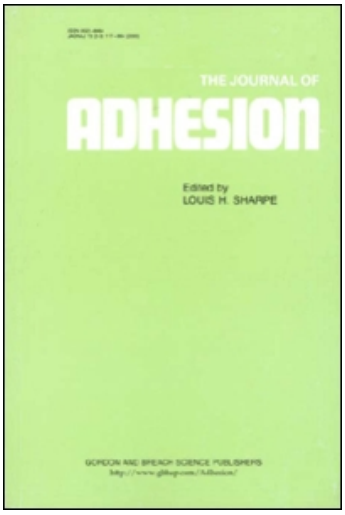

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The Application of Surface Analysis Techniques in the Adhesive Bonding of Oily Automotive Steel

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KEY WORDS Auger depth profiling; bonding oily steel; epoxy bonding; ESCA; galvanized steel; surface analysis.

I INTRODUCTION

There are fewer papers on the adhesive bonding of steel for structural applications than for aluminum and titanium alloys. However, the approach to the adhesive bonding of all three adherends has been similar, that is, the surfaces are pretreated prior to bonding. Trawinski, *et al.*[1,2,3] reviewed several conversion coatings or etching processes used for steel. Haak and Smith[4] selected two surface treatments among nineteen based on minimal cost, simplicity and good durability. Smith[5] has reported work on stainless steel-epoxy bonds under hydrothermal stress. Bischof, *et al.*[6] investigated the effect of surface pretreatment of steel on bonding strength obtained with polyvinyl chloride. Ziane, *et al.*[7] identified four fracture zones resulting from shear loading of epoxy

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bonded galvanized steel following four different surface pretreatments. But in some cases, as in the automotive industry, there is a need to bond oily steel directly without surface pretreatment. Rosty, *et al.*[8] have reported a study of the role of fillers and cure temperature on the shear strength of oily steel bonded with epoxy. None of the reported research utilizes both microscopic and spectroscopic techniques to analyze the fracture surfaces.

In the present work, the emphasis is on the shear strength of epoxy bonded oily automotive steel surfaces subjected to a severe environment and the use of surface analysis techniques to investigate the locus of failure.

II EXPERIMENTAL

Three different kinds of galvanized steels were used in the study and are referred to as MS (Monogal steel from Usinor, France), GH (zinc electroplated steel from Honda, Japan), and A527 (galvanized cold rolled steel from Carolina Steel, USA). The galvanized steel adherends were only wiped with acetone prior to bonding. Two different one-part epoxy adhesives were used and were supplied by CECA, France. The epoxies were cured for 30 minutes at 180°C according to the supplier's specifications.

Bonded samples were prepared using a modified lap shear test, *i.e.*, the Renault lap shear (RLS) test. The test, as shown schematically in Figure 1, consists in joining two 10×1.5 cm coupons (thickness: 0.8 mm) with a bonded area of 2.5×1.25 cm,

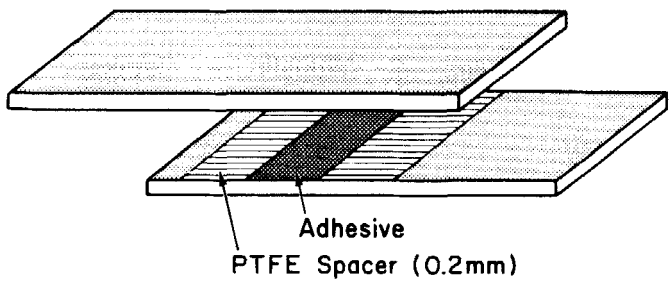

FIGURE 1 Schematic diagram of Renault lap shear test.

the joint thickness being controlled by two 0.2 mm PTFE spacers. After cure the samples were wrapped in cotton, soaked with distilled water and sealed in a Zip-Loc^{R} polyethylene bag and placed in an oven at 70°C for 7 days. The samples were then transferred to a freezer at 20°C for 2 hours and the shear strength determined in an Instron machine. For each sample, the maximum strength was recorded.

Some steel samples were regreased in a 10% ASTM 3 *n*-heptane solution. The regreasing process consisted in dipping the substrate in the solution for a few minutes, letting it drip dry vertically for 90 seconds and then laying it flat before bonding.

The substrate surfaces were analysed prior to bonding and after failure of the joint by either one or several of the following techniques: ESCA (Electron Spectroscopy for Chemical Analysis), AES (Auger Electron Spectroscopy), SEM (Scanning Electron Microscopy) and EDX (Energy Dispersive Analysis of X-rays).

III RESULTS AND DISCUSSION

The shear strengths are listed in Table I. The adhesive A2840 results in higher shear strengths compared to A2241 for all three

TABLE I
Renault lap shear test results

Metal	Regreased	Adhesive	Shear strength (MPa)	Failure mode
A527	N	A2241	9 ± 2	A
A527	Y	A2241	5 ± 2	A
A527	N	A2840	12 ± 1	A
A527	Y	A2840	12 ± 1	A
GH	N	A2241	7 ± 1	FM
GH	Y	A2241	8 ± 1	FM
GH	N	A2840	11 ± 1	FM
GH	Y	A2840	8 ± 1	FM
MS	N	A2241	9 ± 2	C
MS	Y	A2241	8 ± 2	C
MS	N	A2840	11 ± 1	C
MS	Y	A2840	11 ± 1	C

A: Adhesive failure; C: Cohesive failure; FM: Failure in the metal.

steel adherends. Regreased adherends had similar strengths to the degreased samples in all but one case. This indicates that both adhesives are able to displace or absorb the oil from the regreased surface. The mechanism of oil displacement was not investigated in the present work. Adhesive was visible on both fracture surfaces following lap shear tests of the bonded MS adherend samples.

Although visual inspection and SEM/EDX analysis can be useful in the examination of fracture surfaces following lap shear tests, only surface analytical techniques such as ESCA and AES result in a definitive assignment of the locus of failure.

The results of ESCA analysis of the degreased samples are shown in Table II. Zinc is detected on each galvanized surface. Some of the oxygen is due to the oxidation of zinc. Large amounts of carbon contamination are noted.

ESCA has also been used to analyse the fracture surfaces after lap shear tests of the regreased A527 and GH adherend bonded with A2840. The results are listed in Table II. The side with the apparent adhesive layer is termed the "adhesive fracture side" (AFS), the opposite one is the "metal fracture side" (MFS). For A527, the metal fracture side gave an atomic concentration identical to the degreased surface taking the zinc and chromium concentrations together. This shows that this surface is free of any traces of adhesive and thus the failure occurred because the weak boundary

TABLE II
ESCA elemental atomic percentages

				Fracture surface			
	Adherend			A2840/A527		A2840/GH	
Element	MS	GH	A527	AFS	MFS	AFS	MFS
C	48.0	75.0	47.0	67.0	48.0	28.0	24.0
O	35.0	19.0	40.0	22.0	42.0	48.0	47.0
Zn	17.0	6.0	7.0	tr†	13.0	24.0	29.0
Cr			6.0				
Fe		tr†					
Na		tr					
N				2.0			
F				1.0			
Al				3.0			
Si				4.0			

† tr – trace.

layer was located between the substrate and the adhesive. The presence of nitrogen and silicon on the adhesive side is due to the adhesive which was shown to contain these elements. The source of inorganic fluorine and aluminum is not known.

The ESCA analysis of both the adhesive fracture and metal fracture sides of the GH samples is shown in Table II. The results

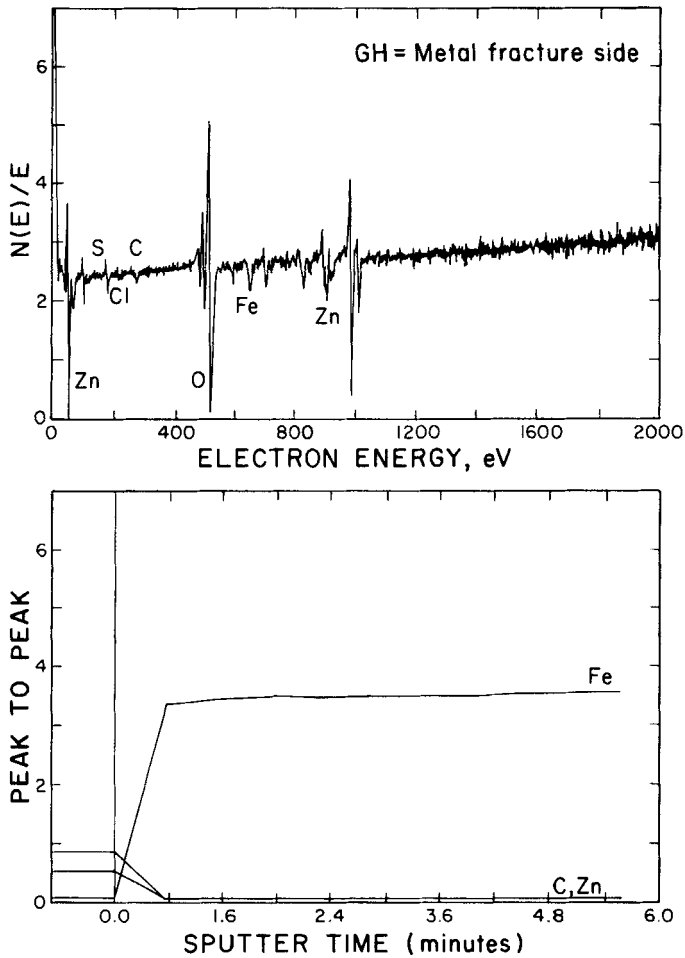

FIGURE 2 AES survey spectrum and depth profile of fracture surface (metal side) of GH steel bonded with A2840 after aging and following lap shear test.

for both surfaces are similar and indicate that the surfaces are coated with carbon which comes from contamination and with oxygen and zinc. The absence of nitrogen and silicon demonstrates convincingly that neither surface contains the A2840 adhesive. It is concluded based on the ESCA results that failure occurred within the galvanized layer. Supporting evidence for the locus of failure was obtained by EDX and Auger analyses.

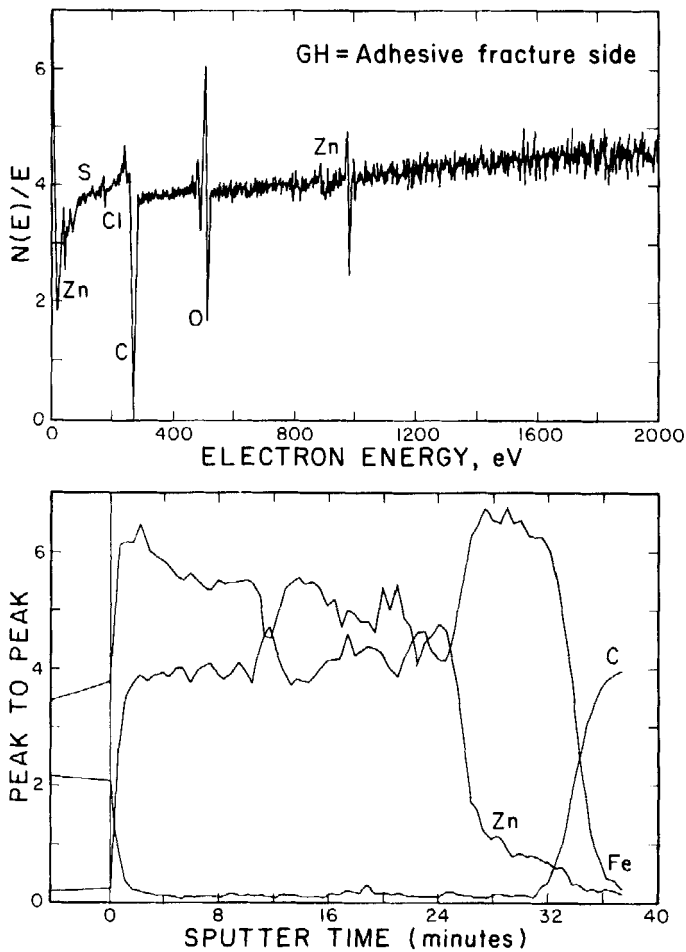

FIGURE 3 AES survey spectrum and depth profile of fracture surface (adhesive side) of GH steel bonded with A2840 after aging and following lap shear test.

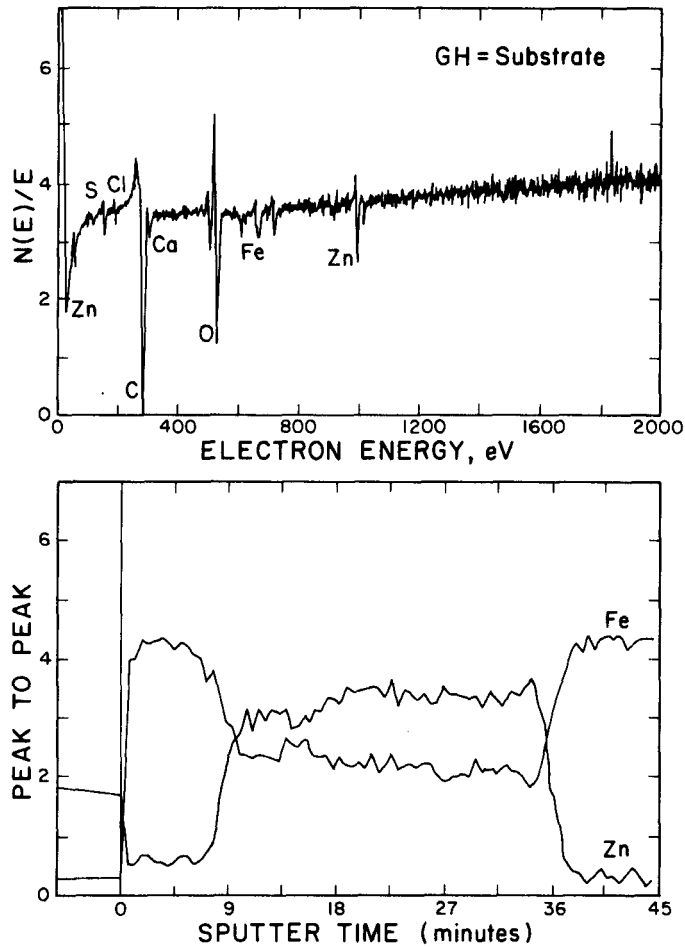

FIGURE 4 AES survey spectrum and depth profile of GH steel prior to bonding.

EDX analysis showed that the adhesive side was a mixture of zinc and iron but only iron was detected on the metal side. An Auger survey spectrum showed the presence of iron which was not detected by ESCA. In order to determine what metallic layer is left on the adhesive, a series of Auger depth profiles were done. The results are shown in Figures 2–4. The profile on the metal side (see Figure 2) shows that the zinc oxide layer disappears after a few

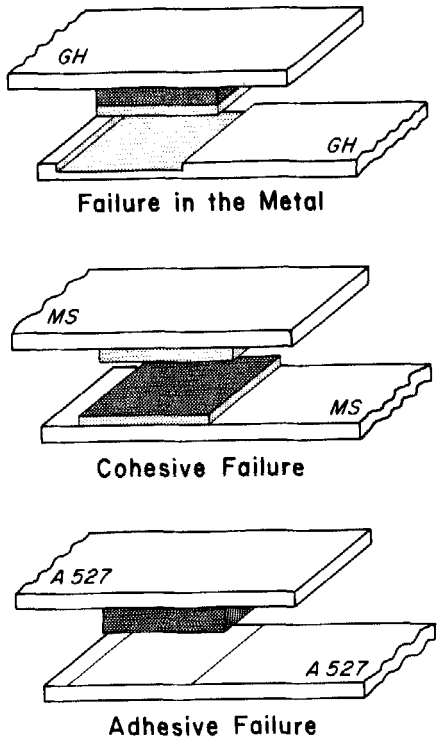

FIGURE 5 Schematic diagram of different fracture modes.

seconds of sputtering followed by an increase in iron characteristic of the bulk of the sample. A profile done on the adhesive side (see Figure 3) indicates that the metallic layer is actually formed of two zinc-iron alloys: a zinc-rich layer which was in contact with the bulk (metal side), and a thinner iron-rich layer on which the adhesive is applied. This pattern is confirmed by a profile done on a degreased substrate (see Figure 4). This means that the weak boundary layer is the interface between the steel substrate and the galvanized coating. A schematic diagram summarizing the different failure modes for the three galvanized steel adherends is shown in Figure 5.

IV SUMMARY

The adhesive A2840 gave consistently higher shear strengths by the Renault lap test on MS, GH and A527 steels compared to A2241. Further, the same shear strengths were obtained for either degreased or regreased samples in all but one case. ESCA was used to obtain the atomic composition of the steel surfaces before and after failure. Comparison of the ESCA spectra of both the adhesive and metal fracture surfaces was made to determine the locus of failure. In the case of A527 steel, the failure was interfacial occurring between the adhesive and the steel surface. However, in the case of GH steel, failure occurred within the galvanized layer. Supporting evidence for this conclusion was based on EDX analysis and AES depth profiles of both the adhesive fracture and metal fracture sides as compared to the substrate. The surface analysis techniques proved to be very useful tools to locate the locus of failure in epoxy bonded galvanized steels.

V. Acknowledgement

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