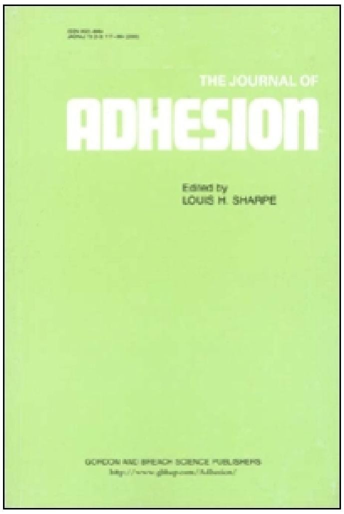

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Hsu, N. N. C. , Noland, J. S. , Brinen, J. S. and Graham, S. W.(1986) 'Some Effects of Heat Processing on Adhesively Bonded Automotive Steel', The Journal of Adhesion, 19: 3, 241 — 256
To link to this Article: DOI: 10.1080/00218468608071226
URL: http://dx.doi.org/10.1080/00218468608071226

J. Adhesion, 1986, Vol. 19, pp. 241–256
0021-8464/86/1904-0241 $18.50/0

Printed in the United Kingdom

Some Effects of Heat Processing on Adhesively Bonded Automotive Steel†

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(*Received February* 12, 1985; *in final form September* 30, 1985)

During a program to develop new structural adhesives that would meet the processing requirements of the current automotive "high heat" bake cycles, substantial differences in performance were noted between the "standard" cold rolled steel (CRS) of SAE1008 and certain Drawing Quality steels (DQSK).

In parallel tests, certain DQSK test specimens (bonded with 200°C heat cycle) failed consistently in the interfacial region, while the CRS samples failed center of bond.

The surface characteristics of the steels and failed adhesive specimens were examined with ESCA, AUGER, and ISS spectroscopic methods. The metal failure surfaces of the DQSK samples were shown to contain relatively high levels of silicon and oxygen, and smaller amounts of boron, with a lower concentration of iron, as compared to CRS which shows iron surface with minor contaminations.

In subsequent testing, with other samples of DQSK SAE1008, this effect was not observed. These samples did not exhibit the same levels of contamination. It is suggested that certain DQSK processes may involve processing steps that are detrimental to the surface properties of the rolled sheet stock.

KEY WORDS Adhesive bonding; Durability; Environmental exposure; Heat Processing; Oily automotive steel; Surface impurities

INTRODUCTION

Cold rolled steel sheets (CRS) and drawing quality special killed (DQSK) cold rolled steel are called out for automotive assembly

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† Presented at the Seventh Annual Meeting of The Adhesion Society, Jacksonville, FL, U.S.A., February 13–15, 1984.

depending upon the amount of forming required of the sheet stock. Since adhesives used in automotive manufacture find applications in hem flange areas, *i.e.*, frequently bonding highly drawn parts to flatter stock, both sheets are important substrates.

Our laboratory development work toward one-part structural adhesives for the automotive hem flange application required that the adhesive be evaluated on oily steel with the cure conditions provided within the boundaries of the bake cycle used to cure the electrocoated primer. Significant differences were observed in substrate behavior between cold rolled steel (CRS SAE1008) and drawing quality special killed steel (DQSK SAE1008). Certain mechanical testing differences can be attributed to the relatively lower yield strength characteristics of DQSK (see Figure 1). In a lap shear test, the substrate deformation places additional stress on the bond line, but the major differences were in failure mode. CRS samples failed center of bond, while the DQSK specimens usually failed interfacially, particularly after environmental exposure. During the same time interval, other DQSK SAE1008 substrates from different sources did not exhibit the same degree of problem, but the whole test history of this product development was complicated by sporadic interfacial failure to the DQSK substrate.

Because of the criticality of the product performance on this substrate, an investigation of the surface of the steels in question was carried out with ESCA, Auger and Ion Scattering spectroscopic techniques.[1-3]

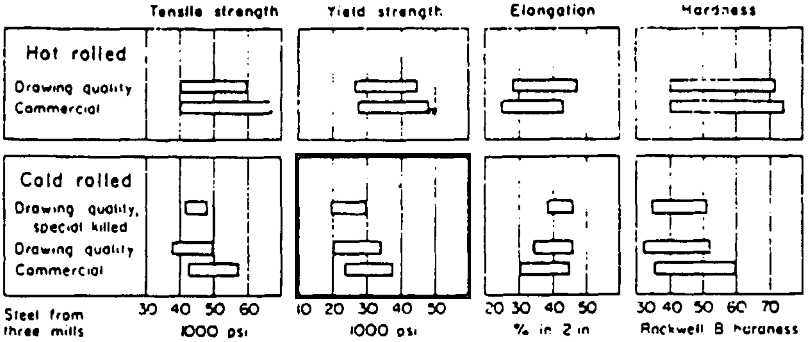


FIGURE 1 Typical range of mechanical properties of low carbon steels furnished by three mills. (Metals Handbook, 8th. Ed., Am. Socy. of Metals).

The investigation showed that the surface characteristics of the DQSK samples which failed interfacially were markedly different from those of CRS and of the DQSK samples which performed satisfactorily. Major differences were the presence of relatively larger quantities of silicon and the detection of boron on the problem DQSK samples.

It is believed that this surface contamination results from certain DQSK processing steps.

EXPERIMENTAL

Lap shear strength:

1" × 4" × 0.06" (2.5 cm × 10.2 cm × 0.15 cm) standard SAE1008 and DQSK SAE1008 cold rolled steel coupons were used. Surface preparations were either MEK-wiped and coated with 8 ml/m^2 of Texaco Almag 1564 oil; or freshly grit-blasted with 80 mesh aluminium oxide grit. Glue line thickness was controlled with 0.1 mm wire. Test specimens were assembled with 12.7 mm overlap and held together with masking tape and Mueller Pee Wee clips.

Specimens were subjected to a "phosphate" resistance test by successive immersions in Parker 348 cleaner, Parker Bonderite EP-1, and a deionized water rinse per General Motors Test Method 45–127,[4] and subsequently oven cured either for a normal cure cycle of one hour at 177°C, or alternatively by a "high heat cycle," *i.e.* one hour at 200°C plus one hour at 177°C.

Tensile shear tests were conducted at room temperature in accord with ASTM D1002. For environmental exposure, the bonded specimens were soaked in 54°C deionized water for 7 days.

The adhesive formulations represented toughened, one-part epoxy systems formulated for bonding oily steel substrates.

SPECTROSCOPIC SURFACE ANALYSIS:

Standard SAE1008 and DQSK SAE1008 cold rolled steel coupons were washed with reagent grade methyl ethyl ketone and allowed to air dry in order to reduce surface oil.

The ESCA data were acquired on a Hewlett-Packard 5950A ESCA spectrometer. This system utilizes monochromatic Al Kα x-ray excitation (1486.6 eV). Samples were mounted in the system covered by a mounting mask. The system routinely runs at a pressure of approximately 1×10^{-8} torr. ESCA survey scans from 0 to 1000 eV and scans from 80 to 280 eV were collected.

The Auger and Ion Scattering data were acquired with a Physical Electronics Model 560 ESCA/SAM instrument equipped with an angle resolved (AR) drum which makes ion scattering possible. The computer is a PDP 1104. The electron gun has a minimum beam size of 2 microns. The system typically runs at a pressure of 1×10^{-9} torr. The steel coupons were mounted on the sample holder such that the electron beam coaxial with the cylindrical mirror analyzer impinges on the sample at an angle 50 degrees from the plane of the surface. The Auger spectra were collected using an area averaged mode. In this mode the electron beam is scanned across the surface at TV rates to obtain an area averaged spectrum. The Auger electronics are stepped through the selected energy range (0–2000 eV) and the total electron counts per energy step are stored in memory. It is possible to signal average the spectra in order to get the desired signal-to-noise level. Auger spectra were acquired in the E'N(E) mode where the transmission function is proportional to E + 1/2 and energy resolution is at 0.6%.

Ion scattering spectroscopy (ISS) used a differentially pumped ion gun and operated at approximately 6×10^{-8} torr. In this study all of the ISS spectra were collected using ^{3}He as the ion source gas, 2.0 KeV ion beam, the 90 degree slot in the AR drum and a scattering angle of 144 degrees. The sputter rate was approximately 1 angstrom per minute.

RESULTS AND DISCUSSION

The degree of the interfacial failure problem presented by a bad lot of DQSK, evaluated with two different one-part, epoxy, high elongation structural adhesives, is illustrated in Table I. While these adhesives on CRS typically exhibit 32–35% strength drop on water soak, the DQSK samples give lower numbers, and a larger proportional drop in wet strength, exhibiting frequent interfacial

TABLE I
Lap shear strengths of automotive steel specimens

SAE 1008 substrate	Surface treatment	Adhesive formulation	Lap shear strength, MPa (PSI) Initial	Lap shear strength, MPa (PSI) After water soak
	MEK-wiped			
CRS/CRS	OIL-coated	A	35.0 (5083) C	22.0 (3200) C
DQSK/DQSK	,,	A	30.2 (4380) C	19.8 (2875) C/S
CRS/CRS	,,	B	29.5 (4280) C	20.0 (2900) C
DQSK/DQSK	,,	B	28.7 (4170) C	16.3 (2367) C/S

Lap specimen = 2.5 CM × 10.2 CM × 0.15 CM: 1.3 CM overlap.
Lap test = ASTM D 1002.
Cure cycle = 1 hour at 177°C.
C = Cohesive failure, S = Substrate surface failure, C/S = Mixed failure.

failure. The surface deterioration was exaggerated by a high heat cycle, as illustrated in Table II. This test cycle, implemented to screen for the effect of accidental over-bake in the automotive process paint ovens, showed a 64% strength drop on the lot of DQSK. When the same substrates were grit blasted prior to bonding, the problem surface was removed, and strength retention was excellent.

Obviously the problem batch of DQSK steel had surface contamination which interfered both with moisture and thermal durability of bonded samples.

TABLE II
Lap shear strengths of automotive steel specimens

SEA 1008 substrate	Surface treatment	Lap shear strength, MPa (PSI) Initial	Lap shear strength, MPa (PSI) After water soak
	MEK-wiped		
CRS/CRS	Oil-coated	35.8 (5200) C	18.9 (2750) C
DQSK/DQSK	,,	30.3 (4400) C/S	11.0 (1600) S
CRS/CRS	Grit-blasted	35.1 (5100) C	22.9 (3325) C
DQSK/DQSK	,,	32.4 (4700) C	25.3 (3675) C

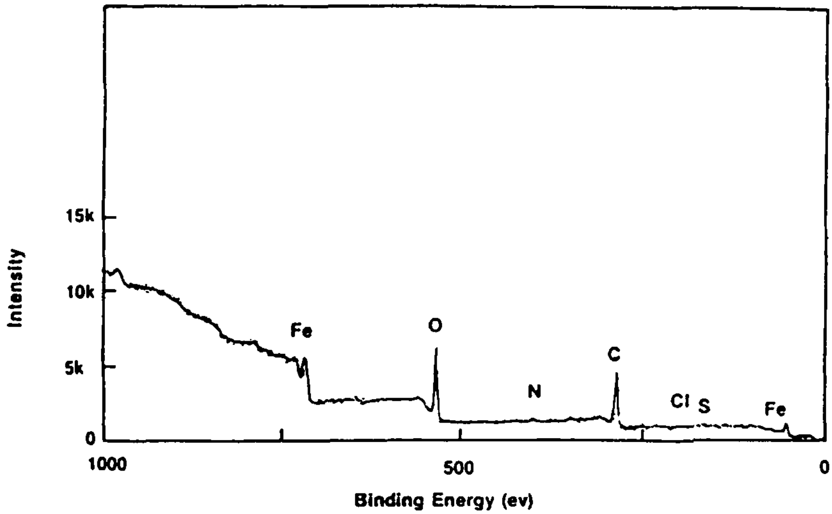
Adhesive = Formulation A.
Lap specimen = 2.5 CM × 10.2 CM .15 CM; 1.3 CM overlap.
Lap test = 1 hour at 200°C + 1 hour at 177°C.
C = Cohesive failure, S = Interfacial failure at substrate.

Examination of these substrates by various electron ion and X-ray spectroscopic techniques showed substantial differences in the two surfaces.

Figure 2 shows the survey scan ESCA spectra of these samples of CRS and DQSK. Both spectra show similar intensities of the major components including Fe, O, N, and C. In addition, the CRS showed the presence of Ca, Na, and Cl. Sulfur is expected to be reduced on the DQSK because one major purpose of the processing which yields DQSK is the reduction of S in the product. ESCA spectra from long scans of the low binding energy (80–280 eV) regions for both CRS and DQSK are shown in Figure 3. In this region the CRS shows the presence of S, Cl, Si, and Pb. The DQSK shows reduced S, plus Cl, Si, Pb, and B. In particular, boron is the most intense peak in the low binding energy region of the DQSK while the CRS shows no boron. The Si peak is weak for both specimens. The presence of B (and Si) on the surface of DQSK was suspect as a cause for the bondability problem. These surface impurities probably are introduced during the Al killing phenomenon. This was further investigated by Auger electron spectroscopy (AES) and ion scattering spectroscopy (ISS).

Typical ESCA spectra are collected using photoelectrons generated from an average of 25 to 50 angstroms depth of the material studied. AES probes only to a depth of 10 to 15 angstroms, so differences in the surface layers of the steels should be more pronounced in AES analysis than they were in studies done by ESCA. Both steels were examined by AES both before and after sputtering approximately 5 to 7 angstroms into the steel surface. The AES spectra are presented in Figure 4.

Unfortunately, it is very difficult to distinguish between boron and chlorine in the AES spectra so the results are reported as B/Cl. The major differences between the CRS before and after sputtering are the decrease of B/Cl, Ca, Na, and Si intensity on the CRS surface during the sputtering process. Using available software it is possible to convert the peak-to-peak heights of the AES spectra into relative atomic concentrations. Table III shows that the C, Si, Ca, and Na concentrations do decrease with sputtering while the O and Fe concentrations increases. However, the changes with sputtering for the CRS are minor.



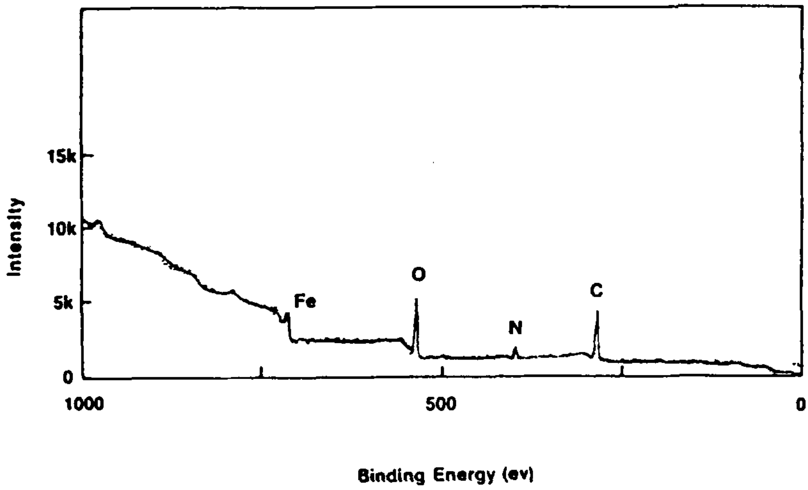


FIGURE 2 ESCA survey scans (0–1000 eV) of CRS (a) and DQSK (b). Spectra were collected using an HP-5950A spectrometer with monochromatized AlKα = 1486.6 eV excitation.

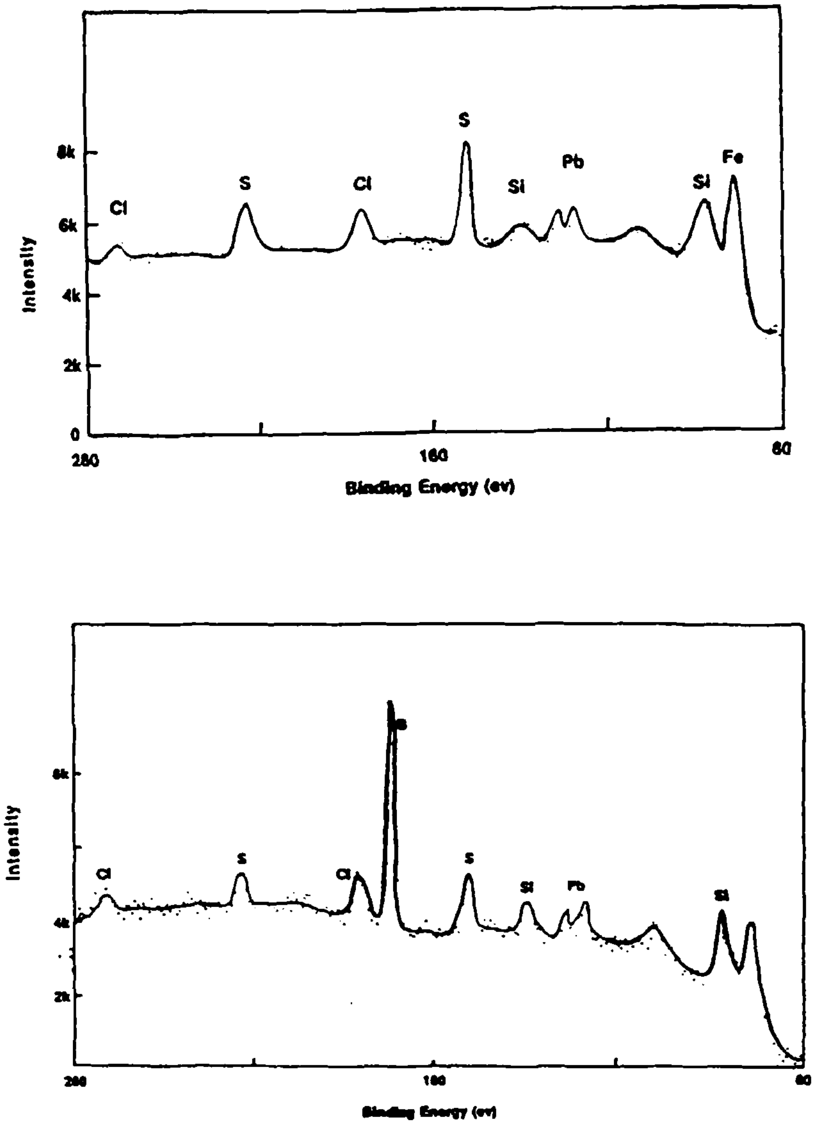


FIGURE 3 ESCA low binding energy region scans (80–280 eV) of CRS (top) and DQSK (bottom). Spectra were collected using an HP-5950A spectrometer with monochromatized AlKα = 1486.6 eV excitation.

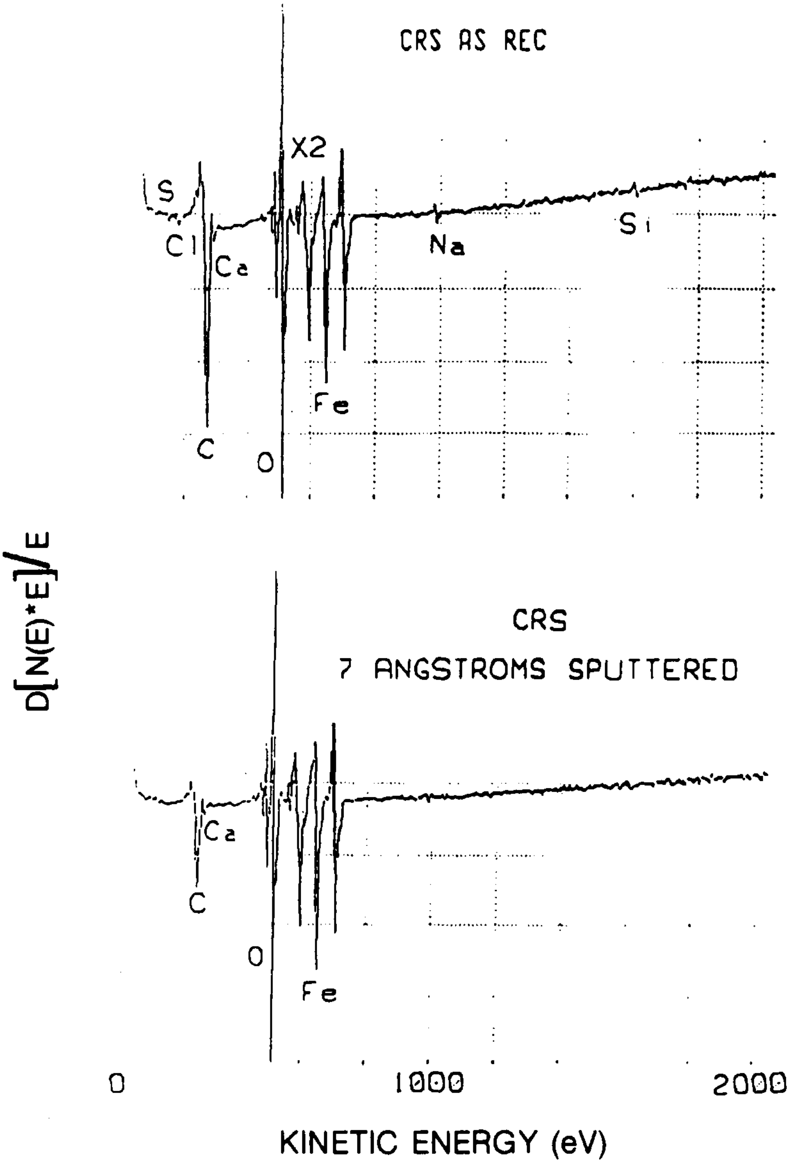


FIGURE 4 AES spectra of CRS both before (top) and after (bottom) sputtering 7 minutes (sputter rate 1–2 angstroms per minute).

TABLE III
Results from the AES studies of CRS and DQSK samples (Results are in atomic percents)

Cold rolled steel (CRS)	C	O	Fe	Si	B/Cl†	N	Ca	Na
Before sputtering	26	47	17	4	1		4	1
After sputtering†	21	53	20	3	<1		2	<1
Drawing quality special Killed steel (*DSQK*)								
Before sputtering	26	26	6	36	2	3		<1
After sputtering‡	23	34	11	24	5	3		<1

† B and Cl are very difficult to separates by AES.
‡ Samples were sputtered 7 minutes at a sputter rate of 1 angstrom per minute.

Figure 5 shows the AES spectra of DQSK before and after sputtering approximately 5 to 7 angstroms from the steel surface. The obvious differences between these spectra include a decrease in the Na and Si intensities with sputtering. From the atomic concentrations presented in Table III, it is obvious that Si concentration decreases dramatically on the DQSK surface with a small amount of sputtering while the Fe and B/Cl concentrations increase significantly. Comparing the CRS with the DQSK, one sees dramatic differences between the two steels which are not eliminated by the sputtering. For example, the B/Cl intensity is much greater on the DQSK than on the CRS and it increases with sputtering on the DQSK but decreases with sputtering on the CRS. These results might be explained if the B/Cl peak were a surface contamination on the CRS which is removed with sputtering, while that peak is primarily due to B on the DQSK, which was incorporated into the steel during processing and is present to a greater depth. Another difference between the steels is the presence of far more Si and less Fe on the DQSK surface than on the CRS surface both before and after sputtering in the AES spectra. The Si is likely to be one of the major reasons for the poor adhesive bonding exhibited by the DQSK. However, because AES averages over a depth of 10 to 15 angstroms it is impossible using only AES to determine how different the topmost layers of the steels are.

Ion scattering spectrometry (ISS) is the most surface sensitive of the tools available to the surface analyst. In fact, ISS looks at the top most atomic layer of a solid surface. Figure 6 shows the CRS

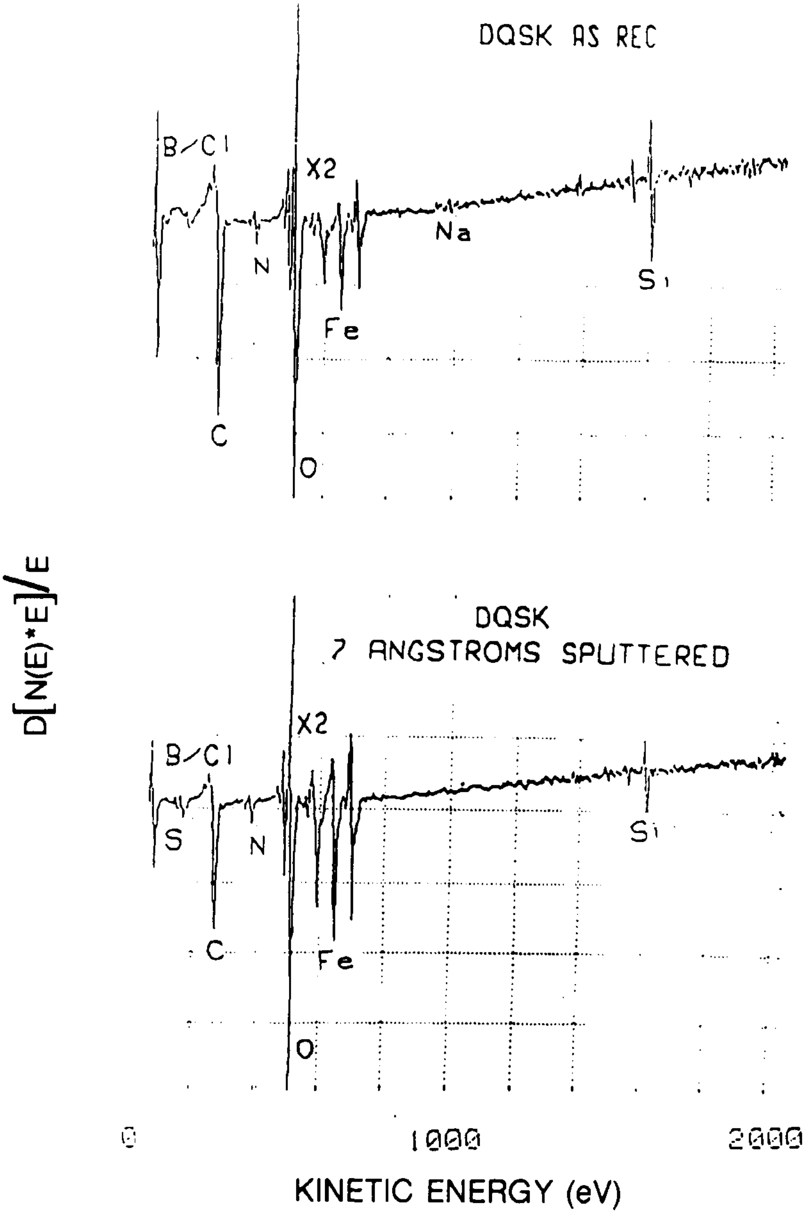


FIGURE 5 AES spectra of DQSK both before (top) and after (bottom) sputtering 7 minutes (sputter rate 1–2 angstroms per minute).

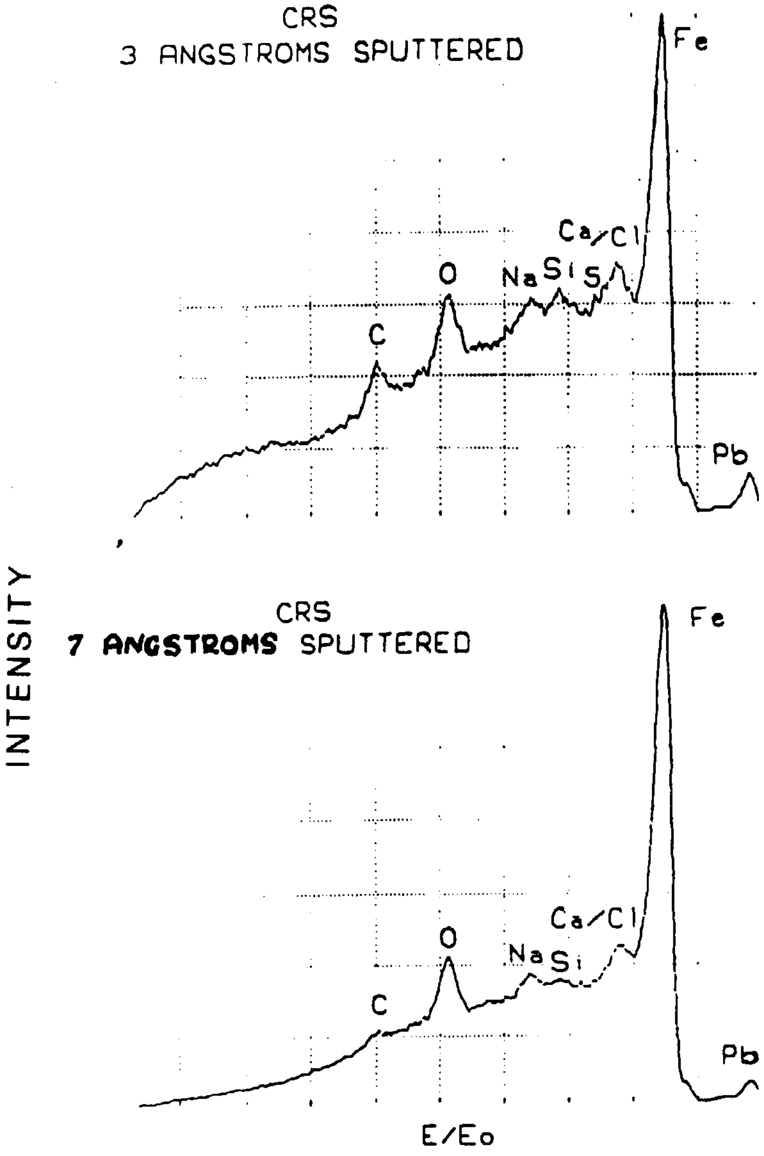


FIGURE 6 ISS spectra of CRS after 3 (top) and 7 (bottom) minutes of sputtering at a sputter rate of 1–2 angstroms per minute.

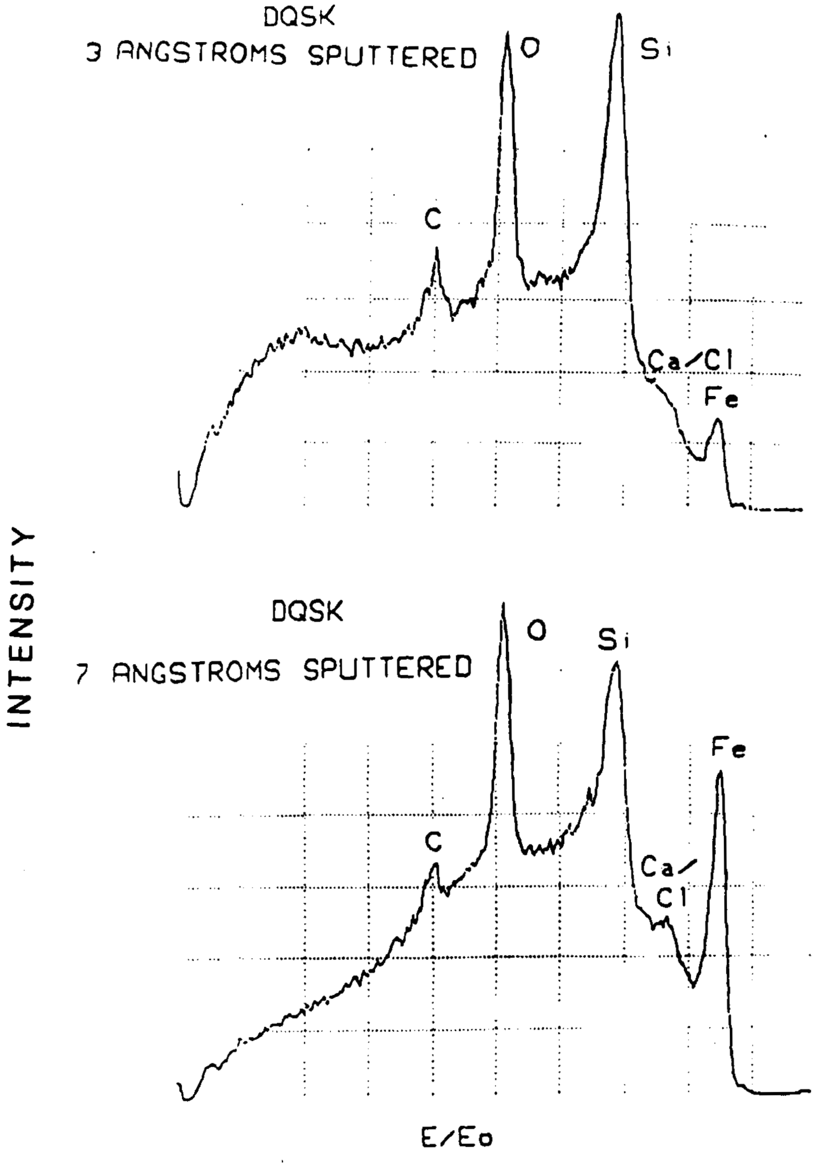


FIGURE 7 ISS spectra of DQSK after 3 (top) and 7 (bottom) minutes of sputtering at a sputter rate of 1–2 angstroms per minute.

after 3 and 6 minutes of sputtering at a sputter rate of 1 angstrom per minute. There are no major differences between the spectra. In both spectra the Fe peak is the most intense and there is also C, O, Na, Si, Ca/Cl, S and Pb have all decreased in intensity relative to Fe peak.

The ISS spectra of the DQSK after 3 and 7 minutes of sputtering are presented in Figure 7. The most intense peaks in the spectra are Si and O with Fe, C, and Ca/Cl also present. The difference in the ISS spectra between 3 and 7 minutes of sputtering is the dramatic increase in the Fe intensity as sputtering time increases. The Si layer present on the DQSK surface is decreased rapidly during the 4 minutes of sputtering but the Si is clearly present in the bonding surface.

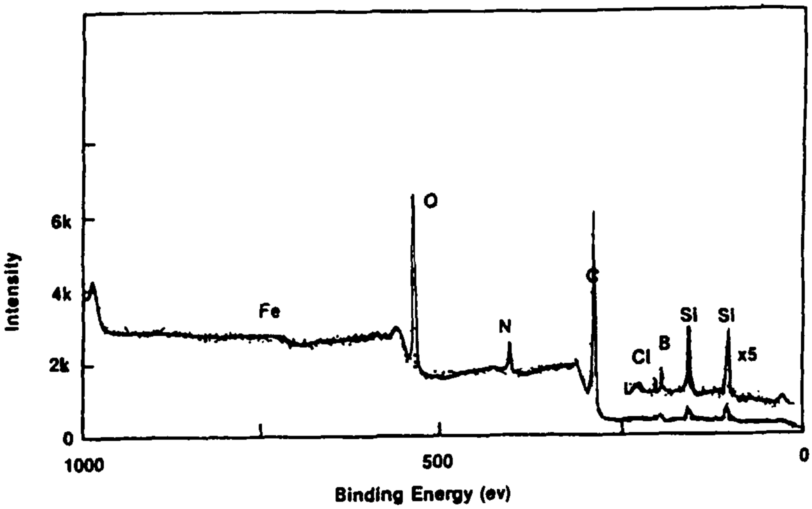
Evidence that these DQSK surfaces are the failure surfaces is presented in Figure 8. ESCA spectra of both the failure surfaces after humidity tests can be compared with the DQK spectra presented in Figures 2 and 3. The adhesive (organic) failure surface shows Si, B, C, N, O, and weak Cl and Fe peaks. The metal failure surface exhibits the same elements, with the signals weaker relative to Fe. These data confirm that the bond failure occurs within the "oxide" layer.

The interfacial strength degradation which was demonstrated in the 200°C heat aging is not accompanied by large changes in the ESCA spectra, but in general the relative intensity of the oxygen peaks increased, both with heat and subsequent humidity exposures.

In subsequent work, other lots of DQSK were found which would fail "center of bond" after the equivalent exposure conditions. Those surfaces were markedly different by ESCA analysis, due to the absence of B and smaller amounts of Si.

CONCLUSIONS

The control of substrates is a problem as old as adhesives. In the automotive field, we are accustomed to bonding "as is, oily steels". In the case of cold rolled steel, the procedure has been quite effective. From our experience, the DQSK steels are considerably more complicated. Based upon these surface analyses, the problems



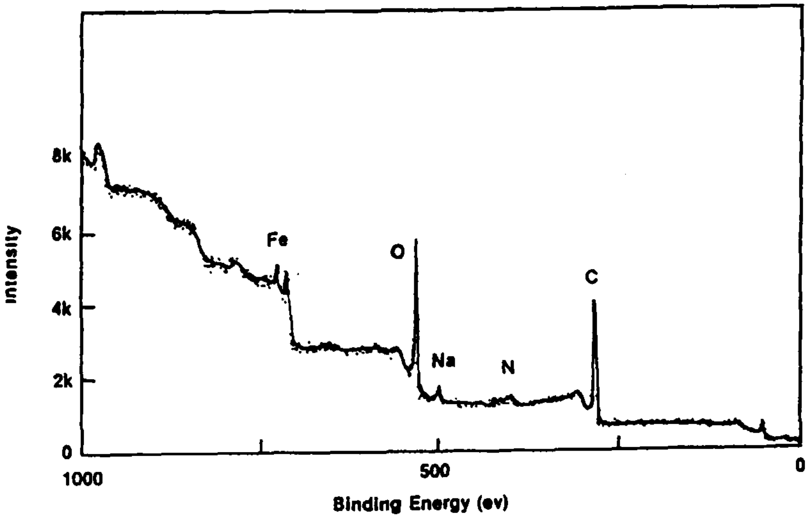


FIGURE 8 ESCA survey scan of the failed adhesive surface (top) and corresponding metal surface (bottom).

of moisture and thermal durability are caused by surface contamination of the DQSK steel with some boron and silicon compounds which could be removed by grit blasting.

From discussions with one of the major automotive steel producers, it is known that the steel manufacturers are aware of the necessity of controlling surface impurities on automotive sheet steel, due to previous problems in automotive finishing. Unfortunately, the small purchaser of steel stock for adhesive substrates must generally purchase from a distributor. Based on this experience, the DQSK SA1008 specification is not sufficient to obtain a reliable supply of material for durable adhesive bonding. In fact, the particular sheets which we examined might not represent aluminium killed cold rolled steel (the "standard" for DQSK in the U.S.), but could represent an imported silicon killed material.

Adhesive bonding of steel represents an important improvement in automotive manufacture. Because of the criticality of substrates to the total adhesive performance, it is important to recognize that characterization and evaluation of each substrate type is critical to satisfactory utilization of structural adhesives.

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