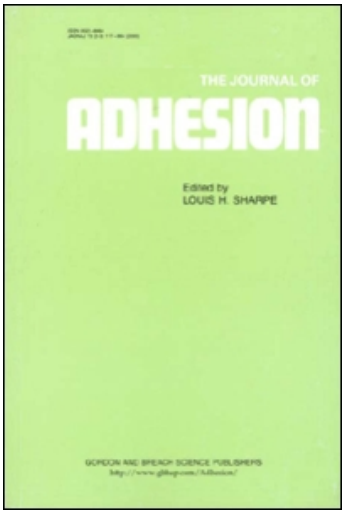

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G. W. Critchlow[a]; D. M. Brewis[a]
[a] Institute of Surface Science & Technology, Loughborough University, Loughborough, Leics, UK

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A Comparison of Chromate-Phosphate and Chromate-Free Conversion Coatings for Adhesive Bonding

G. W. CRITCHLOW* and D. M. BREWIS

Institute of Surface Science & Technology, Loughborough University, Loughborough, Leics LE11 3TU, UK

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Three different conversion coatings have been evaluated. One of these is an established chromate-phosphate treatment (BONDERITE** 705) whilst the others are chromate-free (BONDERITE 777 and EP2472) and not widely used for adhesive bonding. In the present study, the degree of surface modification introduced by these treatments has been determined using Auger electron spectroscopy (AES) and scanning electron microscopy (SEM). Both initial single lap shear and stressed durability results have been obtained using a single part epoxide adhesive. Degreased-only and grit-blasted adherends were used as controls. Overall, the conversion coatings provided better durability performance than the mechanical treatments. The developmental treatment EP2472, a chromate-free conversion coating, out-performed the established chromate-phosphate process at low applied loads ($\leqslant 0.5$ kN). All three conversion coatings performed similarly at the higher loads ($\geqslant 1$ kN).

Keywords: Auger electron spectroscopy; durability; conversion coatings

INTRODUCTION

As indicated in a recent review article by the present authors [1] and in numerous reference works [2, 3], conversion coatings are one of a range of possible treatments which might be applied to the aluminium

*Corresponding author.

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surface to enhance subsequent bond durability. Conversion coatings produce a surface film by interaction with the underlying base material [4]. The passivation and adhesion-promoting properties of such films makes them suitable for a wide range of applications [4–6]. Conversion coatings are used, for example, in the automotive, aerospace and domestic appliance industries; their main application is as a prepaint treatment for metals [4–12]. In addition, their usefulness has been demonstrated for metal treatment prior to adhesive bonding [1–13, 13–19]. Of particular note is the work by Sheasby and co-workers in which the suitability of conversion coatings was investigated for the structural bonding of aluminium-bodied cars [13–15]. Results from this work are mentioned later in the text.

The most commonly-used conversion coatings are based on chromate or chromate-phosphate chemistry [1, 4]. Alternative chromate-free processes are becoming more widely used because of the toxicity of the hexavalent chromium used in the conventional process [5–9, 11, 12].

Characterisation of chromate, chromate-phosphate and other conversion coated surfaces has been carried out by a number of workers [5, 10–12, 18, 20–24]. These studies utilise analytical techniques such as scanning electron microscopy (SEM) [5, 18, 21, 22, 24], secondary ion mass spectrometry (SIMS) [24], Auger electron spectroscopy (AES) [12, 18, 23, 24] and X-ray photoelectron spectroscopy (XPS) [5, 10, 11, 19, 21, 22, 24] to elucidate the film formation mechanisms and to study the physico-chemical characteristics of the films.

The present work is primarily concerned with the thin conversion coatings which are suitable for the enhancement of bond durability rather than the thicker films designed for surface passivation [4]. In this study, aluminium 5251 alloy adherends have been treated using one of three different conversion coatings; BONDERITE 705, a chromate-phosphate process; BONDERITE 777, a zirconia-based process; and EP2472, a novel, chromate-free process. The degree of surface modification imparted by each of these treatments has been studied using AES and SEM. The performance of each treatment has been established in stressed durability trials. Degreased-only and grit-blasted adherends were used for control purposes.

EXPERIMENTAL

Materials

The adherends used were aluminium 5251 alloy (nominal composition by weight: 0.1–0.5% Mn; 1.7–2.4% Mg; 0.15% Cu; 0.4% Si; 0.5% Fe; Al balance) which were cut using a press-tool into coupons measuring $20 \times 55 \times 2$ mm. After surface treatment the coupons were assembled into single lap shear (SLS) joints with 10 mm overlaps. The adhesive used was Araldite 2007, a 120°C curing, single-part, toughened epoxide manufactured by Ciba Polymers. The adhesive was mixed with a $\sim 1\%$ addition of 250 μm "Ballotini" glass spheres prior to bonding to control the glue-line thickness. Three replicates of all joints were prepared, with the exception of the degreased-only joints in which case up to six replicates were used.

Initial joint strengths were measured using a Lloyd 2000R tensometer fitted with a NAMAS calibrated 10 kN load cell. The initial jaw separation was set at 40 mm and a cross-head speed of $6\ \text{mm.min}^{-1}$ was used. Stressed durability data were obtained using Maddison-type stress tubes with joints exposed by immersion in deionised water at 60°C. Details of the apparatus and test methodology used are presented elsewhere [25]. Times-to-failure of the replicate joints were measured at applied loads in the range 0.2 to 1.5 kN.

Surface Treatments

Coupons were degreased by ultra-sonic immersion in "Super Purity" acetone (Romil) for two periods each of 10 minutes duration. Grit-blasted coupons were degreased as previously described followed by grit-blasting using a Guyson Beadblaster operating with 80/120 grade alumina grit; after this, coupons were degreased again. The conversion-coated coupons were degreased as before followed by cleaning with Pyroclean 71 (20g.l^{-1} @ 65°C for 5 minutes) + Aluma Etch 700 (4% w/v NaOH, $7.5\ \text{ml.l}^{-1}$ AE700 @ 50°C for 5 minutes) + rinse + HNO_3 desmut (10% v/v @ 20°C for 30 seconds) + rinse. Following this, the conversion coating was done with BONDERITE 705, BONDERITE 777 and EP2472 according to procedures recommended by Brent

Chemicals. In all cases, a "standard" treatment time of 5 minutes was used and the bath temperature was 20°C.

Surface Analysis

Auger electron spectroscopy (AES) was carried out using a Varian spectrometer with a primary electron beam energy of 3 keV and a current of 0.4 μA into an analysis spot approximately 150 μm in diameter. Depth profiling was carried out by combining AES with sequential argon-ion bombardment using a current density of 50 $\mu A.cm^{-2}$. A Cambridge Stereoscan 360 was used for the SEM investigation.

RESULTS

Surface Analysis

The results of the AES analyses on the three conversion coatings are presented in Figures 1a to 1c which give compositions as a function of depth. In all cases, quantification was achieved using experimentally-

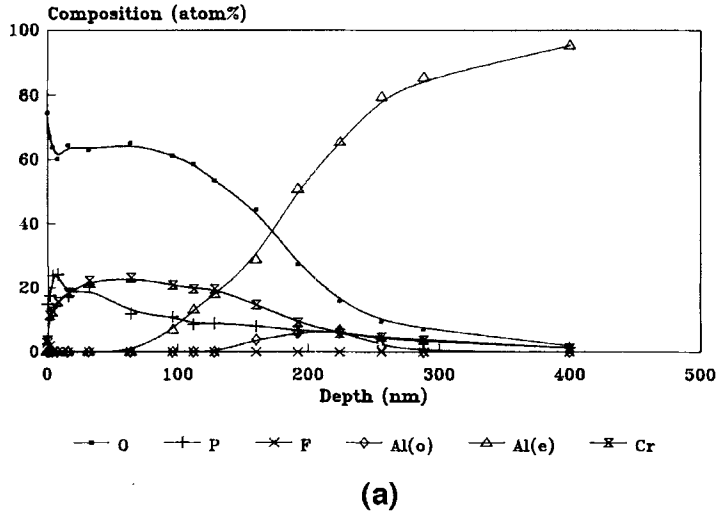
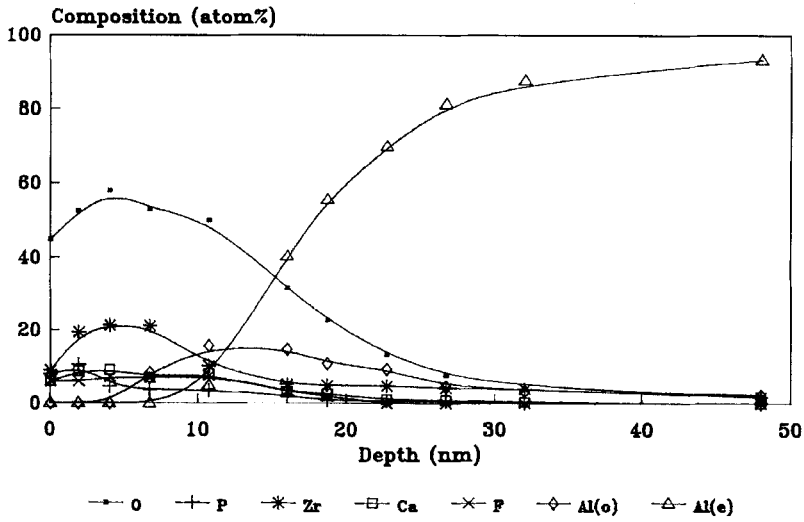
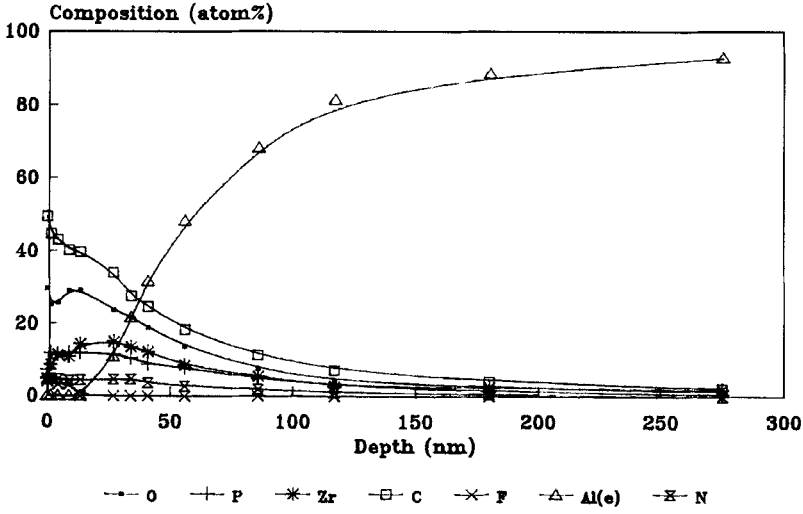


FIGURE 1 AES depth through the conversion coated layer produced after 5 minutes treatment @ 20°C by: a) BONDERITE 705, b) BONDERITE 777 and c) EP2472.



(b)



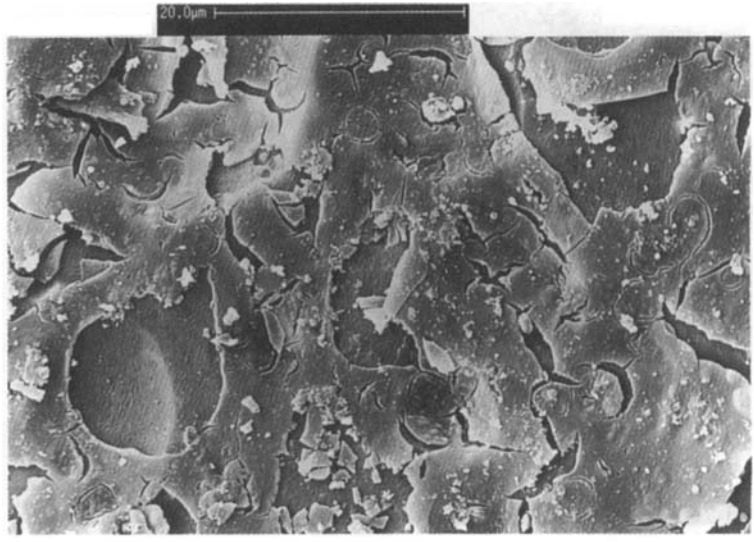
(c)

FIGURE 1 (Continued).

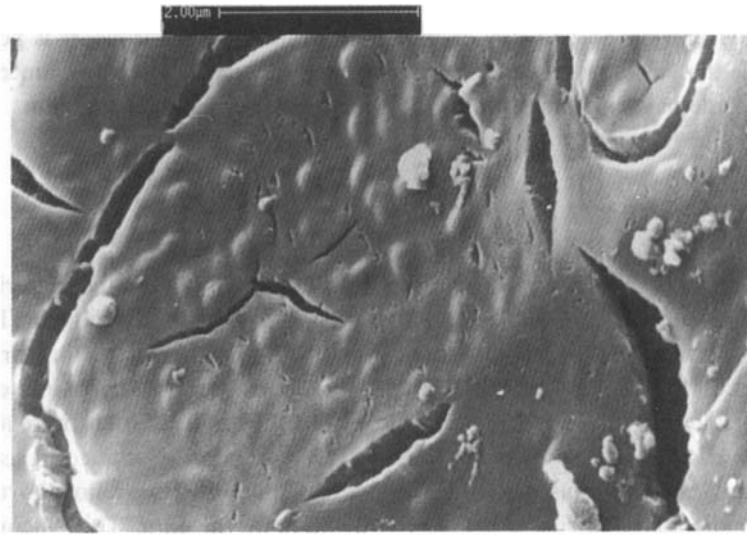
derived relative sensitivity factors based, where appropriate, upon Al_2O_3, P_2O_5, ZrO_2 and Cr_2O_3 reference materials. Depth scale calibration was carried out using a combination of empirical and theoretically derived etch rates. The results of the SEM examination of the conversion coatings are given in Figures 2a to 4b.

BONDERITE 705

The composition of the chromate-phosphate conversion coating (Fig. 1a) is consistent with that reported by other workers [21,23]. A mixed chromium and phosphorus containing oxide is present. Significantly, the AES results indicate that the oxide contains phosphorus in the pentavalent oxidation state with the phosphorus L_3VV peaks at 95 and 110 eV [26]. The high oxidation state (most likely to be as a phosphate) component would be expected to inhibit hydration of the oxide during exposure to water [27,28]. There was, however, no evidence of the fluorine-rich layer at the film-substrate interface which has previously been reported [21,23]. In the present work, a "standard" 5-minute BONDERITE 705 coating was used; there was no attempt at process optimisation. The BONDERITE 705 film was shown by SEM to be $\sim$230 nm thick and to be highly cracked (Figs. 2a to 2c). Treverton *et al.* [21] observed cracks in the surface oxide with the same type of conversion coating. The "mud crack" type morphology was attributed to shrinkage of the coating as water evaporated from between the particles in the gel formed on the metal surface [21]. The SEM images indicate that large areas of the coating have become detached (Figs. 2a and 2b) to reveal the rippled appearance of the underlying etched metal. In addition, these images reveal that there is a significant amount of surface detritus which has not been removed in the final rinse stage (Figs. 2a and 2c). According to the mechanism of film formation proposed by Treverton *et al.* [21] the chromate-phosphate conversion coating comprises small, spherical particles of chromium (III) oxide which join together to form a filament-like structure. The film porosity introduced by such features would be desirable for improved bond durability, providing both an extended interface across which interactions can occur and also the possibility of micro-mechanical interlocking. However, within the limited resolution of the SEM, the surface

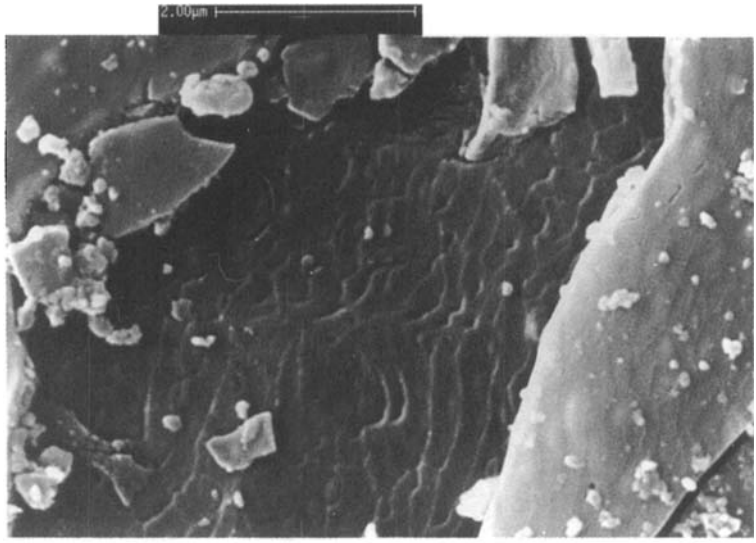


(a)



(b)

FIGURE 2 SEM micrographs of the BONDERITE 705 treated surface.



(c)

FIGURE 2 (Continued).

texture on the BONDERITE 705 treated adherends in the present study appears to be wavy or undulating rather than porous. It is possible that, as a consequence of the extended treatment time, the filaments of oxide have agglomerated to form a close-packed, continuous film.

BONDERITE 777

The results of AES analysis on the BONDERITE 777 treated material are given in Figure 1b. The AES results show that the BONDERITE 777 conversion coating produces a much thinner film than that produced by the BONDERITE 705 process, being approximately 15–20 nm thick (*cf.* ~230 nm). The AES results indicate that there are two distinct phases within the layer, the inner 7–8 nm comprises mainly Al_2O_3 whilst the outer 7–8 nm is mainly ZrO_2. Phosphorus, calcium and fluorine are present throughout the film. The calcium could possibly derive from the rinsing stage; however, since it was not observed in either of the other conversion coatings this is unlikely. As with the BONDERITE 705, the phosphorus present in the

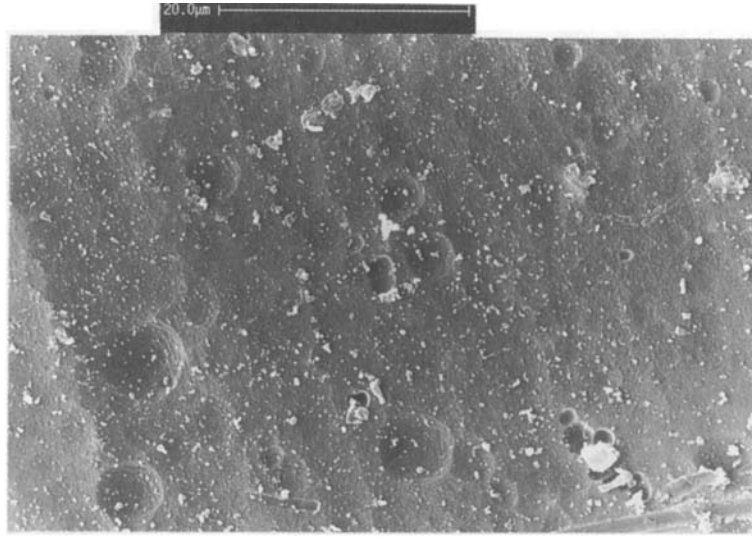
BONDERITE 777 film was in the high oxidation state and, therefore, might be expected to provide a degree of hydration resistance to the film. The SEM images, in Figures 3a and 3b, indicate that the BONDERITE 777 process produces a scalloped surface texture with sharp ridges in between. The size of these features is in the range 0.5 to less than 0.1μm across. The surface appears to be uniformly treated with none of the patchiness observable after the BONDERITE 705 treatment. Small particles of debris were also present on this surface.

EP2472

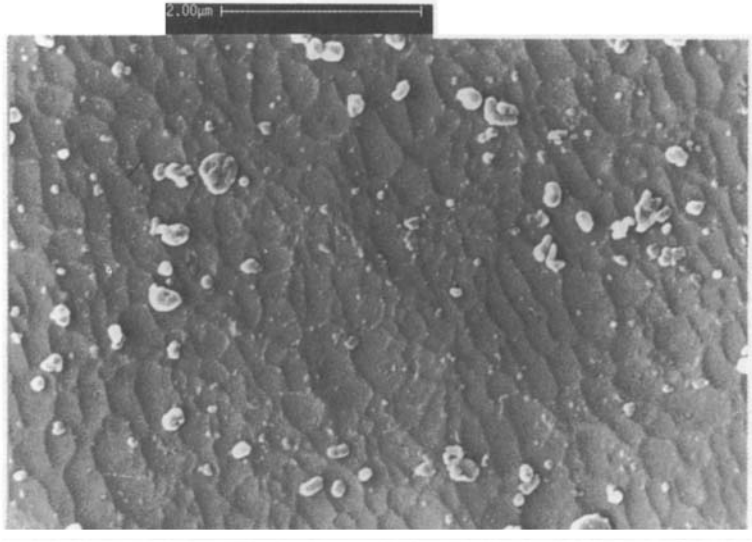
AES results, presented in Figure 1c, indicate that the EP2472 process produces a film containing both organic and inorganic components. This type of structure, a combination of zirconium-based chemistry with a polymer, has been reported by Schram *et al.* [24] There are, however, a number of differences between the films produced by the EP2472 conversion coating, used in the present work, and the Alodine 4830/4831 process studied by Schram *et al.* Firstly, the EP2472 film contains phosphorus which is absent in the Alodine 4830/4831 film. Also, there is much more zirconium in the EP2472 conversion coating compared with the Alodine 4830/4831. In addition, the EP2472 film is much thicker (~ 50 nm) than the Alodine 4830/4831 film (< 10 nm) previously reported [24]. The SEM images (Figs. 4a and 4b) indicate that there is uniform coverage of the substrate by the EP2472 film. On a macro-scale the surface texture appears to contain a series of large scallops up to ~ 20 μm in diameter (Fig. 4a). On a micro-scale the surface appears highly nodular (Fig. 4b). The nodules are approximately 0.1 μm in diameter or less.

Bond Testing

Initial joint strengths for the five treatments under investigation are given in Table I. The degreased-only adherends produced, by far, the worst initial joint strengths. Of the others, the chromate-phosphate treatment (BONDERITE 705) was out-performed by grit-blasting whilst the chromate-free treatments (BONDERITE 777 and EP2472) performed best of all.

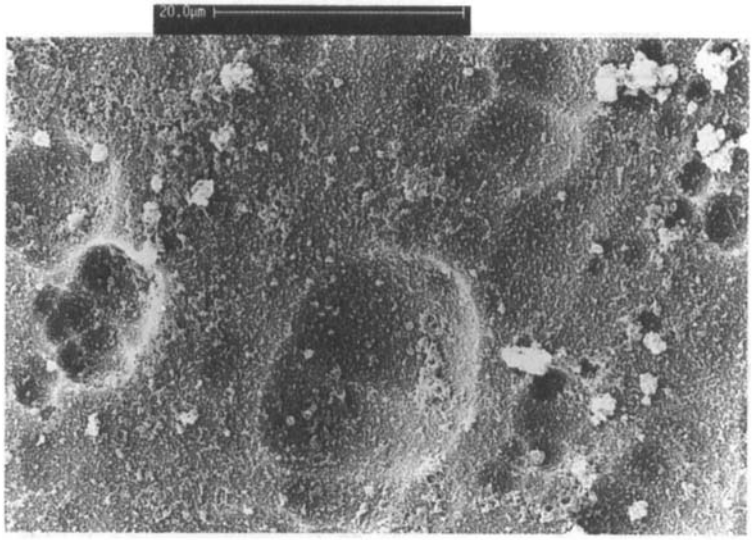


(a)

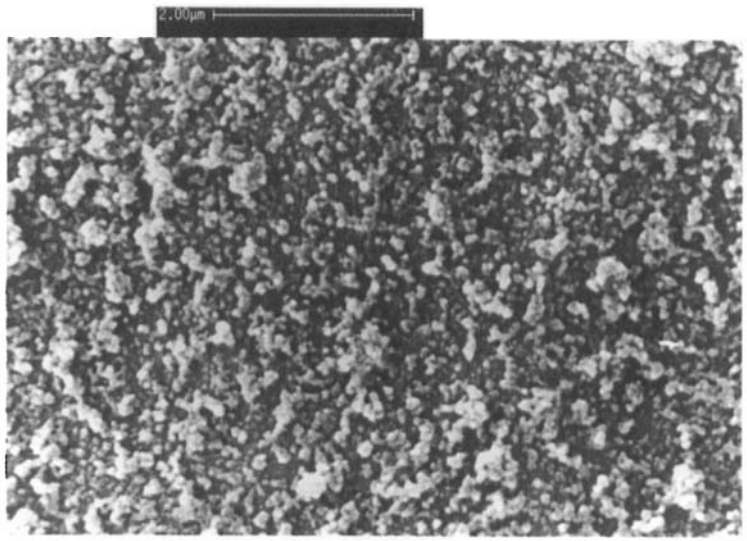


(b)

FIGURE 3 SEM micrographs of the BONDERITE 777 treated surface.



(a)



(b)

FIGURE 4 SEM micrographs of the EP2472 treated surface.

TABLE I Initial SLS joint strengths as a function of surface treatment

Treatment	*Joint strength (N) (±1 std. dev.)*
Degrease-only	1895±184
Grit-blast	4687±160
BONDERITE 705	4057±313
BONDERITE 777	5677±194
EP2472	5444±379

The results of stressed durability trials are illustrated in Figure 5, which presents the mean times-to-failure of SLS joints as a function of applied load. As expected, with all treatments, the mean time-to-failure decrease with increasing applied load. The degreased-only joints had the lowest times-to-failure at every applied load. This effect is particularly evident at the higher loads. For example, a mean time-to-failure times of approximately 20 hours was recorded with the degreased-only adherends at an applied load of 1 kN; this compares with more than 450 hours with the other treatments. At all applied loads the mechanical treatment (grit-blasting) was out-performed by

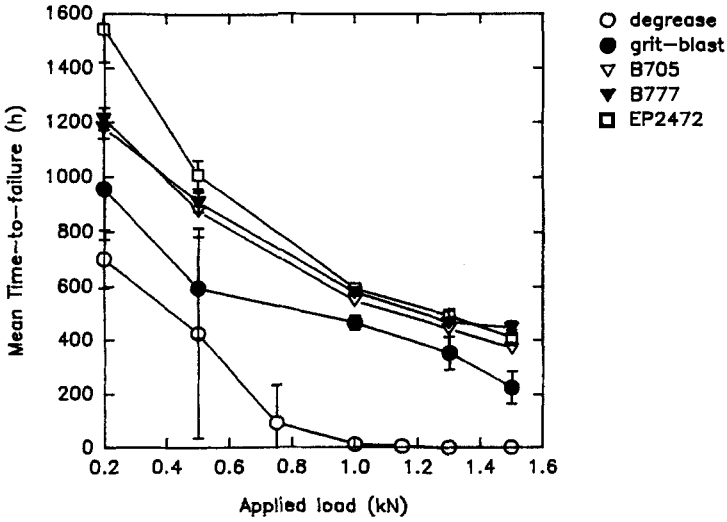


FIGURE 5 The mean times-to-failure (T_f) of stressed SLS joints as a function of applied load and surface treatment.

the conversion coating treatments. At loads of 0.2 and 0.5 kN the EP2472 treated joints had the longest time-to-failure with the B705 and B777 performing similarly. At loads of 1 kN or greater, all three conversion coatings perform similarly.

DISCUSSION

Surface characterisation and bond durability results have been presented for the three different conversion coating treatments. In the present work, degreased-only, grit-blasted and chromate-phosphate conversion coating treatments were included for comparative purposes. The chromate-phosphate process has been shown by Sheasby *et al.* [13–15] to be an effective surface treatment for aluminium. In his work, conversion coatings were incorporated into an integrated design and manufacturing process for adhesively-bonded car bodies from aluminium sheet. As a part of the evaluation process, zirconium- and chromium-based conversion coatings were considered alongside chromic acid etching (CAE) for the treatment of aluminium prior to bonding. In unstressed durability tests SLS joints were exposed to salt-spray for up to 60 weeks. Overall, the zirconium-based conversion coating performed comparably with the CAE with residual strengths of $\sim$6 MPa after 60 weeks exposure. The chromium-based conversion coating performed much better with residual strengths of $\sim$16 MPa after the same exposure. The superior performance of the chromium-based conversion coating was confirmed by stressed humidity tests, whereby SLS joints were exposed to temperature cycling between 43–48°C and 5 MPa applied stress. In these tests, using the same (unnamed) adhesive, zirconium-based conversion coated joints lasted $\sim$15 days whilst with the chromium-based treatment joints lasted $>$320 days. In the UK patent GB 2 139 540 A, chromate-phosphate conversion coated joints are compared with those prepared with the Boeing BAC 5555 phosphoric acid anodise (PAA) process. With aluminium 2117 and 5251 alloys the conversion coating produces comparable initial joint strengths to the PAA with values in the range $\sim$15–16 MPa. Furthermore, with unstressed joints exposed to salt-spray exposure for 8 weeks the surface treatments performed similarly with strength retention levels in the range $\sim$60–70%.

Work by Minford also highlights the beneficial effects of conversion coatings [1, 16, 17]. In one study [16], Minford compared the performance of Alodine 1200, a chromate conversion coating, with degreasing, grit-blasting and a number of acid etches. With a two-part epoxide the conversion coating gave poor initial control strengths (8.7 MPa) but demonstrated excellent durability with 90% strength retention after 8 years exposure in an industrial atmosphere. However, after 2 years exposure to a seacoast atmosphere the conversion coated joints retained ~34% of their initial joint strengths. Acid etched joints used in the same trials had 0% strength retention after this time. The poor initial joint strengths and relatively good durability were also reflected in tests with a single-part epoxide. Initial joint strengths were 18.4 and 36.8 MPa for conversion-coated and acid-etched joints, respectively. However, after 4 years exposure to the seacoast environment the conversion coating showed 97% strength retention, whilst the acid-etched joints retained no joint strength. In the present work, the chromate-phosphate conversion coating out-performed both the degrease-only and grit-blasting treatments, in line with Minford's results [16].

Maddison and Critchlow [18] demonstrated that, with the BONDERITE 705 treatment, a degree of process optimisation is essential in order to maximise joint strengths and bond durability. In their work, surface analysis was carried out on adherends treated for between 5 and 60 seconds. The chromate-phosphate conversion coating (BONDERITE 705) was shown to remove the previously existing magnesium-rich oxide on the aluminium alloy surface. This effect was followed by controlled film formation with a constant rate of growth for treatment times up to 60 seconds. Variations in joint performance, as measured by impact testing, were observed with treatment times up to 1000 seconds. Of significance was the development of micro-cracks in thicker films (of ~1 μm) which were associated with poor joint performance.

In the present work, no process optimisation was carried out, as "standard" treatment times were used. The SEM images from the BONDERITE 705 treated surface (Figs. 2a to 2c) indicate that over-treatment might have occurred with a cracked, non-continuous and non-porous oxide layer produced. There are a number of possible explanations for the improved durability results produced by the BONDERITE 705 treated, as compared with the grit-blasted adhe-

rends; there is some micro-mechanical interlocking with surface features not resolved by SEM; there is increased chemical interaction between the epoxide and the chromate-phosphate conversion coated compared with the grit-blasted surface, or the BONDERITE 705 conversion coating produces a more hydration-resistant surface. Locus of failure studies are currently underway to determine the failure mechanisms and, thereby, to indicate which of these factors produce the improved durability.

The surface texture produced by the BONDERITE 777 process is comparable with that produced by the Forest Products Laboratory (FPL) (CAE-based) etch [29,30]. The possibility of micro-mechanical interlocking and the increased area over which interactions can occur have been proposed as being responsible for the generally good durability performance of the FPL etch [29,30]. These benefits could also be responsible for the good durability performance of the BONDERITE 777 treated joints. The FPL etch is not recommended for bonding of primary structures because of doubts over the uniformity of treatment [31] and the inability of the oxide layer to resist attack by moisture [31,32]. The potential for increased hydration resistance and the apparently uniform coverage provided by the BONDERITE 777 process means that this treatment could possibly provide additional benefits to those offered by the FPL etch.

The EP2472 conversion coating contains both inorganic and organic components. The inorganic component is based upon zirconium and phosphorus chemistry, whilst the nature of the organic part is unknown. It is likely that when the EP2472 treated adherend is bonded, a region of graded composition is formed between the metal adherend and the polymeric adhesive, rather than there being a discreet interface between the adhesive and the adherend. Irrespective of any surface interaction with the adhesive, the highly micro-rough, nodular surface created by the EP2472 process would, if fully wetted by the adhesive, provide an ideal surface topography for bonding.

It is recognised that, in order to evaluate fully the effectiveness of the BONDERITE 777 and EP2472 treatments, more extensive trails should be conducted. Such trials should include exposure of joints to variations in ambient conditions, loading and ageing times. The treatments used in the present study should be compared directly with the established phosphoric acid anodise and chromic acid etches. Some of

these trials are currently underway. In order to understand more fully the joint failure mechnisms, work will be carried out to determine the loci of failure.

CONCLUSIONS

- Surface analysis by AES and SEM highlight differences in topography and chemistry between the three "standard" conversion coatings (with 5-minute treatment times at 20°C).
- Initial joint strength results indicate that both the mechanical and chemical treatments provide significant improvements compared with the degreased-only control.
- All three conversion coatings out-performed both the degrease-only and the grit-blast treatments in the stressed durability trials.
- In the stressed durability trials, the chromate-free treatments out-performed the established chromate-phosphate conversion coating at low applied loads (0.2 and 0.5 kN). All three conversion coatings performed similarly at loads $\geqslant 1$ kN.
- The effects of applied stress in combination with elevated temperatures and water immersion on adhesive joints has yet to be fully investigated. These three factors are experienced by many joints in service and, therefore, it is appropriate that they should be studied in combination if durability results are to reflect service conditions. It is likely that at low applied loads the increased exposure times to water and elevated temperatures prior to failure enables water ingress to be a contributory factor in joint failure. However, at high applied loads creep of the adhesive might be the dominant failure mechanism.

Acknowledgment

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