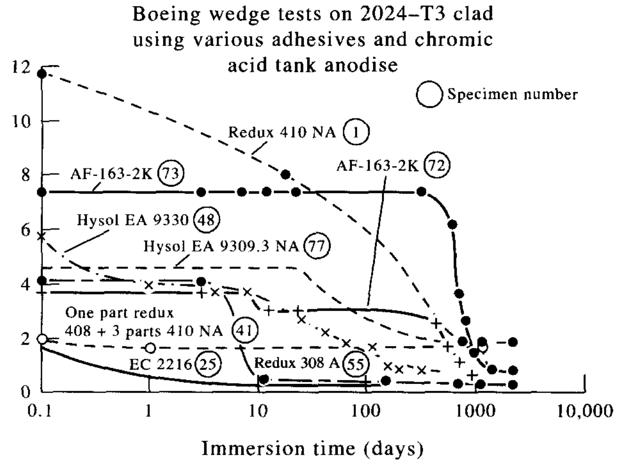

Figure 1 Fracture energy *versus* immersion time

Tables 2 and *3* indicate where tests have been completed (i.e. split apart) and also where tests have been terminated (i.e. wedges removed). Those listing a fairly small number of days were left immersed, after the wedges had been removed, up to the full 5.5years of this test programme. They were opened up with a screwdriver each time readings were taken on the other specimens. All those not recorded as split were still in one piece at the end of this programme whether they still had wedges in or not.

For tests continued to long times with the wedges in place it was realised that, owing to water plasticisation, the stresses at the crack tips had reduced, possibly to zero in some cases. Kinloch[12] says this is highly likely with adhesives that undergo 'creep'. If a micrometer is used to measure the end of adherend deformation then the 'crack length' is different from that indicated visually. This technique was used after long times when visible crack propagation appeared to have ceased. For those tests continued without wedges, it was originally assumed that corrosion would produce disbond after some length of time. After 5.5years this did not occur in specimens with wedges or those without. The tests without wedges were opened up with a screwdriver blade, if they would open that far, whenever readings were taken and these crude tests indicated that all these specimens could still sustain considerable load.

Two of the materials used were outside their recommended shelf life.

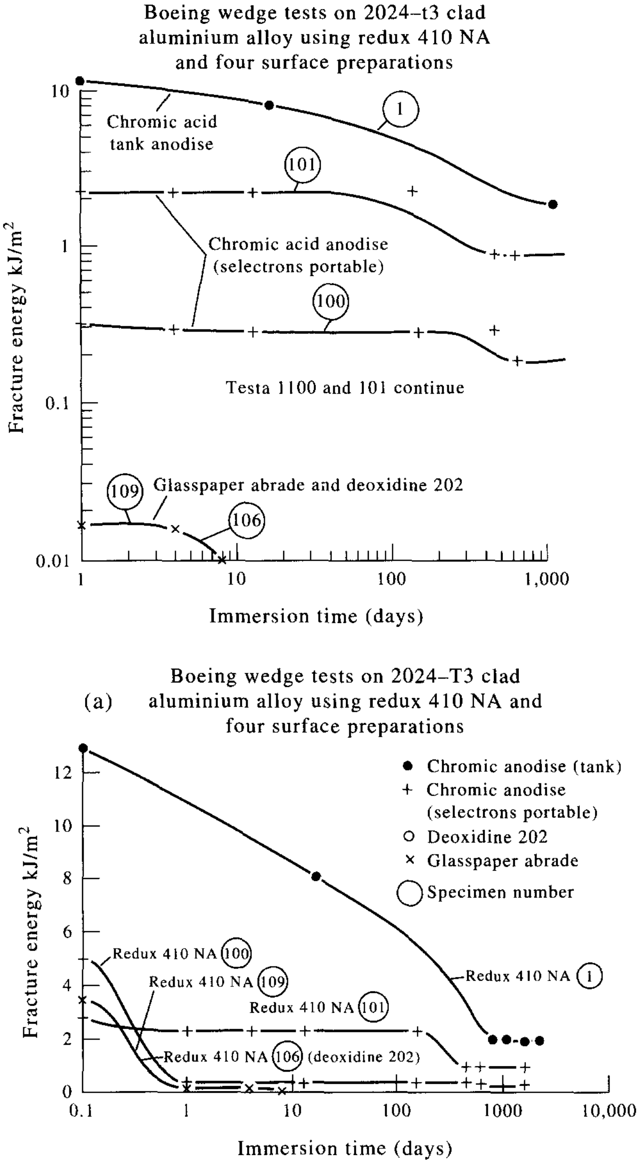

Figure 2 Fracture energy *versus* immersion time

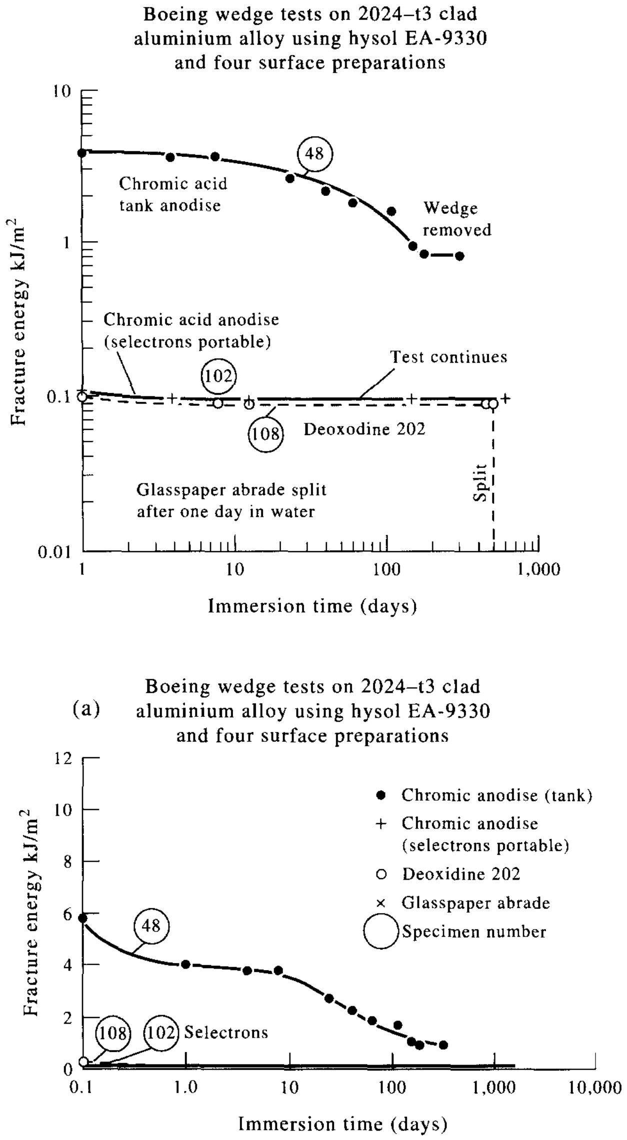

Figure 3 Fracture energy *versus* immersion time

(1) Cyanamid FM 123-2 is listed only in *Table 2*, because its performance was expected to be seriously affected. In fact, the results obtained were as good as other similar materials and this adhesive would most probably have shown better results than the others had it been used fresh. It was about 9months over its recommended shelf life. Testing was worthwhile because, although no flow was visible and some degree of both toughness and durability was found, it did prove that shelf lives and storage conditions must be taken seriously. It is a common belief (possibly at least partially true) that manufacturers give a cautious limit to shelf life, but the results obtained confirm that any material over its shelf life should be tested before use. Unfortunately, at the time of testing, fresh material was not available for comparison. Lap-shear results on fresh material are always good.

(2) A lesser and more uncertain effect was found with time-expired Hysol EA 9330. This was only 3months over its shelf life at 25°C (77°F), but its date of manufacture was 1year before date of supply and shelf life is counted from date of supply. In this case the fracture energy was unexpectedly low for the Selectrons anodise, about normal for Deoxidine 202 and low on glass paper abrade when compared with the same proportional reductions shown by Redux 410NA on the same surface preparations.

However, Allen *et al.*[33] have shown that different adhesives behave differently on various surface preparations. In this case it cannot be proved that there was any effect of shelf life. Some adhesives seem to prefer one surface preparation and others another. It was felt that the above observations should be recorded although it is not unusual to use adhesives only 3months over their shelf life in less demanding applications. Storage life and conditions also need to be carefully controlled for two-part paste adhesives.

Table 4 presents fracture energies at various stages of

Table 4 Fracture energies at various stages of crack growth using Hysol EA 9390 and Hysol EA 9394 for comparison with values obtained on CFRP in Ref. 38. Tests with 2024-T3 clad aluminium alloy, chromic acid anodised (unsealed)

Adhesive	Specimen number	Glueline thickness (mm)	Initial fracture energy (kJm^{-2})	Fracture energy, 24 h dry (kJm^{-2})	Final fracture energy (kJm^{-2})
Hysol EA 9394, 95°C cure	01C	0.37	0.55	0.55	N/A
	02C	0.45	0.24	0.24	0.18 1388 days
	03C	0.35	0.55	0.55	0.41 1388 days
Hysol EA 9394, RT cure	1C	0.47	0.17	0.17	N/A
	2C	0.47	0.2	0.2	0.18 1388 days
	C	0.52	0.2	0.2	0.07 1388 days
Hysol EA 9390, 95°C cure	4C	0.40	0.05	0.05	N/A
	5C	0.40	0.038	0.038	N/A
	6C	0.20	0.045	0.045	N/A

Hot curing improves the fracture energy of EA 9394 on aluminium alloys

Specimens 01C to 6C in *Table 4* were tested as part of a subsequent programme to assess the durability of Hysol EA 9394 and 9390 when bonded to composite substrates. The objective of these tests was to obtain the fracture energies and likely durabilities for direct comparison with this programme

It can be seen that EA 9394 is a reasonably tough adhesive and 9390 is a fairly brittle matrix resin for composites

Specimen 01C, bonded with EA 9394 cured at 95°C, was split after 24h and showed apparent adhesive failure in the area cracked by wedge insertion but cohesive failure in the area split with a chisel

Specimen 1C, bonded with EA 9394 cured at RT, gave mainly cohesive failure during wedge insertion and when split with a chisel. The crack progressed in a series of jumps during wedge insertion in all three tests: 1C, 2C and 3C

Specimens 4C, 5C and 6C, bonded with EA 9390 cured at 95°C, were all split with a chisel and gave apparent adhesive failure in every case. Armstrong[10] found that brittle adhesives tend to undergo apparent adhesive failure even on anodised surfaces, whereas adhesives with a greater toughness always show cohesive failures

crack growth for Hysol EA 9390 and Hysol 9394 adhesives on chromic acid anodised 2024-T3 clad aluminium alloy adherends. These may be compared with values obtained on CFRP.

DISCUSSION

Many authors have considered the problem of adhesive bond durability over a long period of time. All have concluded that surface preparation is important and that phenolic adhesives are generally better than epoxies[12]. A great deal of effort has gone into the development of epoxies because of their lower curing temperatures and bonding pressures and, hence, lower manufacturing costs. However, in this area of activity as in many others, 'you get what you pay for'. Competition forces prices down and usually quality as well unless tight specifications exist.

In adhesive bonding, in common with other manufacturing procedures, a cheaper production process may lead to a shorter service life although a lower initial price may be achieved. A lower life cycle cost may require a higher purchase price to be paid for a better process. The problem is that aircraft are being expected to last longer and longer, and when the life of a part does not exceed the life of the aircraft then repair or replacement becomes necessary. This will almost certainly cost more than producing a more durable part in the first place. Aircraft are usually sold on purchase price and low direct operating costs. The cost of maintenance over the life cycle is seldom given as much consideration as it deserves.

A large number of factors seem to affect durability; these may be listed as follows.

1. The type and quality of surface preparation.
2. Adequate warming of film adhesives to room temperature, whilst inside their sealed bags, to avoid condensation on the film when it is removed for lay-up.
3. The time between switching off the anodising current and rinsing.
4. The type and quality of rinse waters[34].
5. The temperature of the rinse water.
6. The time of drying and the time between drying and the application of a primer or adhesive. Any contamination caused by dust, dirt or handling between drying and priming will reduce bondability.
7. The chemical type of the adhesive or primer used and any additives. Redux 775, a phenolic adhesive, has a saturation water uptake of 44% and yet is more durable on aluminium alloys than epoxies with only 2%! It would be very useful to find an explanation for this. The adhesive chemical type is clearly important in relation to the adherend. pH is probably more important than previously thought. If so, it could present a problem if steel parts are bonded to aluminium parts because it is not possible to have an adhesive pH suitable for both. However, a double-layer film could be used with one side of pH suitable for aluminium and the other side suitable for steel.

(8) The mechanical properties of the adhesive.
(9) The cure temperature.
(10) The bonding pressure.
(11) If performance is measured by fracture energy, then glueline thickness is important[35].
(12) The viscosity of the resin at the time of bonding affects the degree of 'wetting' and, in the case of a porous anodise, the degree of penetration of the pores. According to Kinloch, 'An adhesive should exhibit a zero or near zero contact angle on the adherend to be bonded. At some time in the cure cycle the viscosity should be low, i.e. a few centipoises'.
(13) As better surface preparations produce greater durability, it would seem that the difference between the surface energy of the adhesive and the substrate may be of significance.
(14) Stress and service temperature must be within a range acceptable to the adhesive system. Adhesives must be tested over their complete intended service temperature range to check their performance and also the effect of the substrate. Lewis and Gounder[18], quoting Kreiger and Politi, state that at high temperatures the metal surface catalyses degradation of the adhesive. They also showed that atmospheric oxygen was detrimental when compared with a nitrogen atmosphere. XPS work by Harwell shows increased amounts of oxygen on the metal side of all interfacial failures.
(15) The alloy type, its chemical content and heat treatment are also important.
(16) Various workers have considered diffusion of water into the adhesive to be important. Conclusion 3 and *Figures 9–11* confirm this.

FURTHER TESTING AT HARWELL

Having drawn such conclusions as were possible from this work, after 5.5years of water immersion, it was decided to hand over the specimens to AEA Technology at Harwell for further testing and microscopic examination of the failure surfaces. Where a sufficient length of adhesive bond remained the specimens were re-tested in the wedge mode, by driving the wedge in further, and failure mode and other information obtained. Where there was insufficient length of bond remaining a form of lap-shear test was used. Lap joints were made from wedge specimens by cutting a pair of parallel grooves, 25mm apart, one in each adherend. They were tested in an Instron hydraulic instrument at a crosshead speed of 0.5mm/min.

The lower values of fracture energy obtained by Harwell, after a further period of immersion up to a total of almost 7years, suggests that even longer term testing may be needed. Another possibility is that the re-test methods were not identical to the original and this may explain the differences. The Harwell report[36] should be studied in detail as much useful information was obtained. The finding of most importance was some evidence that the anodic oxide layer may fail within itself. Previous work by several authorities has concluded that disbond occurs first and that corrosion follows. This work, at much higher magnification, shows that the oxide layer itself may fail before the adhesive bond and the following figures are included to illustrate this point. *Figures 4–6* (Figures 24–26 in the Harwell report[36]) were obtained from sample 25, bonded with 3M EC 2216. *Figure 4*, at ×1300 magnification, shows signs of corrosion. The surface appears to have a granular structure coupled with the formation of rectangular platelets and a corner intersection can be seen. Inspection of the adhesive surface from an area adjacent to a corrosion patch, *Figure 5*, shows that some of the aluminium oxide has been removed with the adhesive. This suggests that corrosion has taken place prior to the failure of the adhesive joint and may have contributed to its failure. *Figure 6* shows a region of cohesive failure in the adhesive. Similar photographs for Hysol EA 9330 in *Figures 7* and *8* (Figures 31 and 32 in the Harwell report[36]) confirm the previous findings. *Figure 7* shows a typical 'pitted' surface resulting from anodising and some flaking of the anodise. *Figure 8* shows the same effect more clearly: large platelets, typically 0.1mm square, have formed and in places been removed. These results indicate that the quality of anodising may need to be improved to give a more durable oxide and/or that corrosion-inhibiting primers are an essential part of the bonding process. They also suggest that adhesives should not contain any materials likely to cause corrosion of the oxide.

Another important finding from the microscopic examination was that the adhesive in contact with the substrate forms a skin, which may have different properties from the bulk adhesive. This was described as an 'interphase' and its form may depend on the substrate to which the bond is made[36].

CONCLUSIONS

An attempt to analyse *Figure 1*, which shows the decline of fracture energy with immersion time for a range of adhesives, revealed the following points of interest.

(1) Redux 410NA, Hysol EA 9309.3NA and the mixture of 3 parts of Redux 410NA and one part of Redux 408, all level out at 1100days at about the same point. Hysol EA 9330 levelled out somewhat lower. All these adhesives are room-temperature-curing two-part pastes.
(2) Redux 408 and Redux 410NA contain a corrosion inhibitor. Results of corrosion tests indicate that Hysol EA 9309.3 does not. In spite of that fact, they all level out at about the same fracture energy after 1100days. Redux 410NA could have

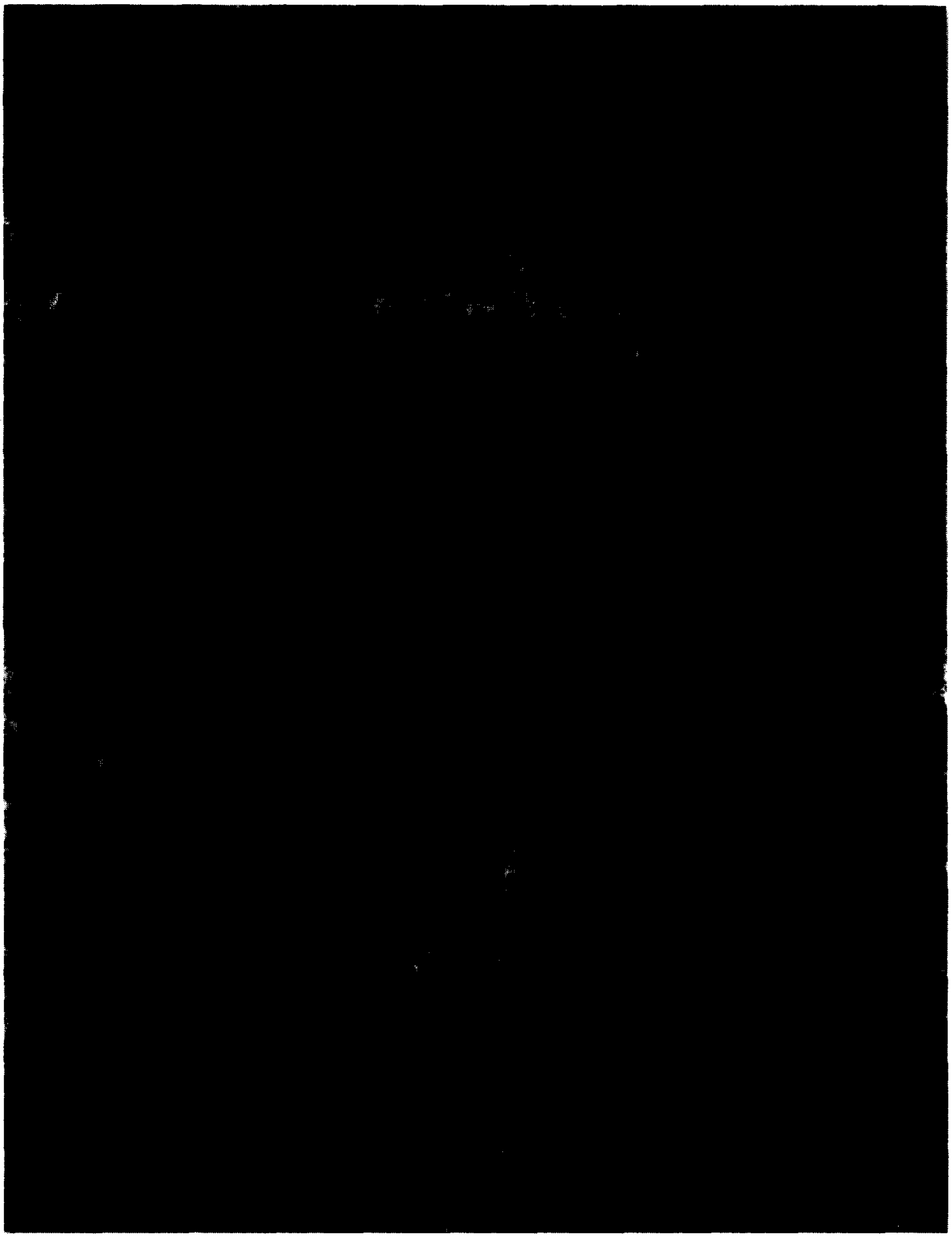

Figure 4 3M-EC2216 corrosion showing junction of platelets

been plotted at a higher value but, although the crack had not visibly propagated at long times, the adhesive in the stressed area had swollen. The use of a micrometer to locate the point where the specimen ceased to be parallel gave a different 'crack length' from the one obtained by observing the end of the crack. This method of measuring crack length was reported by Cognard[27]. The Redux 408 + 410NA blend shows the least loss of fracture energy from the starting figure. It would be useful to find an explanation for this.

(3) AF 163-2K and Redux 308A are both cured with dicyandiamide. They both show a steep drop in fracture energy after a period of time, 3days in the case of Redux 308A and an average of 300days in the case of AF 163-2K. Dicyandiamide has been associated with corrosion[24] but in this case there is no proof of the cause of the sudden drop in fracture energy. However, it is probably of significance that the diffusion coefficient of Redux 308A is more than an order of magnitude higher than that of AF 163-2K and its solubility coefficient is twice as high. Multiplying diffusion coefficients and solubility coefficients for AF-163 and Redux 308A shows that the permeability of Redux 308A is six times higher than that of AF 163 (see data in Armstrong[10]). This suggests that a critical water content may be needed to start the corrosion process because the drop in fracture energy is sudden and rapid. The initial drop in the

Figure 5 3M-EC2216 some oxide removed with adhesive

curve for Redux 308A occurs after 3days whereas the initial drop for AF 163 occurs after 300days.

While the shape of the curves in *Figure 1* is similar, they are affected by glueline thickness, which affects the initial fracture energy. It is also worthy of note from *Figure 1* that specimen 73 (AF 163, glueline thickness = 0.5mm, initial fracture energy = 7.4kJm^{-2}) levels out at a higher fracture energy than specimen 55 (Redux 308A, glueline thickness = 0.45mm, initial fracture energy = 4.1kJm^{-2}).

It is also clear from *Figure 1* that where two layers of film adhesive were used, this having the effect of doubling the fracture energy in some cases, then the final fracture energy after 2000days was also different in about the same proportion. Only with anodising did a high starting fracture energy result in a higher final fracture energy. Presumably this is because the lower surface preparations always give interfacial failure. At this point it was decided to plot the time to the first steep drop in fracture energy against diffusion coefficient, D, solubility coefficient, S, and permeability, $D \times S$. All these showed clearly that low values of D and S are essential to long-term durability, see *Table 5*. They all show signs of levelling off at long times. The curve for solubility coefficient suggests that a saturation water uptake of 1% or less would be a good target for development. A diffusion coefficient target of

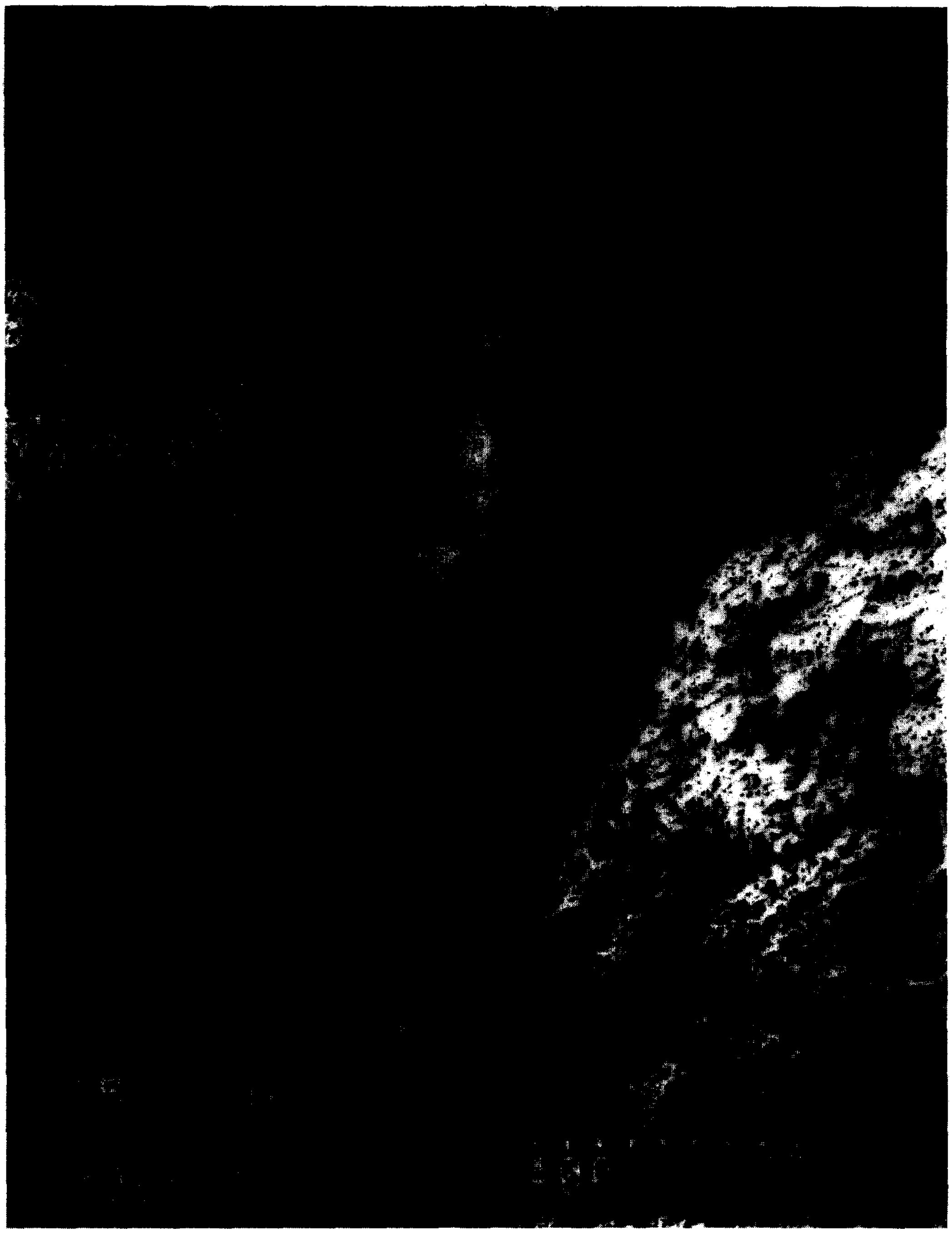

Figure 6 3M-EC2216 cohesive failure in the adhesive

$7\times10^{-14}\text{m}^2\text{s}^{-1}$ would be worth aiming for. Bowditch *et al.*[37], working with adhesives for use underwater, quotes UW 45 as having an S value of 0.5 and a D value of $5\times10^{-14}\text{m}^2\text{s}^{-1}$. Thus the target can not only be achieved but has been bettered and indicates that, if used out of water, the durability of bonds to aluminium alloys could be increased between 10 and 100 times without the use of primers if adhesives with permeability values as low as that of UW 45 were used! UW 45 has been marked on *Figures 9–11* for reference only. The curve for the mixture of one part of Redux 408 and 3 parts of Redux 410NA (both chromate inhibited) in *Figure 1* suggests that good inhibitors extend durability considerably. Alternatively, or additionally, it may confirm the value of adding some phenolic material to the blend. Redux 408 is an epoxy/novolac. This is good news, especially if the targets for D and S prove difficult or impossible to achieve at the same time as other essential properties. Redux 410NA and EC 2216 were added to *Table 5* to show the effect of inhibitor (410) and primer (EC 2216).

(4) The two hot-cured adhesives levelled out at a lower fracture energy than most of the room-temperature-curing ones at long times. This is a rather surprising result, worthy of some further investigation. Cold-setting adhesives on a good preparation may be far more durable than is

Figure 7 HYSOL EA9330 typical "pitted" surface from anodising showing surface flaking of the oxide

generally credited.

(5) The results comparing the four surface preparations show chromic acid anodising to be superior to the others and, except for the portable anodise, vastly superior (see *Figures 2* and *3*).

(6) Selectrons (now Sifco Selective Plating (UK) Ltd) portable anodising shows a large variation between specimens (see *Figures 2* and *3*). At present this work is always done with fresh solution. In view of the findings reported by Kinloch[12], it would seem that the Selectrons solution should have the correct amounts of copper and aluminium added to it before use.

More research to find an optimum formulation for this solution is recommended. The best results with Selectrons anodise were quite good and far better than with Deoxidine 202 or glass paper abrasion. However, a solution giving better and more consistent results needs to be developed. The Harwell micrographs showed this to give a much lighter anodise than the tank method.

(7) An adhesive/surface preparation combination for good durability might be defined by specifying a value of fracture energy below which it may not fall after 1000days or some other specified immersion time. At least 1000days seems to be necessary in this wedge test method in order to find the final and rather low value.

(8) The curve for 3M's EC 2216 is of interest in that it levels out quite near to that of the other adhesives,

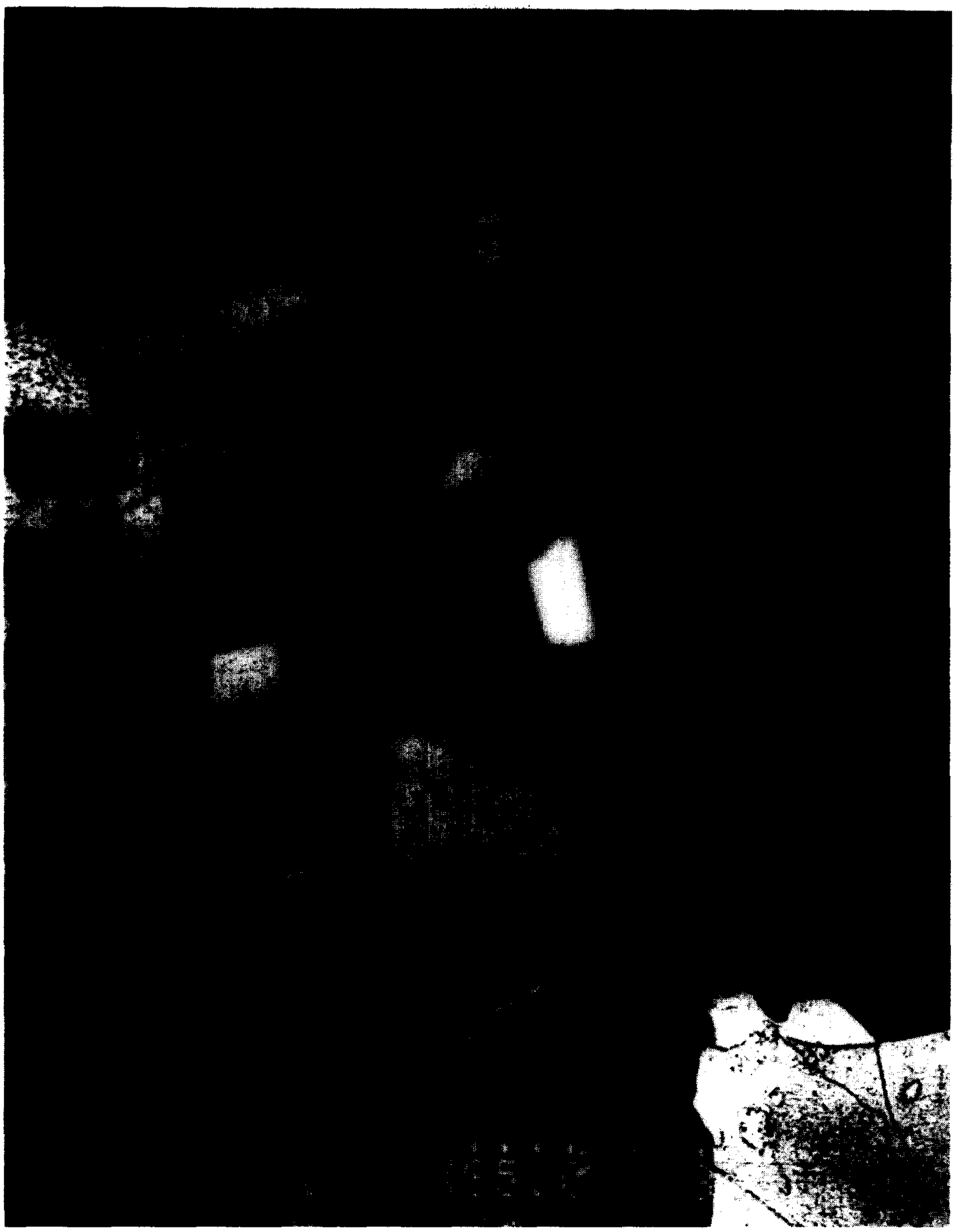

Figure 8 Surface flaking of the oxide-joint bonded with HYSOL EA9330

Table 5 Diffusion and solubility coefficients for *Figures 9–11*

Adhesive	D ($10^{-14}m^2s^{-1}$)	S (%)	DS	Days to drop
AF 163	8.04	1.89	15.2	300
Redux 308A	27	3.6	97.2	3
EA 9330	16.3	13	208	6
EA 9309.3NA	11.4	5	57	22
EC 2216	15.75	5.7	90	—
Redux 410NA	13.8	4.4	61	Inhibited
FM 1000	110	16	1760	Nylon/epoxy
UW 45	5	0.5	2.5	Underwater adhesive

Data from Armstrong [10] and Bowditch[37]

Note: (1) EC 2216 has served well on Fokker aircraft in rivetted and bonded fuselage lap joints when used with Redux 101 phenolic primer. (2) Redux 410NA, when mixed with Redux 408 (also chromate inhibited) on a chromic acid anodised specimen, survived for 1100days before the steep drop occurred. Redux 408 is an epoxy/novolac. See *Figure 1*

although it starts at a lower level. This adhesive has been very successful in the Fokker F.27 fuselage lap joints when used with Redux 101 phenolic primer. It has a much lower modulus than many other adhesives and in lap-shear tests has been found to be relatively sensitive to the quality of surface preparation. EC 2216 has a $D \times S$ value similar to that of Redux 308A, which suggests that its good durability is due to the use of a phenolic primer rather than the adhesive itself.

(9) It is very clear that short-term tests do not give the true order of merit for the durability of adhesives or rather adhesive bonds, although they do sort out differences in surface preparation quality.

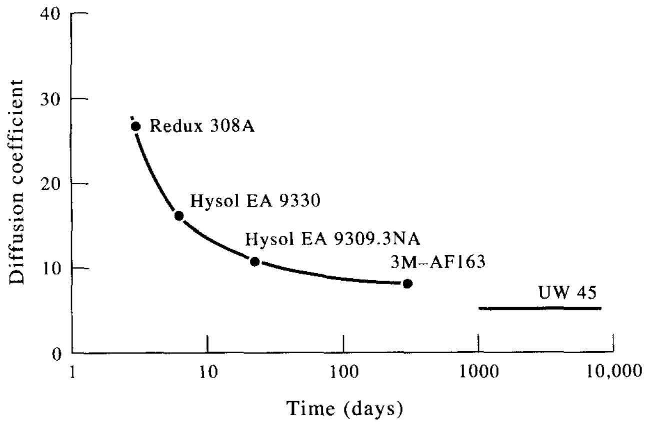

Figure 9 Diffusion coefficient v time to steep drop in fracture energy, see Fig. 1 and Table 4

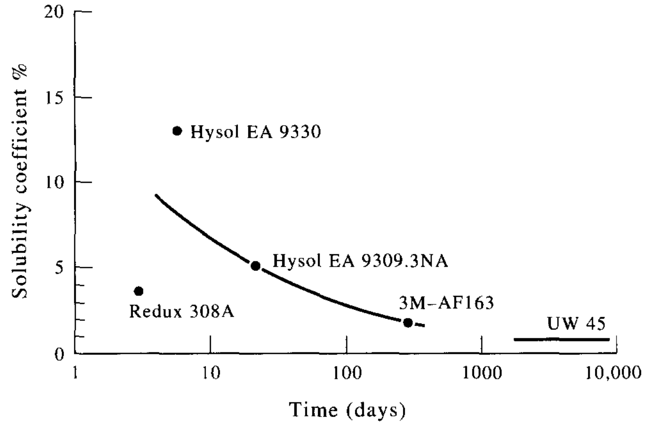

Figure 10 Solubility coefficient v time to steep drop in fracture energy, see Fig. 1 and Table 4

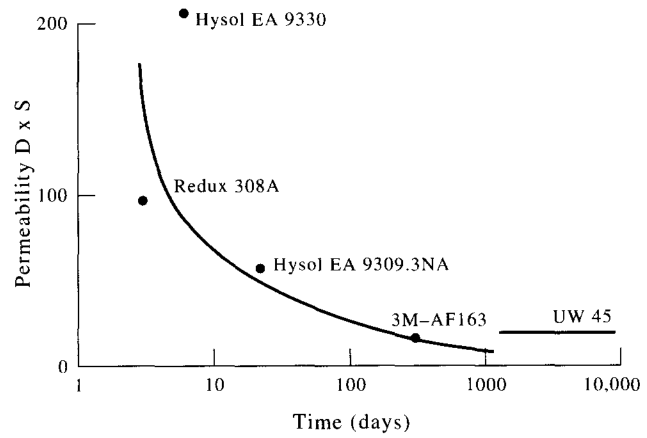

Figure 11 Permeability v time to steep drop in fracture energy, see Fig. 1 and Table 4

(10) The adhesive showing the least reduction in fracture energy over 5.5years of immersion was the 'home-made' blend of one part of Redux 408 with three parts of Redux 410NA. Redux 408 is an epoxy novolac and therefore contained some phenolic resin in addition to strontium chromate corrosion inhibitor.

(11) The above conclusion agrees with the conclusion of Brockmann *et al.*[24] that the long-term durability of adhesive bonds to aluminium alloy may best be achieved by concentrating on the development of phenolic resins.

(12) A further conclusion is that future research effort for the improvement of durability could probably best be spent on methods of improving portable anodising techniques rather than on a search for adhesives that do not require a good surface preparation.

(13) In this test high fracture toughness seems to give improved durability.

(14) It could be useful to carry out similar tests to these on phenolic and acrylic adhesives for comparison.

(15) This programme could be repeated in abbreviated form using primers to see how much difference they make.

(16) It could also be repeated using cyclic immersion tests, as the increased availability of oxygen at the bondline would probably reduce the durability considerably.

(17) The work at Harwell suggests that corrosion does take place before disbond. If the oxide layer is where degradation begins and failure occurs, this suggests that anodising processes, especially the portable variety, may need to be optimised and more carefully controlled.

(18) The above finding indicates that the durability of bonds may depend on the durability of the oxide more than on the durability of the adhesive itself. As adhesives are improved, development may need to move to the oxide layer and both its strength and durability may need to be increased. Primers that protect the oxide could increase in importance.

(19) The results from Harwell also show an 'interphase' and some skinning of the adhesive at the surface. From this it appears that each adherend surface may affect the 'interphase' differently and that even more careful matching of adhesives to substrates may be necessary.

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