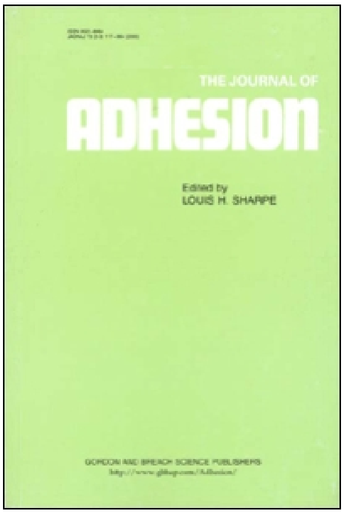

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Allen, K. W. and Alsalim, H. S.(1976) 'Surface Preparation of a Stainless Steel for Adhesive Bonding', The Journal of Adhesion, 8: 3, 183 — 194

To link to this Article: DOI: 10.1080/00218467608075082

URL: http://dx.doi.org/10.1080/00218467608075082

J. Adhesion 1977, Vol. 8, pp. 183–194

Printed in Scotland

Surface Preparation of a Stainless Steel for Adhesive Bonding

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(*Received May 27, 1976*)

The surface preparation of stainless steel of identified martensitic structure has been studied in relation to the strength of adhesive bond with an epoxy–phenolic, an epoxy and a polyimide adhesive. Attention has been given to replacing the inefficient mechanical removal of deposited carbon ("smut") by chemical means. Seven different chemical treatments by acids or acid combinations were tried. Hydrofluoric or sulphuric acids modified by nitric or oxalic acids respectively were most satisfactory followed by chromic acid desmutting.

INTRODUCTION

In the normal state in which metals are available in industry the surface is covered with a layer which has quite different properties from the bulk. This layer may contain processing lubricant, mill scale, selective oxidation products, or incidental contaminants and is usually so thick that it entirely governs the behaviour of the surface. Hence the strength of an adhesive joint is limited by forces between this layer and the adhesive, or between this layer and the metal or by the cohesive strength of the layer; whichever is the weakest. Generally this surface layer in its original state has a deleterious effect on adhesive bond strength and is modified or removed by suitable treatment before bonding.

The effects of surface treatment of metal adherends upon adhesive joint properties have been extensively investigated. As these investigations have usually been directed to the needs of the aerospace industry, the metals most extensively studied have been the alloys used there. These include stainless steels and the various alloys based on aluminium, magnesium or titanium. The published reports are surprisingly vague about the exact nature of the alloys studied particularly for stainless steel, despite the very wide variation in composition and properties of stainless steels.

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Treatments are divided into physical or mechanical methods (such as sandblasting) and chemical or pickling methods. Sometimes these are used successively but our concern has been entirely with the latter methods.

THE ADHEREND

The present work was done with Firth-Vickers steel FV-520 B which is a precipitation hardening stainless steel of composition:

	weight %	atomic %
C	<0.07	0.4
Si	<0.7	1.4
Mn	<1.0	1.0
Nb	0.2 ~ 0.7	0.3
Cu	1.2 ~ 2.0	1.2
Mo	1.2 ~ 2.0	0.8
Ni	5.0 ~ 6.0	5.2
Cr	13.2 ~ 14.7	15.0
Fe	72.8 ~ 77.4	75.0

In addition to its martensitic structure, depending upon its thermal treatment this alloy may contain δ-ferrite and carbide phases. The samples used in the torsional adhesive joint testing had all been treated to give peak

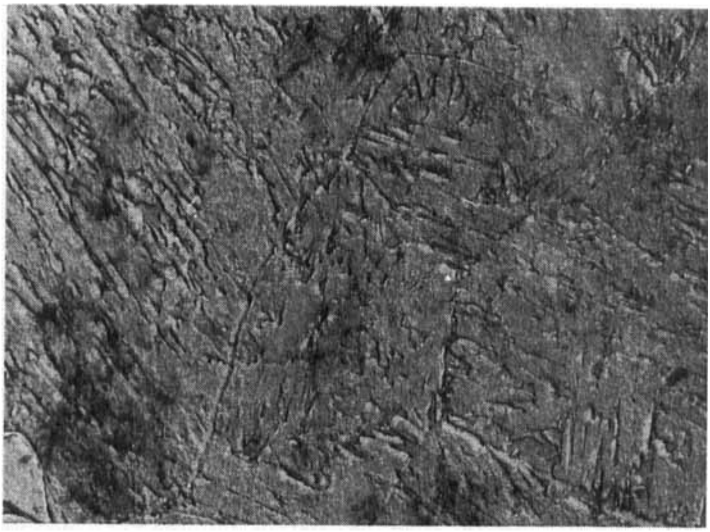

FIGURE 1 Electron micrograph (×2500) of FV 520B stainless steel after etching for 5 seconds in hydrochloric acid/nitric acid/water (2:4:10) at 50°C. Shows grain boundaries and martensitic laths.

hardness which should give a structure free from δ-ferrite and carbide. This was confirmed by electron micrographs taken after electropolishing and etching in nitric acid reagents. These showed grain boundaries and martenistic laths but no other phases (Figure 1); but other samples used for preliminary studies revealed these additional phases occasionally.

DESMUTTING

All the treatment solutions which effectively attacked the steel leave a deposit of graphite on the surface. This phenomena is well known and the deposit is commonly referred to as "smut" and its removal as "desmutting".

It is essential that smut is removed because, as will be seen later, its presence on surfaces to be bonded reduces bond strength by about 50%.

The usual method recommended for desmutting is mechanical brushing by a wire or stiff bristle brush. However, careful examination by optical and stereoscan methods revealed that this removed the carbon from the top of the asperities only, leaving that in the crevices unaffected.

It was found that when a freshly etched specimen was dipped in a concentrated (30% w/v) solution of nitric acid a vigorous reaction lasting a few seconds occurred. During this reaction a colourless (unidentified) gas was evolved and the smut was removed. After a few seconds the reaction completely ceased. No change in the topography of the surface could be detected by careful examination of selected areas.

Since concentrated solutions of nitric acid are essentially hazardous, a search was made for alternative methods. Solutions of sodium dichromate, of acidified potassium permanganate and of hydrogen peroxide all produced no effect. A dilute solution of chromic acid had no effect at room temperatures, but when heated to over 50°C desmutting was complete in about seven minutes. A solution containing 10% w/v sulphuric acid and 10% w/v chromium trioxide and used at 70°C was adopted as standard. This would normally complete desmutting in about three minutes.

Either of these chemical methods is preferable to the mechanical: they remove almost all the graphite, and they leave the surface passive with a thicker coherent oxide layer and less chance of subsequent corrosion. The chromic acid method seems to lead to rather stronger bonds (10%) than the nitric acid method.

SURFACE TREATMENTS AND THEIR EFFECTS

The chemical treatments which have been suggested for treatment of steel surfaces before adhesive bonding can be broadly grouped into those including chromates, reducing acid solutions, and solutions of mineral acids with

TABLE I

Reflection electron diffraction of FV 520B after various treatments and desmutting

H_2SO_4 then desmutted in:				H_2SO_4 + Oxalic acid then desmutted in:				HCl then desmutted in:				HCl + $FeCl_3$ then desmutted in:				ASTM data for:	
Nitric acid		Chromic acid		Nitric acid		Chromic acid		Nitric acid		Chromic acid		Nitric acid		Chromic acid		α-Fe	
dÅ	Int	dÅ	Int	dÅ	Int	dÅ	Int	dÅ	Int	dÅ	Int	dÅ	Int	dÅ	Int	dÅ	Int
2.008	m	2.018	m/st	2.065	st	2.045	st/m	2.060	m	2.018	st	2.065	st	2.033	st	2.027	100
1.422	m	1.450	m	1.430	m	1.437	m	1.420	m	1.430	m	1.437	m	1.440	w	1.433	19
1.166	m	1.172	m	1.168	m	1.171	m	1.169	m	1.166	m	1.166	m	1.160	m	1.170	30
1.011	vw	1.022	vw	1.012	w	1.014	vw	1.000	vw	1.011	w	1.014	w	1.012	w	1.013	9
0.906	w	0.901	w	0.909	w	0.907	w	0.906	w	0.910	w	0.909	w	0.907	m	0.906	12
0.822	vw	0.811	vw	0.820	vw	0.831	vw	0.822	w	0.8		0.814	w	0.818	w	0.827	6

various modifiers particularly oxidising agents. The alloy FV 520B became passive in all the chromate solutions and was only very slowly affected by the solutions containing oxidising agents, so it was decided to investigate the following treatments:

1) Sulphuric acid alone.
2) Sulphuric acid plus oxalic acid.
3) Sulphuric acid plus sodium sulphate.
4) Hydrochloric acid alone.
5) Hydrochloric acid plus sodium chloride.
6) Hydrochloric acid plus ferric chloride.
7) Hydrofluoric acid.

Specimens in the form of discs (*ca.* 4 mm in diameter) were electropolished in a sulphuric–phosphoric acid mixture, rinsed in water and in acetone and dried before they were treated in the appropriate solution at its boiling point. After they had been treated, they were desmutted, rinsed in alkaline water, in distilled water and in acetone and finally dried at 100°C for 45 minutes. Then they were examined by reflection electron diffraction at glancing angle. The untreated electropolished surface produced no lines because of charging of the oxide film, nor did any treated surface before desmutting because of the amorphous nature of the carbon layer. The results for the treated and desmutted surfaces are given in Table I, from which it will be seen that the only diffraction lines obtained correspond to the martensite structure of α Fe of the bulk substrate; indicating that the surface layer must be too thin to be effectively studied by this technique. However, in one instance after treatment with sulphuric and oxalic acids and desmutting with chromic acid a pattern corresponding to niobium carbide was obtained (interpretation kindly confirmed by Mr. T. W. Baker of A.E.R.E. Harwell, using his computer programme). Unexpected as this was, apparently niobium carbide is a common corrosion product of stainless steels. Those specimens which had been desmutting with chromic acid gave sharper diffraction lines than those desmutted with nitric acid, suggesting cleaner surfaces with less amorphous deposits remaining.

Supplementary to these, the surface of the alloy in an air-oxidised state was examined because this is the condition in which it is delivered. This corresponded to a mixture of Cr_2O_3 and α Fe_2O_3 with no lines unaccounted for.

BONDING AND TESTING TECHNIQUES

The adhesive bond properties were tested in torsional shear using napkin ring test pieces of FV 520B alloy of outer radius 0.793 cm and inner radius 0.635 cm, providing a bonding area of 0.707 cm^2. These were polished using the jig provided with successive grades of emery paper to 600 Å, and then further polished with diamond paste. This was followed by cleaning with warm water, degreasing with trichloro ethylene and drying at about 100°C for at least 45 minutes.

The rings were either used in this condition, or were subjected to a chemical treatment and desmutting, then rinsed in alkaline water, water alone and finally in acetone before they were dried.

Bonds were assembled at room temperature in a jig, were cured and were allowed to cool to room temperature under pressure before removing from the jig. At least 24 hours was allowed to elapse between completion of curing and testing.

The adhesives used and curing conditions were:

Hidux 1197A (Bonded Structures Ltd.) an epoxy-phenolic adhesive, cured 2½ hours at 165°C under 4.5 ~ 5.0 kg/cm^2 pressure.

Redux 319 (Bonded Structures Ltd.) a modified epoxy adhesive, cured 2¼ hours at 175°C under 3.0 ~ 4.5 kg/cm^2 pressure.

Nolimid IP–A380 (Rhône Poulenc) a polyimide adhesive used with a primer, cured 6½ hours at 295°C under 3.0–3.5 kg/cm^2 pressure.

All these adhesives contained aluminium powder as filler, and the first and last were supported on a glass cloth.

IP–A380 adhesive required a primer liquid which was brushed on to the dry treated surface. The specimens were placed in an oven at 85°C for an hour and then were allowed to cool to room temperature before the joints were assembled.

It was found that there was always a period after the specimen had been immersed in the acid solution before any reaction was apparent. This induction period is believed to correspond to the penetration of a passive film and is of very variable length even with apparently identical alloy samples and acid solutions. For example, with sulphuric acid it was about one second on one occasion and several hours on another. Because of this unpredictable and apparently random length of induction period, the duration of etching time was always measured from the point when a reaction could be seen and not the moment of immersion.

Bonding with Hidux 1197C

The strength of an adhesive bond depended both upon the nature of the treatment of the alloy surface and also upon the length of time (and hence the extent) of the etching. It was evidently important to investigate the length of time for which a specimen needed to be etched to give maximum bond strength for each treatment individually.

The following treatments were used:

i) 10% w/v sulphuric acid.
ii) 4% w/v hydrofluoric acid.
iii) 4% w/v hydrofluoric acid and 2% w/v nitric acid.
iv) 10% w/v hydrochloric acid.

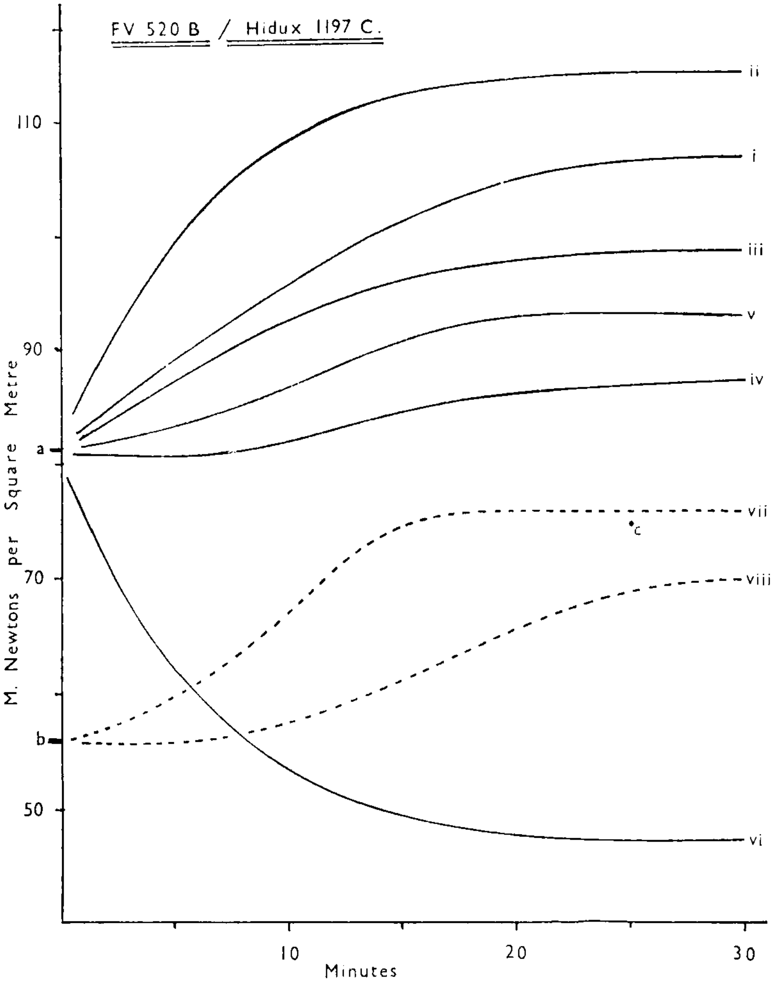

FIGURE 2 Bond strength obtained with FV 520B and Hidux 1197C with different chemical treatments carried out for various lengths of time. ——, first batch of Hidux 1197C; - - -, second batch of Hidux 1197C; a,b, bond strengths corresponding to plain polished adherends using first and second batches of Hidux 1197C respectively; c, bond strength corresponding to treatment with 10% w/v H_2SO_4 and using second batch of Hidux 1197C. Key to treatments according to text.

v) 10% w/v hydrochloric acid and 5% ferric chloride.
vi) 4% w/v hydrofluoric acid but with *no* desmutting.
vii) 10% w/v sulphuric acid and 20% w/v oxalic acid.
viii) 1:1:1 parts by weight of sulphuric acid, phosphoric acid, water, and 5% w/v potassium iodide or bromide.

All these, except (vi) were followed by nitric acid desmutting.

Unfortunately, a different batch of Hidux 1197C had to be used for tests (vii) and (viii) and this gave considerably lower (55.9 against 81.4 MN/m^2) values for bond strengths with untreated polished adherends. It was established that the proportional changes resulting from various treatments were closely similar. The reasons for this variation are unimportant in the present context and simply meant that two sets of reference values had to be used.

The results of all these trials are shown in Figure 2, and the values of the maximum attainable bond strengths are given in Table II.

TABLE II

Maximum bond strengths obtained with FV 520B and Hidux 1197C after various treatments[a]

Adherend treatment	Bond strength Mean value and standard deviation MN/m^2		% change
Adhesive Batch 1			
Plain polished	81.36	(1.81)	—
10% H_2SO_4	106.48	(0.49)	+30.9
4% HF	116.53	(1.47)	+43.1
4% HF + 2% HNO_3	97.30	(2.56)	+19.6
10% HCl	85.88	(1.42)	+ 5.7
10% HCl + 5% Fe Cl_3	92.27	(0.92)	+13.4
4% HF *Not desmutted*	49.05	(3.97)	−39.7
Adhesive Batch 2			
Plain polished	55.89	(2.80)	—
10% H_2SO_4	75.48	(1.32)	+35.1
10% H_2SO_4 + 20% $(COOH)_2$	75.29	(2.10)	+34.7
$H_2SO_4/H_3PO_4/KI$	67.26	(3.54)	+20.3
$H_2SO_4/H_3PO_4/KBr$	69.73	(1.33)	+24.8

[a] All include desmutting with nitric acid except where stated.

Following these trials, the effects of adding varying amounts of salts to the acid solutions were investigated. In all cases etching was carried out at boiling point and for 20 minutes. With 10% hydrochloric acid the addition of up to 20% w/v sodium chloride had no significant effect on the bond strength obtained.

With 10% w/v sulphuric acid the addition of sodium sulphate caused a steady decrease in the bond strength obtained, going down to a limiting value at 20% w/v salt of about 80% of that obtained with the acid alone.

Also with 10% sulphuric acid the addition of oxalic acid was studied. Here it was found that up to 30% w/v oxalic acid had no effect on bond strength obtained. The effect of the oxalic acid was, as has been seen earlier, to reduce the time of etching needed to obtain maximum bond strength from about 25 minutes to 15 minutes. A further advantage arising from the addition of oxalic acid was that less smut was produced and it was easier to remove it.

Bonding with Redux 319

Since it was now clearly established that maximum bond strengths could be obtained by etch treatment for 20 minutes, this part of the work was concerned only with the relative bond strengths obtained by different treatments and also different desmutting techniques.

TABLE III

Maximum bond strengths obtained with FV 520B and Redux 319 various treatments and desmutting

Adherend treatment and desmutting	Bond strength Mean value and standard deviation MN/m^2	% change
Plain polished	81.8 (1.3)	—
10% H_2SO_4		
mechanical	61.3 (1.0)	−26
chromic acid	91.6 (2.0)	+11
10% H_2SO_4 + 20% $(COOH)_2$		
nitric acid	90.8 (2.4)	+10
chromic acid	95.3 (2.7)	+16
4% HF		
mechanical	71.8 (2.1)	−13
chromic acid	89.3 (3.4)	+9
$H_2SO_4/H_3PO_4/KI$		
mechanical	57.3 (2.0)	−30
nitric acid	59.9 (2.0)	−27
chromic acid	63.9 (3.4)	−22

The results of this are shown in Table III. This shows the greater efficiency of chromic acid desmutting which gave a gain of about 5% in the bond strength over that obtained with nitric acid, and the inadequacy of mechanical desmutting. The failure of the treatment including phosphoric acid and potassium iodide is also very obvious.

Bonding with Nolimid IP-A380

Only two treatments were explored with Nolimid IP–A380 and the results are given in Table IV. In these cases chromic acid was used for desmutting.

TABLE IV

Maximum bond strengths obtained with FV 520B and Nolimid IP–A320 after various treatments. (All include desmutting with chromic acid.)

Adherend treatment	Bond strength Mean value and standard deviation MN/m^2	% change
Plain polished	50.7 (2.0)	—
10% H_2SO_4 + 20% $(COOH)_2$	64.5 (2.7)	+27
4% HF	65.9 (2.4)	+30

MODE OF FAILURE AND SURFACE TOPOGRAPHY

With Hidux 1197C and treated surfaces the failure was always cohesive within the adhesive layer but the position of failure with respect to the interface varied. The stronger bonds failed close to the glass cloth carrier while the weaker bonds failed nearer to the interface with the metal.

The results with Nolimid IP–A380 were similar in this respect.

Redux 319 gave somewhat different results since it has no carrier but again the failure was cohesive except from the treatment including potassium iodide, where it was mainly adhesive. However these bonds were so much weaker that evidently the mechanism was quite different, possibly due to gases trapped in the very porous surface.

The different treatments gave surfaces of very different roughness and Figures 3 and 4 show the two extremes the former resulting from treatment with sulphuric acid, phosphoric acid and potassium iodide and the latter from treatment with sulphuric acid and oxalic acid. Clearly the surface shown in Figure 4 would be expected to give stronger bonds; its pits can be more readily filled with adhesive, and its asperities can penetrate more deeply into the adhesive matrix. This last effect would be particularly relevant if there is any separation and inhomogeneity of the adhesive near the interface; as is known to occur with Hidux 1197C.

The fracture behaviour with Nolimid IP–A380 and plain polished, untreated adherents is unusual and interesting. Failure occurs both apparently adhesively at the interface and also cohesively within the adhesive. This

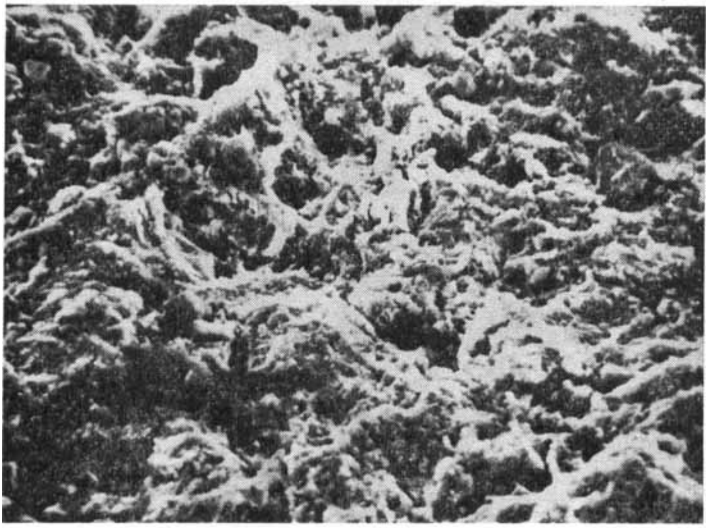

FIGURE 3 Photo micrograph (×1000) of FV 520B stainless steel after treatment with sulphuric acid/phosphoric acid/potassium iodide. Desmutted with chromic acid. Shows spongy surface with re-entrant pitting.

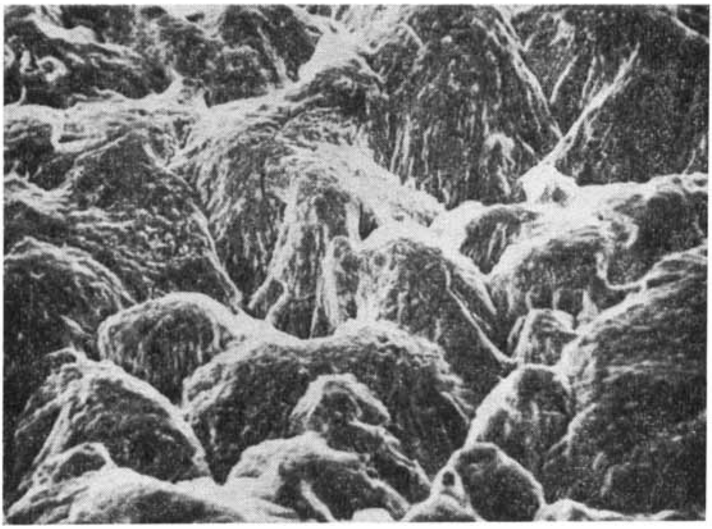

FIGURE 4 Photo micrograph (×1000) of FV 520B stainless steel after treatment with sulphuric acid/oxalic acid. Desmutted with chromic acid. Shows well defined surface with open depressions.

fracture through the adhesive was of a step nature with a series of apparently flat areas of differing thickness, suggesting that perhaps it is crystalline at least towards the interface.

CONCLUSIONS

Generally speaking it is clear that while etching with any reducing acid will lead to improved strength in adhesive bonds for the materials discussed, hydrofluoric acid or sulphuric acid are preferable. These may be modified by the addition of nitric acid to reduce the vigour of attack of the hydrofluoric acid or oxalic acid to reduce the time needed to reach the condition for maximum strength with sulphuric acid.

With all the acids there is an induction period before etching begins. The length of this may be quite variable, from a few minutes up to an hour. It is necessary to continue etching for 20 minutes after the induction period is passed and etch reaction has commenced.

Desmutting after etching and before bonding is essential to remove carbon and debris if satisfactory joints are to be achieved. Chemical desmutting with either nitric acid or chromic acid is very much more satisfactory than mechanical methods and either yield stronger adhesive bonds.

Acknowledgements

The authors wish to express their thanks to Professor W. C. Wake for his invaluable help throughout this work which was carried out with the support of the U.K. Ministry of Defence Procurement Executive.