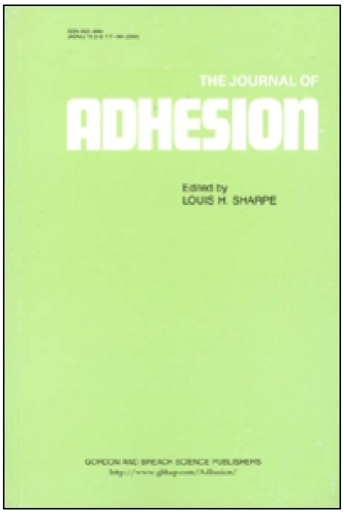

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Adhesive Bonding of Oil-Contaminated Steel Substrates

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Durability of adhesive bonds formed by curing epoxies against oil-contaminated steel substrates using amidoamine curing agents was determined during exposure to boiling water. The most durable bonds were obtained using amidoamine curing agents with relatively low amine numbers and by blending silane coupling agents such as γ-glycidoxypropyltrimethoxysilane (γ-GPS) and N-(2-aminoethyl)-3-aminopropyltrimethoxy silane (AAMS) into the adhesives. When X-ray photoelectron spectroscopy (XPS) was used to characterize the failure surfaces of the adhesive joints after exposure to boiling water, it was determined that adhesives prepared using amidoamine curing agents with low amine numbers were able to displace the oil from the steel surface but adhesives prepared with amidoamine curing agents with high amine numbers were not. Results obtained from XPS also showed that the amino groups on the substrate fracture surfaces of joints prepared using curing agents with low amine numbers were protonated whereas the amino groups in the bulk adhesive were not, indicating that there was a chemical interaction between the curing agent and the hydrated surface of the substrate. It was also shown using infrared spectroscopy that the amidoamine curing agents formed salts with calcium compounds in the oil.

KEY WORDS Epoxy/amidoamine adhesives; oil contamination; cold rolled steel; silanes; X-ray photoelectron spectroscopy; infrared spectroscopy.

I. INTRODUCTION

Most applications of adhesive bonding to metal substrates require considerable pretreatment of the metals. The objective of the pretreatment is to remove organic contaminants and to provide an oxide that adheres strongly to the base metal, is resistant to moisture, and porous enough to permit mechanical interlocking with the adhesive. Thus, for example, aluminum substrates are frequently anodized in phosphoric acid prior to bonding. However, there are many instances where it is not practical or feasible to pretreat metals extensively prior to bonding. Examples are found in field repair of bonded structures or in manufacturing operations involving metals that have been treated with oils normally used in drawing, stamping and milling operations.

In order to form a strong adhesive bond with an oil-contaminated metal surface, the adhesive must absorb or displace the oil from the metal surface. Debski *et al.* have shown that it is thermodynamically possible for a model epoxy resin based on bisphenol-A to displace a standard apolar mineral oil from the metal surface.[1] They have also shown that the epoxy resin cured with 6% dicyandiamide could absorb the oil from the metal surface and that the oil plasticized the adhesive and inhibited its crosslinking.

Bowen and Volkmann tested the performance of epoxy adhesives cured against oil-coated, cold rolled steel. They found that epoxy systems cured with amidoamine curing agents were superior in tensile shear strength to those cured with aliphatic amine curing agents.[2] They suggested that epoxies cured with amidoamine curing agents had greater affinity for the oily metal surface than those cured with simple amines due to the oleophilic character of the aliphatic fatty acids moieties found in amidoamine curing agents.

Rosty *et al.* conducted a series of studies on adhesive bonding of cold rolled steel coated with oils. [3–5] The adhesives tested were Cybond 4533, Conastic 830, Versilok 200, 202, and 204, Depend, Epibond 1210, and Dymax 845. It was found that joints prepared using Cybond 4533 and Conastic 830 exhibited the best durability when unstressed test specimens were exposed to an atmosphere of 60°C and 100% relative humidity and those prepared using Cybond 4533 showed the greatest durability under stress.[3] Rosty *et al.* reported that the viscosity of the oil affected the lap shear strength of the joints. The higher the viscosity of the oil, the lower the lap shear strength.[4]

Rosty also used lap shear tests to determine the effects of fillers and curing temperature on the performance of an adhesive system consisting of a DGEBA-type epoxy cured with an amidoamine having a relatively high amine number. Greater lap shear strengths and oil absorption were observed for samples cured at higher temperatures because of increased assimilation of the oil by the adhesive and a greter extent of curing at higher curing temperatures.[5] The addition of fillers improved the bond strength of the epoxy system on the oily steel surface.[5] Neither Rosty nor Bowen and Volkmann investigated the possible chemical reactions occuring between adhesives and oils and how they affected the strength and long-term durability of adhesive joints.

Commercon and Wightman used surface analysis techniques such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) to analyze the fracture surfaces of joints prepared by bonding oil-coated galvanized steel with commercial epoxy adhesives and exposed to 100% relative humidity at 70°C for 7 days.[6] They found that the locus of failure for galvanized cold rolled steel was interfacial between the adhesive and the steel surface and that for zinc electroplated steel was within the galvanized layer.

Maeda *et al.* used XPS and glow discharge spectroscopy to study the bond durabilities of several commercial adhesives on galvanized steel sheets coated with a mill oil.[7] They found that the surface segregation of Al and Pb on the galvanized steel was enhanced by grain boundary diffusion during thermal cure of the adhesive and subsequent immersion in hot water. This process caused the formation of a weak boundary layer resulting in bond strength deterioration. Durability of the bonds was markedly improved by reducing the Al and Pb segregation through the use of Pb-free galvanizing baths or by spraying pure zinc powder onto the steel surface during post-galvanization.

Natale investigated the performance of several epoxy adhesives on lubricated galvanized sheet steels using tensile-shear joints.[8] It was found that the ambient and environmental durability performance of the joints was strongly dependent on the adhesive/adherend/lubricant combination. Similar conclusions were reached by Arnold from an investigation of the bond strength and durability of lap shear joints prepared using a modified one-part epoxy adhesive and sheet steels which were contaminated by mill oils. He found that the joint strength and durability were dependent on the adhesive and the type of steel used.[9]

Organofunctional silanes are usually used as adhesion promoters for organic resins, particularly when good durability in humid environments is required. Theories proposed to explain the mechanisms by which the silane coupling agents function are numerous and support for the presence of chemical bonding in the silane/substrate interface is well known.[10,11] Silanes can be applied to substrates such as glasses or oxidized metals as primers from aqueous solutions or used as additives to the adhesives to improve the initial strength and durability of adhesive bonds. When silane coupling agents are incorporated into adhesive formulations, hydrolysis of the silane is then limited to the surface hydroxyl groups unless aqueous impurities exist in the organic medium.[12]

Plueddemann has evaluated the durability of adhesive bonds by measuring the time required for adhesive films cured against glass slides to delaminate during exposure to boiling water or water at 70°C. Performance of silanes as coupling agents was evaluated by adding silanes directly to the adhesives or by pretreating the glass slides with dilute aqueous solutions of the silanes. Results showed that the performance of individual silane primers or additives for epoxies differed markedly depending on the epoxy formulation.[13] A Japanese patent showed that the addition of epoxide-terminated polydimethylsiloxane to epoxy/dicyandiamide adhesives cured against steel surfaces coated with silicone release agents provided very good bond strength.[14] A German patent showed that joints prepared by curing an epoxy/dipropylenetriamine adhesive against substrates contaminated with hydraulic fluid had good strength and durability during exposure to hydraulic fluid at elevated temperatures when an aminosilane was added to the adhesive.[15]

The purpose of this paper is to present preliminary results concerning the formulation and analysis of room temperature cured epoxy adhesives for oil-contaminated steel substrates. It is shown that epoxy/amidoamine adhesives, modified with an epoxy-functional silane, provide strong, durable bonds to oil-contaminated steel substrates as long as the amine number of the curing agent is relatively low.

II. EXPERIMENTAL

The adhesive system used in this study was Epon 828 (Shell Chemical Co.) cured with the amidoamines V-15, V-25, and V-40 (Shell Chemical Co.) having amine numbers 230–246, 330–360, and 370–400, respectively. The substrate was 1020 cold rolled steel (CRS) purchased locally. Two silane coupling agents, N-(2-aminoethyl)-3-amino-propyltrimethoxy silane (AAMS) and γ-glycidoxypropyltrimethoxysilane (γ-GPS), were obtained from Dow-Corning. The oil used to "contaminate" the coated steel surfaces was Ferrocote-61 (FC-61), a ship-out oil manufactured by Quaker Chemical Co.

All the steel substrates were cleaned in a solution of 30 g/l of Parker 338 cleaner at 60°C for 30 minutes and followed by ultrasonic cleaning in the same solution for 15 minutes. This procedure was repeated and then the steel substrates were rinsed in deionized water. Results obtained from XPS showed that this was a very effective process for removing the contaminants from the steel surface.[16]

Screening tests similar to those described by Plueddemann were conducted. 1020 CRS substrates were cut into small pieces 1.0 cm × 2.0 cm. After the substrates were cleaned by the methods described above, oil was wiped onto the surfaces. Then the epoxy adhesives were applied to the oily steel surfaces, cured at room temperature for 18 hours, and post cured at 50°C for 5 hours. The epoxy and curing agents were mixed stoichiometrically. Thus 120 parts per hundred (phr) V-15 was added to the epoxy. V-25 was added as 90 phr and V-40 was added as 75 phr. In some cases 2, 5, or 10 wt% AAMS or γ-GPS was added to the adhesives.

After curing, the samples were put in boiling water for testing. Periodically samples were removed from the water and examined to determine if any delamination had occurred. If no delamination occurred, the samples were returned to the water and the tests were continued. If delamination had occurred, the failure surfaces were examined by XPS.

Specimens similar to those used for the screening tests were immersed in liquid nitrogen, causing delamination to occur near the adhesive/oxide interface. The resulting fracture surfaces were then examined by XPS so as to determine the composition of the interphase in as-prepared specimens.

A Perkins–Elmer Model 5300 ESCA system was used to obtain the XPS spectra. Mg K_α X-rays were used to generate the spectra. Survey spectra were obtained using a pass energy of 44.75 eV and 0.5 eV/step. Multiplex spectra were obtained with a pass energy of 17.9 eV and 0.05 Ev/step.

Joints were prepared for measurement of lap shear strength as specified in ASTM standard D-1002. Steel coupons were cut into pieces 10.2 × 2.5 cm, cleaned, and oiled. Adhesive systems that had performed well in the screening tests were used to bond the adherends with a 1.3 cm overlap to form single lap shear joints. A 0.1 mm spacer was used to keep the bond-line thickness constant. After curing, residual adhesive was trimmed from the edges of the bondline using a razor blade. Some of the specimens were then tested to failure on an Instron using a strain rate of 1.3 mm/min. Other specimens were immersed in boiling water for a period of time and then tested. Five specimens were used for each measurement.

Transmission infrared spectroscopy was used to determine if any reaction occurred between the oil and individual components of the adhesives. Thus, the epoxy, curing agent, or silane was mixed with the oil at a ratio of 2:1 and applied to the surface of the KBr pellet so that the IR spectra could be obtained. Specimens were also prepared by spreading mixtures of the adhesives and 0, 20, 40, and 60 wt% oil on KBr pellets. After curing the adhesives as described above, these specimens were also examined by infrared spectroscopy. All infrared spectra were obtained using a Perkin–Elmer 1800 Fourier-transform infrared spectrophotometer at a resolution of 4 cm^{-1}.

III. RESULTS AND DISCUSSION

A Screening tests

The durability of bonds formed by curing Epon 828 on oily CRS substrates using stoichiometric amounts of V-40 and different amounts of γ-GPS is shown in Figure 1. With no silane added, the adhesive delaminated from the substrate after about 8 hours exposure to boiling water. As the amount of silane added to the adhesive was increased, the delamination time increased. With 10% silane, the delamination time was 14 hours.

When the performance of adhesives prepared using different curing agents was evaluated using the screening test, the results shown in Figure 2 were obtained. The durability of the epoxy/V-15 system was greatest while that of the epoxy/V-40 system was least. When a fixed amount of γ-GPS, 2%, was added to the adhesive systems, the durability increased (see Figure 2). The increases in delamination times were relatively small for the epoxy/V-40 and epoxy/V-25

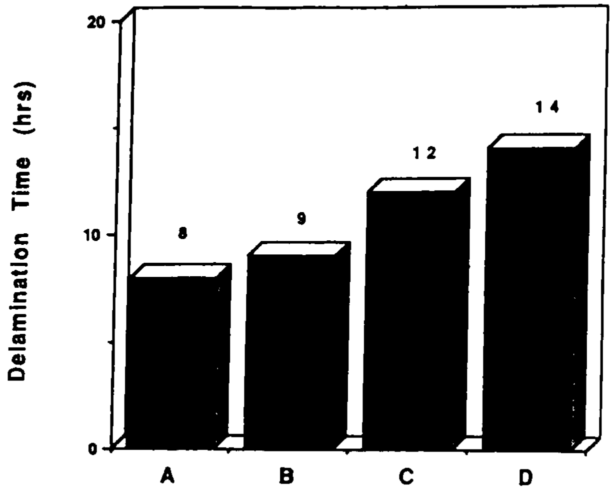

FIGURE 1 Effects of γ-GPS on the time to failure of epoxy/V-40 adhesive on oiled steel substrates: (A)—no siliane, (B)—2%, (C)—5%, (D)—10% γ-GPS.

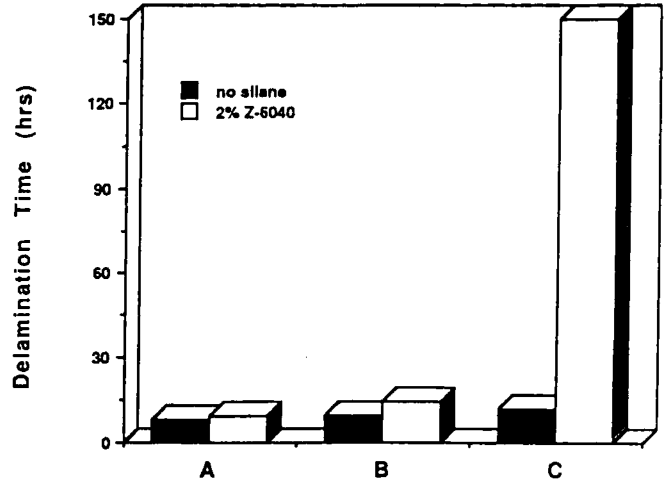

FIGURE 2 Effect of curing agent on the time to failure of bonds between epoxy/amidoamine adhesives and oiled steel substrates. The curing agents were (A)—V-40, (B)—V-25, (C)—V-15.

systems and were only about two and four hours, respectively. However, a significant improvement was obtained for the epoxy/V-15 system. After 160 hours in boiling water, there was no sign of delamination for the epoxy/V-15 system with 2% γ-GPS added.

The difference in performance of the various adhesive systems shown in Figure 2 is undoubtedly related to the amine numbers of the curing agents. V-40 has the highest amine value and V-15 has the lowest. Adhesives cured with V-15 were most oleophilic and were most effective in bonding to oil-contaminated steel. Bowen also found that oleophilic adhesives were most effective in bonding to oil-contaminated steel substrates.[2]

In order to determine the effect of stoichiometry on the durability, screening tests were carried out on specimens prepared using various ratios of epoxy and V-40 (see Figure 3). However, it was found that any increase in the amount of V-40 in the adhesive (75 phr of the curing agent is stoichiometric for this system) resulted in a decrease in durability. This deterioration of durability was probably related to excess unreacted curing agent in the adhesive.

γ-GPS and AAMS were both effective in improving the durability of adhesive bonds to the oil-contaminated steel substrates. Thus, when 5% AAMS was added to the epoxy/V-15 system, delamination did not occur within 160 hours and the test was discontinued. However, when 10% AAMS was added, the durability seemed to decrease somewhat, probably because of excess unreacted amino groups.

B Lap shear strength

According to the results of the screening tests, the performance of the adhesive system cured with V-15 was better than that of the adhesives cured with V-25 or

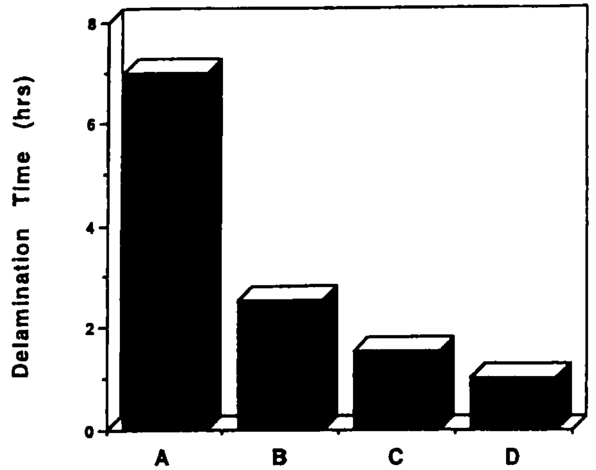

FIGURE 3 Effect of the epoxy/curing agent ratio on the durability of the epoxy/V-40 adhesive on oiled steel. The ratios were (A)—100:75, (B)—100:95, (C)—100:115, and (D)—100:135. A ratio of 100:75 is stoichiometric for this curing agent.

V-40. Moreover, the addition of γ-GPS resulted in very large increases in the durability of the epoxy/V-15 system. However, the screening tests did not provide any quantitative measure of the strength of the joints before and after exposure to boiling water. Accordingly, the lap shear strength of the epoxy/V-15 adhesive cured against oil-contaminated CRS surfaces was measured before and after immersion in boiling water. The results are shown in Figure 4.

The initial lap shear strength of joints prepared using the epoxy/V-15 adhesive was 968 ± 104 psi. However, when 5% γ-GPS was added to the adhesive, the

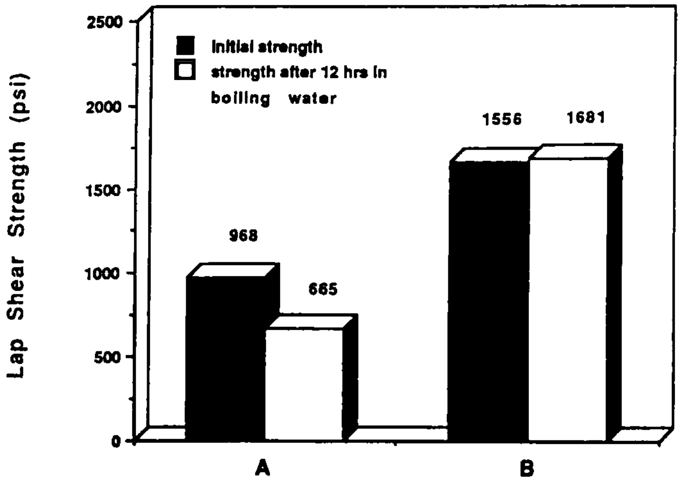

FIGURE 4 Effect of γ-GPS on the initial strength and durability of lap joints prepared using the epoxy/V15 adhesive and oiled steel adherends. In (A) there was no silane added to the adhesive but in (B) 5% γ-GPS was added.

shear strength increased to 1666 ± 123 psi. After immersion in boiling water for 12 hours, the shear strength of joints prepared without silane decreased to 665 ± 455 psi. However, the strength of joints prepared using a similar adhesive containing 5% γ-GPS actually increased to 1681 ± 137 psi after 12 hours in boiling water. These results confirmed those obtained from the screening tests and showed the great improvement in durability that was obtained by adding γ-GPS to the epoxy/V-15 adhesive system. Although the standard deviation in the shear strength of the epoxy/V-15 system without silane was high (455 psi) after exposure to boiling water, the difference in lap shear strength before and after immersion in boiling water was significant at the 85% confidence level.

C Infrared spectroscopy

The differences in the composition of V-15, V-25, and V-40 were identified from the infrared spectra shown in Figure 5. The most significant difference in the spectra was the intensity of the band near 1650 cm^{-1} which was related to amide groups. This band was strongest in spectra of V-15 and weakest in spectra of V-40, indicating that V-15 has more amide groups, and thus less amino groups, than V-40.

Samples of the epoxy resin cured with V-15, V-25 and V-40 in the presence of different amounts of oil were examined by infrared spectroscopy so as to determine the influence of the oil on the crosslinking behavior of the epoxy adhesives. The spectra of the epoxy/V-15 adhesive system cured in the presence of 0, 20, 40 and 60% oil are shown in Figure 6. There was little evidence that the oil affected the curing reaction since the band near 910 cm^{-1}, which is characteristic of epoxy rings, was not observed in any of the spectra. This

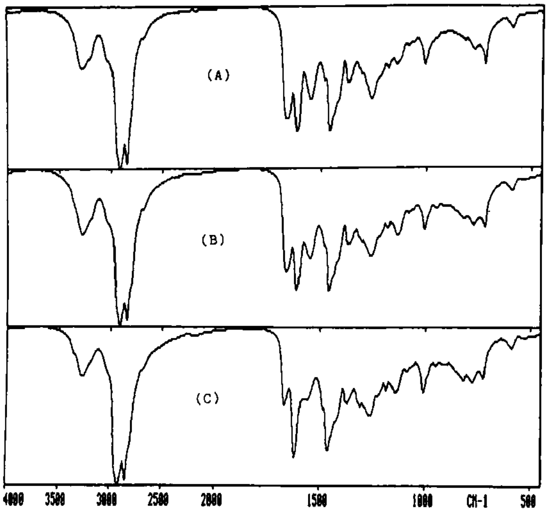

FIGURE 5 Infrared specta of (A)—V-15, (B)—V-25, and (C)—V-40 curing agents.

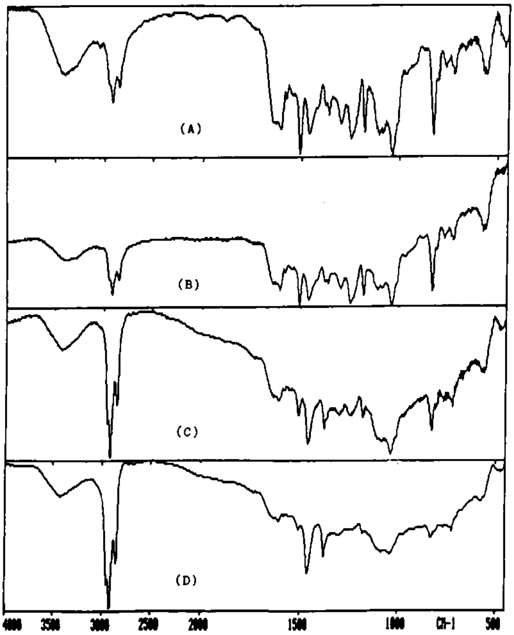

FIGURE 6 Infrared spectra of Epon-828 cured by V-15 in the presence of (A) 0, (B) 20, (C) 40, (D) 60 wt.% FC-61 oil.

indicates that even after the addition of 60% oil, the curing reaction still occurred in the bulk of the epoxy. This result is consistent with those obtained from DSC measurements.[17] Similar results were obtained from an analysis of the spectra of the epoxy/V-25 and epoxy/V-40 adhesive systems. However, this conclusion does not imply that the composition of the epoxy/steel interphase will not be affected by the oil, since some materials are more abundant in the interphase than in the bulk (see below).

In testing the reaction of individual components of the adhesive systems with the oil, it was found that the epoxy and γ-GPS were not compatible with the oil. When the epoxy and γ-GPS were mixed with the oil, phase separation was observed. However, all of the curing agents were compatible with the oil and no signs of phase separation were observed when they were mixed with the oil. Chemical reactions between the amino groups in the curing agents and AAMS and the calcium salts in the oil were detected by infrared spectroscopy. The calcium in the oil was probably present as a calcium sulfonate which is usually found as a corrosion inhibitor in slushing oils.[18,19] The spectrum of V-15 mixed with 50% oil on a KBr pellet is shown in Figure 7 to demonstrate the reaction between amines and calcium salts in the oil. The spectrum of oil on a KBr pellet is shown in Figure 8 for comparison purposes. The small bands near 1600 cm^{-1} were related to aromatic ring structures in the calcium sulfonate. Most of the remaining bands were associated with aliphatic chains in the oil. When the spectrum in Figure 7 was compared with those in Figures 5 and 8, new bands

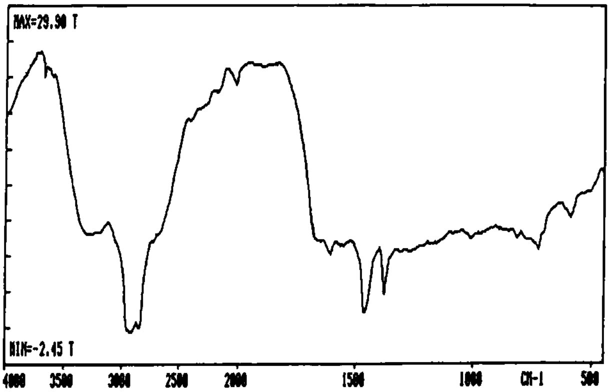

FIGURE 7 Infrared spectrum of V-15 mixed with 50 wt.% FC-61 oil.

were observed near 3679 cm^{-1} and in the region between 2500 and 2000 cm^{-1}. All the other bands are due to either V-15 or oil. The small bands between 2500 and 2000 cm^{-1} were attributed to amine salts. Aryl sulfonates are easily attacked by nucleophilic reagents.[20,21] Bunnett showed that a nucleophilic reagent such as aniline can attack 2,4-dinitrophenyl-p-toluenesulfonate and form sulfonic acid and sulfonamide-like compounds.[22] The compounds formed are dependent on the polarizability and steric effects of the attacking nucleophile. Kirkien-Konasiewicz *et al.* also showed that $—SO_3^-$ and R_3N^+ could be formed by the reaction of 2,4-dinitrophenyl-p-toluenesulfonate with tertiary bases of the pyridine type.[23] Similar reactions apparently occur between amidoamine curing agents and calcium sulfonate in the oil. The bands in the region between 2500 cm^{-1} and 2000 cm^{-1} are related to amine salts formed by the reaction described above.

Numerous investigations of amine salts by infrared spectroscopy have been reported.[24–26] Chenon and Sandorfy studied the salts formed by reacting HCl, HBr and HI with primary, secondary, and tertiary amines.[24] They found that

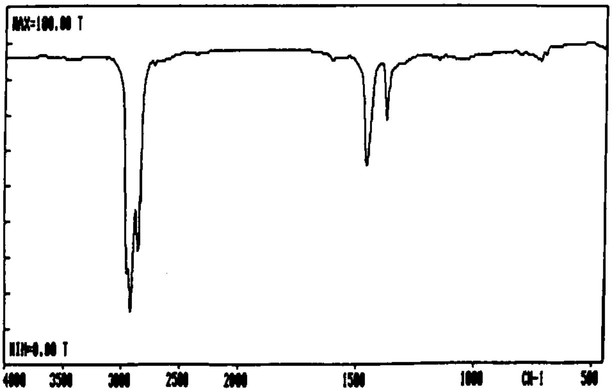

FIGURE 8 Infrared spectrum of FC-61 oil.

bands between 2800 and 2000 cm^{-1} were due to stretching modes of hydrogen-bonded aliphatic and aromatic amine hydrohalides. These bands could shift as much as 100 cm^{-1} due to the effects of substituents and hydrogen bonding. Chenon and Sandorfy observed a strong band near 2000 cm^{-1} in all their spectra and assigned it to a combination between the scissoring band and a very anharmonic band. We observed a similar band near 2027 cm^{-1} in the spectra of the reaction product of V-15 and the oil (see Figure 7). The band near 3679 cm^{-1} could be due to the OH stretching mode of aryl sulfonic acids or $Ca(OH)_2$ formed by the route stated above. However, further analysis is required to confirm these suggestions.

D XPS analysis

XPS survey spectra obtained from oil-contaminated steel substrates were characterized by a very strong band near 285 eV and by a weaker band near 530 eV that were characteristic of C(1s) and O(1s) electrons, respectively. Weak bands related to calcium and sulfur were observed in the multiplex spectra.

Survey spectra obtained from the substrate failure surfaces of samples from the screening tests are shown in Figure 9. The spectra shown in Figure 9C consisted mostly of the peaks near 285 and 530 eV that were characteristic of C(1s) and O(1s) electrons from the oil. Carbon and oxygen were the only two elements detected on the failure surfaces of screening specimens cured with V-40. This implied that the epoxy/V-40 adhesive did not absorb or displace the oil and that the locus of failure was in a weak layer of oil between the substrate and the adhesive. The XPS survey spectrum obtained from the metal failure surface of a screening specimen prepared from the epoxy/V-15 adhesive is shown in Figure 9A. Peaks related to carbon and oxygen were still observed near 285 and 530 eV. However, the shape of the peak near 530 eV was different from those observed for the oil or for the metal failure surfaces of epoxy/V-40 screening specimens and contained a component near 529.7 eV that was characteristic of the oxide. Additional peaks, characteristic of nitrogen, iron, and calcium were observed near 400, 712, and 340 eV, respectively. Nitrogen was from the curing agent while the iron was from the steel substrate and calcium was from the oil. It was evident that the epoxy/V-15 adhesive absorbed or displaced the oil and that the locus of failure was near the substrate/adhesive interface. The XPS survey spectra obtained from the substrate failure surface of a screening specimen prepared from the epoxy/V-25 adhesive is shown in Figure 9B. This spectrum was intermediate between those shown in Figures 9A and 9C. That is, the peak characteristic of carbon near 285 eV was still strong, indicating that failure was mostly in a layer of oil. However, the band characteristic of oxygen, near 530 eV, was relatively strong and contained the component near 529.7 eV that was characteristic of the oxide, indicating that at least some absorption or displacement of the oil had occurred and that the failure was partially near the adhesive/substrate interface.

Differences between the failure surfaces can be seen more clearly from the atomic concentrations which are summarized in Table I. For the epoxy/V-40

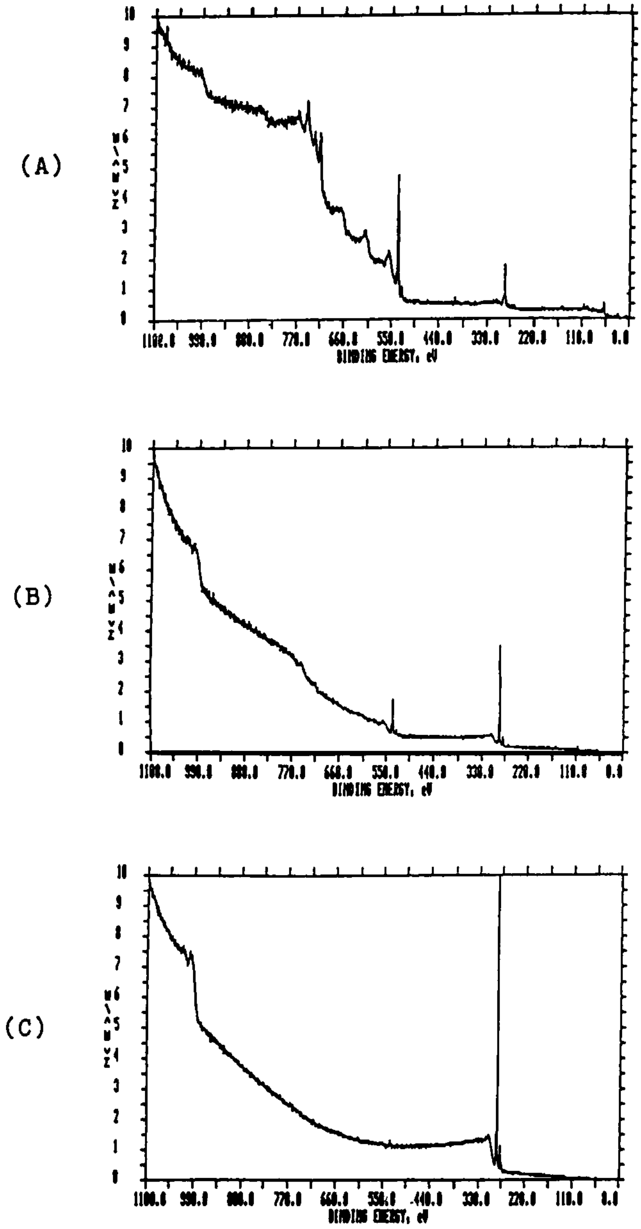

FIGURE 9 XPS survey spectra of substrate failure surfaces of joints prepared using epoxy/amidoamine adhesives and oiled steel adherends. The curing agents were (A) V-15, (B) V-25, and (C) V-40. The take-off angle was 15° in all cases.

TABLE I
Atomic concentrations of the failure surfaces of specimens prepared using amidoamine curing agents and oiled steel substrates

	Atomic concentration (%)					
Curing agent:	C	O	N	Fe	Ca	Si
V-40						
Substrate failure surface	98.7	1.3				
Adhesive failure surface	97.2	2.0	0.8			
V-25						
Substrate failure surface	76.9	17.1	1.6	1.3		3.1
Adhesive failure surface	94.1	3.8	1.4			0.8
V-15						
Substrate failure surface	45.0	41.0	3.2	8.2	3.2	
Adhesive failure surface	75.3	17.7	4.6	2.1		

specimen, there were 98.7% C and 1.3% O on the substrate failure surface and 97.2% C, 2.0% O, and 0.8% N on the adhesive failure surface. Since both failure surfaces were composed almost entirely of carbon, it was evident that failure was within a layer of oil. This conclusion was confirmed by the C(1s) multiplex spectrum which contained only one symmetric peak near 284.6 eV that was characteristic of hydrocarbon linkages in the oil.

For the epoxy/V-15 sample, 45.0% C, 41.0% O, 3.2% N, 8.2% Fe and 3.2% Ca were detected on the metal failure surface and 75.3% C, 17.7% O, 4.6% N and 2.1% Fe were detected on the adhesive failure surface. The N/C ratio from the metal failure surface was 0.07 which was very close to the value of 0.06 obtained for the epoxy failure surface, indicating that failure was partially cohesive within the adhesive and that the epoxy/V-15 adhesive had absorbed or displaced the oil.

The performance of the epoxy/V-25 adhesive was intermediate between those of the epoxy/V-15 and epoxy/V-40 adhesives. This was confirmed by comparing the atomic concentrations for the various failure surfaces. There were 1.6% N and 1.3% Fe on the metal failure surface of the epoxy/V-25 specimen. These values were larger than those of the epoxy/V-40 specimen but smaller than those of the epoxy/V-15 specimen, indicating that the performance of the epoxy/V-25 adhesive in absorbing or displacing the oil was intermediate between those of the epoxy/V-40 and epoxy/V-15 adhesives.

Similar comparisons were made regarding the XPS spectra obtained from the substrate failure surfaces of epoxy/V-40 screening specimens prepared using varying amounts of γ-GPS (see Figure 10). When the spectrum shown in Figure 9C is compared withe those in Figure 10, it is evident that more oxygen,

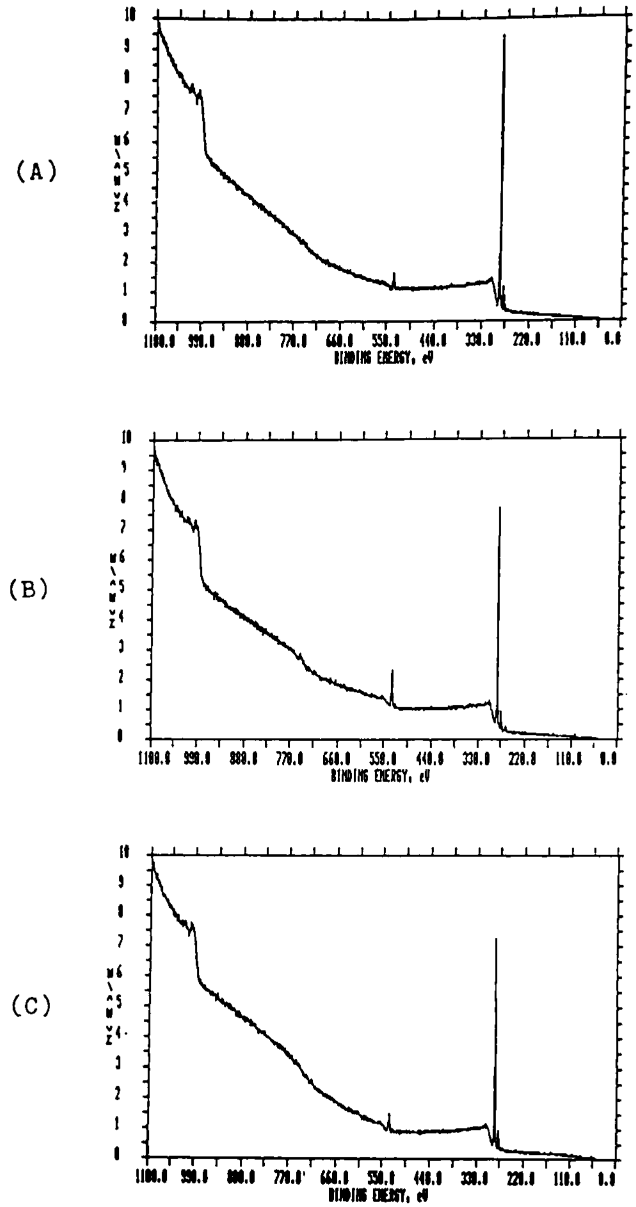

FIGURE 10 XPS survey spectra obtained from the substrate failure surfaces of specimens after the screening tests. The adhesive was epoxy/V-40 containing (A)—2, (B)—5, and (C)—10 wt.% γ-GPS and the substrate was oiled steel. The take-off angle was 15°.

TABLE II
Effect of γ-GPS on the atomic concentrations of failure surfaces of specimens prepared using the epoxy/V-40 adhesive and oiled steel substrates

		Atomic concentrations (%)				
	Silane (%)	C	O	N	Fe	Si
Substrate failure surface	0	98.7	1.3			
	2	95.1	3.8	0.6		0.5
	5	89.4	8.2	0.9	0.5	1.0
	10	92.1	5.8	0.8	0.8	0.6
Adhesive failure surface	0	97.2	2.0	0.8		
	2	96.9	2.1	0.8		0.2
	5	81.0	13.6	2.5	1.0	1.9
	10	91.6	5.5	2.1	0.6	0.3

characteristic of the oxide, was observed on the substrate failure surface of screening specimens prepared using the epoxy/V-40 adhesive when γ-GPS was added to the adhesive than was observed with no silane was added. The effect of γ-GPS on th composition of the failure surface is shown more clearly in Table II. No nitrogen was detected on the substrate failure surfaces of screening specimens prepared using the epoxy/V-40 adhesive without γ-GPS. However, when 2% γ-GPS was added to the adhesive, the nitrogen content of the failure surface was 0.6%, indicating that the addition of small amounts of γ-GPS enabled the adhesive to absorb or displace at least some of the oil. When 5% γ-GPS was added to the adhesive, 0.9% N and 0.5% Fe were detected on the substrate failure surface and when 10% γ-GPS was added, 0.8% N and 0.8% Fe were detected. The atomic concentrations of the adhesive failure surfaces also showed that the epoxy/V-40 adhesive absorbed or displaced more oil from the surface as the silane content of the adhesive increased. Little oxygen or nitrogen was observed on the adhesive failure surface of specimens prepared from the epoxy/V-40 adhesive containing 2% γ-GPS but the N content was greatly increased on the adhesive failure surfaces of specimens prepared with the epoxy/V-40 adhesive containing 5 or 10% γ-GPS.

In order to obtain information regarding the composition of the adhesive/steel interphase in as-prepared joints, screening specimens were prepared using oil-contaminated substrates and immersed in liquid nitrogen. The residual stresses in the specimens were sufficient to cause debonding very near the interface, allowing the adhesive and substrate fracture surfaces to be examined using XPS. For comparison purposes, similar specimens were prepared using clean steel surfaces. The atomic concentrations observed on the substrate fracture surfaces are summarized in Tables III and IV.

In spite of the differences in the curing agents, fracture seemed to be very close to the substrate surface for the specimens prepared using clean substrates. From angle resolved XPS, it was shown that adhesive closest to the surface contained more nitrogen than that farther away. The N/C ratio of the epoxy/V-15 adhesive on the subtrate fracture surface was 0.03 for a take-off angle of 15°, 0.06 for an

TABLE III
Atomic concentrations of substrate fracture surfaces of specimens prepared using epoxy/amidoamine adhesives and clean adherends

Curing agent	Take-off angle (°)	Atomic concentrations (%)				
		C	O	N	Fe	Si
V-15	15	74.9	18.7	2.5	2.0	1.9
	45	58.5	31.1	3.7	5.1	1.6
	75	51.0	35.4	3.4	8.8	1.5
V-25	15	76.1	17.0	3.3	1.2	2.5
	45	67.2	23.1	5.5	2.9	1.4
	75	56.5	30.5	5.5	6.0	1.5
V-40	15	65.5	24.2	4.9	1.4	4.0
	45	48.6	36.2	5.5	9.4	0.3
	75	47.2	37.0	5.4	10.2	0.3

angle of 45°, and 0.06 for an angle of 75°. For the epoxy/V-25 adhesive, the ratios were 0.04 at 15°, 0.08 at 45°, and 0.10 at 75° and for the epoxy/V-40 adhesive the ratios were 0.07 at 15°, 0.11 at 45°, and 0.11 at 75° take-off angle. The N/C ratios obtained at a take-off angle of 75° were higher than those obtained from free films except for the epoxy/V-15 specimens. The nitrogen content was higher on the substrate fracture surfaces of the epoxy/V-25 and epoxy/V-40 specimens than on those of the epoxy/V-15 specimens.

Differences in the amine content and viscosity of the curing agents caused the differences in composition of the fracture surfaces to occur. V-40 had the largest amine number and the lowest viscosity. Evidently, there was a tendency for the curing agent in the epoxy/V-40 adhesive to segregate to the interface.

When the C(1s) and O(1s) multiplex spectra obtained from the substrate fracture surfaces of specimens prepared with clean substrates were compared, some interesting phenomena were observed (see Figure 11). The C(1s) spectra consisted of three components near 284.6, 286.0, and 287.9 eV. The component near 284.6 eV was related to carbon bonded to other carbon or to hydrogen. The components shifted upward by about 1.4 and 3.3 eV were related to carbon making single bonds with oxygen and nitrogen and to amide groups, respectively. The area under the three components varied depending on the curing agent. For the epoxy/V-15 adhesive, the relative area under the amide peak was 6.7%. For

TABLE IV
Atomic concentrations of fracture surfaces of specimens prepared using oiled adherends. The take-off angle was 45° in all cases

Curing agent	Atomic concentrations (%)				
	C	O	N	Fe	Si
V-15	43.5	40.6	3.6	9.5	0.7
V-25	98.4	0.8	0.3	0.5	
V-40	98.6	1.4			

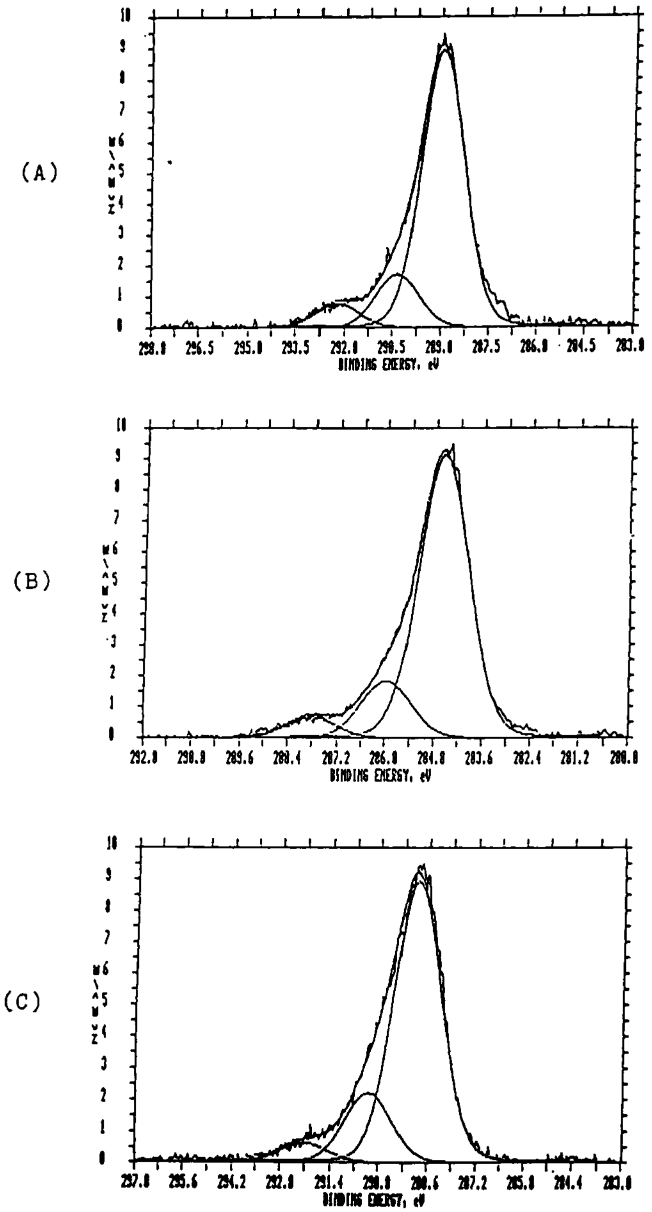

FIGURE 11 Carbon mulitplex spectra obtained from the substrate fracture surfaces of specimens prepared using the epoxy cured by (A) V-15, (B) V-25, and (C) V-40. The substrates were cleaned steel and the take-off angle was 45°.

the epoxy/V-25 and epoxy/V-40 adhesives the area was 5.7 and 5.5%, respectively.

These results indicated that there were more amide groups close to the steel surface for the epoxy/V-15 specimens than for the epoxy/V-25 and epoxy/V-40 samples. This result was not surprising since V-15 has more amide groups than the other two curing agents.

Table IV lists the atomic concentrations observed on the substrate fracture surface of the screening specimens prepared using oil-contaminated steel substrates. The N/C ratio for the epoxy/V-15 specimen was 0.08, which was higher than that for specimens prepared using clean substrates. Moreover, the area under the amide component of the C(1s) spectrum was 9.7% of the total area under the C(1s) peak. Therefore, the N/C ratio and the number of amide groups increased when the epoxy/V-15 adhesive was cured against the oil-contaminated steel surface, indicating that adhesives cured with V-15, which has more amide groups and less amine groups than the other curing agents, were better able to absorb or displace the oil than adhesives cured with V-25 and V-40.

Results summarized in Table IV showed that only a slight amount of nitrogen was detected on the substrate fracture surface for the epoxy/V-25 adhesive cured against an oil-contaminated substrate and none was detected for the epoxy/V-40 adhesive. These results were consistent with those obtained from analysis of the failure surfaces of screening specimens (see Table I).

Additional important information was obtained from the N(1s) multiplex spectra obtained from the substrate fracture surfaces of joints prepared by curing the adhesive against clean substrates (see Figure 12). The N(1s) spectra were resolved into two components. The component at the lowest binding energy was attributed to free amino groups but the component shifted about 2.0 eV to higher binding energies was attributed to protonated amino groups. About 15.2% of the amino groups were protonated for the epoxy/V-15 adhesive whereas about 20.5 and 19.6% were protonated for the epoxy/V-25 and epoxy/V-40 adhesives. However, references to Figure 13 indicates that none of the amino groups were protonated when the epoxy/V-15 adhesive was cured against an oil-contaminated steel substrate. These results are consistent with those obtained by Baldwin *et al.* showing that the active sites for adsorption of polyamide resins onto oxidized metal surfaces were the amino and imidazoline linkages and that the amide linkages were inactive.[27] The protonated amino groups may be an indication of degree of crosslinking of the epoxy system near the steel surface.

By comparing the atomic concentrations given in Table III and V, it was determined that the N/C ratios for all three adhesive systems decreased considerably during exposure to boiling water. However, from a comparison of Tables I and IV it was concluded that the N/C ratio remained about the same when the epoxy/V-15 adhesive cured against oiled steel was exposed to boiling water. These results imply that curing agent was dissolved away from the interface during exposure to boiling water when protonated amino groups were detected on the steel surface. This may indicate that protonated amino groups are associated with partially cured epoxy resins in the steel/epoxy interphase.

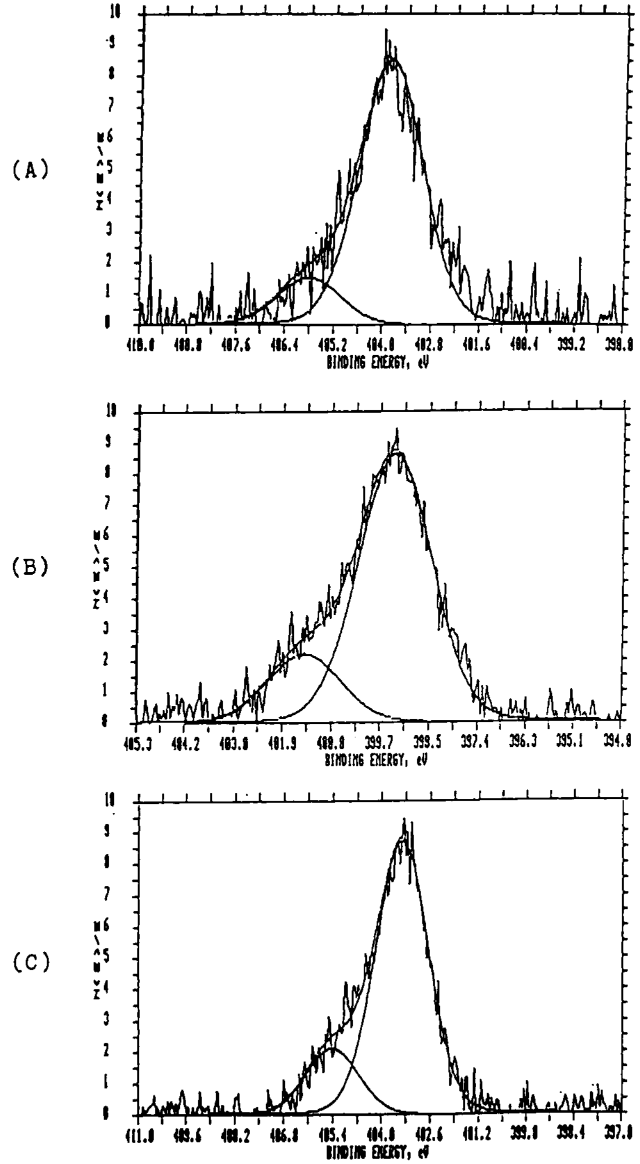

FIGURE 12 Nitrogen (1s) multiplex spectra obtained from the fracture surfaces of epoxy adhesives cured against clean steel substrates using (A) V-15, (B) V-25, and (C) V-40. The take-off angle was 45°

When the epoxy/V-15 adhesive was cured against an oiled steel substrate, the protonated amino groups disappeared, perhaps indicating less unreacted material present in the steel/epoxy interphase. This may indicate that amide groups diffuse through the oil more easily than the amino groups, so the formation of protonated amino groups was decreased. The other possible reason is that the oil

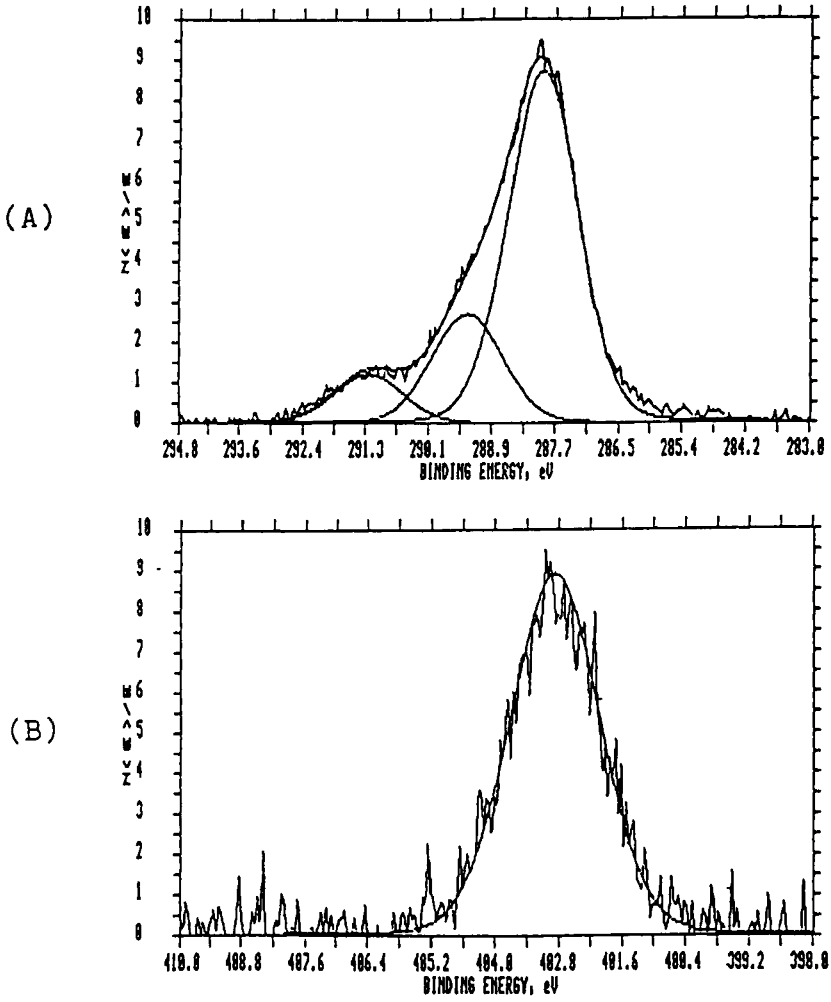

FIGURE 13 (A)—C(1s), and (B)—N(1s) multiplex spectra obtained from the fracture surfaces of epoxy/V-15 specimens cured against oil-contaminated steel substrates. The take-off angle was 45°.

will react with amino groups in the curing agents to form salts. As a result, the number of amino groups protonated by reaction with the steel surface was decreased.

In the screening tests, all the samples were immersed in boiling water and epoxy resins were probably postcured to some extent. By comparing the atomic concentrations obtained from the fracture and failure surfaces of specimens prepared by curing the epoxy/V-25 adhesive against on oiled steel surface, it was shown that only 0.3% nitrogen was present on the fracture surface before the screening test but 1.6% was detected on the failure surface after the screening test. This implies that partially cured epoxy resins were driven to the steel surface

TABLE V
Atomic concentrations of fracture surfaces of specimens prepared using clean adherends. The take-off angle was 45° in all cases

	Atomic concentrations (%)				
	C	O	N	Fe	Si
V-15	47.0	39.8	1.3	10.7	1.2
V-25	50.8	37.5	1.9	7.6	2.3
V-40	22.3	54.4	1.4	13.9	5.3

and bonded with steel surface. Two processes are probably involved. One was due to the dissolution of oil in boiling water and the other was that partially cured epoxy resins diffused to the steel surface. The dissolution of oil in boiling water was confirmed by XPS measurement. 90.9% C, 7.8% O and 1.3% Ca were detected by XPS before immersion in boiling water. However, after 2 hours in boiling water, only 90.5% C, 7.8% O, 0.2% Ca and 1.5% Fe were detected, showing that some oil and calcium were dissolved in boiling water. The difference in nitrogen content on steel surfaces before and after screening tests was also observed for epoxy/V-40 adhesives containing 2% γ-GPS.

It is interesting to consider whether absorption or displacement of the oil was the most dominant mechanism. Recently, we have carried out an investigation similar to that described here except that galvanized steel substrates were used.[17] During that investigation it was determined that much more oil remained on the substrate failure surfaces of specimens after screening tests than was observed for steel substrates. These results imply that displacement was the dominant mechanism. However, additional work will be required to determine the contribution of absorption.

IV. CONCLUSIONS

The durability of adhesive joints prepared by curing epoxide adhesives against oil-contaminated steel substrates using amidoamine curing agents depended on the amine number of the curing agent. During immersion in boiling water, epoxide adhesives cured with amidoamines having high amine numbers delaminated from oil-contaminated steel substrates before those cured with amidoamines having low amine numbers. Results obtained from X-ray photoelectron spectroscopy showed that adhesives prepared using curing agents having high amine numbers were unable to displace the oil from the substrate. Failure of such specimens during immersion in boiling water was within a layer of oil between the adhesive and substrate. Adhesives prepared with curing agents having low amine number were able to displace oil from the steel surface. Little oil was detected on the failure surfaces of those samples after the screening tests.

More nitrogen was detected on the substrate fracture surfaces of joints prepared from clean adherends than in the bulk adhesives. Moreover, the amino groups were protonated whereas those in the bulk adhesive and on the substrate fracture surfaces of joints prepared using oiled substrates were not. These results indicate that the curing agent segregates to the metal substrate and that amino groups in the curing agent are protonated by hydroxyl groups on the surface of the oxide.

Addition of the silanes γ-glycidoxypropyltrimethoxysilane (γ-GPS) and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAMS) improved the lap shear strength and durability of adhesive bonds between epoxy resins and oiled steel substrates. More epoxy resin was detected on the substrate fracture surfaces of joints prepared using oiled steel substrates when silanes were blended into the adhesive than when no silane was used, indicating that silanes can help epoxy resins displace the oil.

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