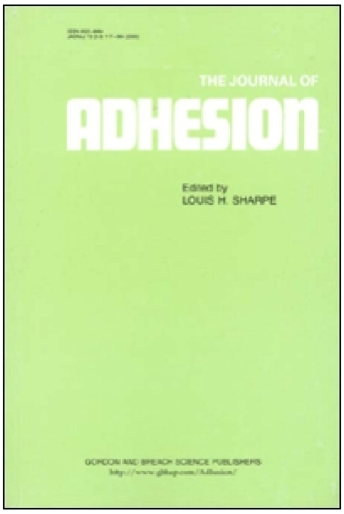

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Adhesive Bonding of Clean and Oil-Contaminated Electrogalvanized Steel Substrates

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The performance of two-part, amidoamine-cured epoxy adhesives on clean and oil-contaminated electrogalvanized steel (EGS) was studied using screening and lap shear tests. On exposure to boiling water, the cured epoxy adhesives with amidoamines having higher amine value delaminated from the clean and oil-contaminated EGS surfaces before those cured with amidoamines having low amine value. The results of X-ray photoelectron spectroscopy (XPS) showed that the adhesives cured with amidoamines having high amine value were unable to displace the oil from the EGS substrate. However, the durability and the strength of the adhesive bonds on the oiled EGS could be improved by adding proper amounts of silane or wetting agent to the adhesive. The preferential adsorption of amino curing agents occurred on the clean EGS surface, confirmed by XPS and reflection absorption infrared spectroscopy, and this decreased the durability of the bonds in boiling water. In addition, from XPS analyses of various specimens, different amounts of cured resins were detected in the adhesive/EGS interfacial regions which affecting the durability of the adhesive bonds. In addition, the amidoamine curing agents may form complexes on the EGS surface.

KEY WORDS: electrogalvanized steel; X-ray photoelectron spectroscopy; oil contamination; preferential adsorption; durability; epoxy adhesive

I. INTRODUCTION

Structural adhesives have been used increasingly in the automotive industry for replacing conventional spot-welding methods, because adhesive bonding can offer advantages such as good fatigue and corrosion resistance, and reduced stress concentration.[1-3] However, this application usually requires the adhesive systems to be capable of bonding to metal surfaces contaminated with treating oils or oils and greases present in factory environments.

To form a useful adhesive bond on an oil-contaminated metal surface, the adhesive needs to penetrate into the oil layer and make intimate contact with the metal surface underneath. Debski *et al.* proposed two mechanisms to guide the formulation of oil-accommodating adhesives: (1) the adhesive should be capable of displacing the oil from the metal surface; (2) the adhesive should be capable of absorbing the oil and

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diffusing onto the metal surface.[4] They also showed that an epoxy resin cured with 6% dicyandiamide could absorb the non-polar standard ASTM 3 mineral oil from the metal surface and form a strong bond.[4]

Natale analyzed the bonding durability of three epoxy adhesive systems on five automotive steel substrates (cold-rolled steel, zinc, and zinc-iron coated steels made by electroplating and hot-dip processes) by using lap-shear specimens exposed to ambient conditions and accelerated corrosion cycles.[5] The substrates were contaminated by combinations of two mill oils and three stamping lubricants. It was concluded that the strength, strength retention, and failure modes of the adhesive bonds were dependent on the specific adherend/oil/adhesive used. Strength losses of lap shear joints prepared were mainly attributed to corrosion at the adherend/adhesive interface.

Similar conclusions were drawn by Arnold, who studied the performance of a modified one-part epoxy adhesive on mill-oil-contaminated steel substrates.[6,7] Substrates included cold-rolled steel, electroplated, and hot-dipped galvanized steels. The lap-shear strength of the joints was measured and the results indicated that the durability of the joints depended on the corrosion resistance of the substrate. Joints prepared using electrogalvanized steel adherends had better durability than those made using cold-rolled steel adherends due to the slower corrosion rate of the electrogalvanized steel.

Ziane *et al.* investigated the tensile strength of three commercial epoxy structural adhesives on cold rolled steel, galvanized steel, and galvannealed steel substrates, which were surface treated by eight different methods.[8] The tensile strength was measured using a special stud-specimen. It was found that the tensile strength of the stud joint was dependent on the particular combination of the adhesive, the substrate, and the surface pretreatment method.

Foister *et al.* have also studied the performance of five different epoxy adhesives on the electroplated and the hot-dipped galvanized steels (ultrasmooth and minimum spangled). Both clean and mineral seal oil coated substrates were investigated.[9] For a given epoxy adhesive, higher adhesive bonding strength and higher strength retention after water immersion were obtained on the electroplated galvanized steel substrate than on the hot-dipped galvanized steel. They also showed that for a two-part, imidazole-cured epoxy adhesive system and a one-part, dicyandiamide cured epoxy system, greater strength and strength retention values were obtained on the reoiled ultrasmooth substrate than on a clean ultrasmooth substrate.

Foister *et al.* also examined the surface morphology, oxide chemistry, bond failure modes, and failure loci of the above systems using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), X-ray diffraction, and scanning electron microscopy (SEM).[10] Poor adhesive strength and strength retention on hot-dipped galvanized substrates were related to their lower surface roughness and higher surface chemical heterogeneity compared with electroplated galvanized substrates. Higher bond strength and durability were obtained on a more stable electroplated galvanized surface, which was mainly composed of rough crystals of ZnO. The locus of failure was found to be identical for clean and reoiled surfaces for a given epoxy adhesive and this substrate. Lap shear failure loci were cohesive in the adhesive layer for initial and control samples, but adhesive at the adhesive/substrate interface for samples aged by water immersion or exposing to corrosion accelerating environments, for both one-part and two-part epoxy adhesives. It was concluded that the initial bond strength was mainly influenced by surface morphology, but durability was mainly affected by the surface chemistry of the substrate. Similar conclusions were also reached by Holubka *et al.*[11]

Commercon and Wightman also used XPS and AES to analyze the fracture surfaces of modified lap shear joints prepared with two commercial epoxy adhesives cured on ASTM-3 oil-coated galvanized steel, which were exposed to 100% R. H. at 70 °C for 7 days.[12] They found that the locus of failure for joints prepared from galvanized cold-rolled steel substrates was between the adhesive and the steel surface, but for zinc electroplated steel the locus of failure was within the galvanized layer.

Maeda *et al.* studied the performance of epoxy adhesives on clean and mill-oil-contaminated, hot-dipped galvanized steel surfaces under dry and wet conditions using single lap shear joints, XPS, and glow discharge spectroscopy.[13] They found that segregation of both lead and aluminum to the substrate surface during hot water immersion stimulated corrosion of the galvanized steel and decreased the strength of the adhesive bond.

In addition to these, many other investigations on the performance of epoxy/EGS bonding systems have also been published.[14–19] In a previous study, it was shown that a two-part epoxy adhesive system consisting of Epon-828 (Shell) and an amidoamine curing agent could form strong and durable adhesive bonds on oil-contaminated 1020 cold-rolled steel substrates. Great bonding durability was obtained by addition of 2 wt.% of γ-glycidoxypropyl-trimethoxysilane to the adhesive.[20,21] In this study, the performance of a similar adhesive system on clean and oil-contaminated electrogalvanized steel substrates was investigated.

II. EXPERIMENTAL

The epoxy adhesives used were Epon-828 with amidoamine curing agents V-15, V-25, and V-40 (with amine values 230–246, 330–360, and 370–400, respectively) from Shell Chemical Co. The substrate was electrogalvanized steel (EGS) obtained from Armco, Inc. The silane coupling agents, N-(2-aminoethyl)-γ-aminopropyl-trimethoxysilane (γ-AEAS) and γ-glycidoxypropyl-trimethoxysilane (γ-GPS) were obtained from Dow-Corning. Another silane, γ-mercaptopropyl-trimethoxysilane (γ-MPMS), was purchased from Petrarch Systems. The wetting agent, Epodil-L, was supplied by Pacific Anchor. The oil used to contaminate the EGS surface was a "ship-out" oil, Ferrocote-61 (from Quaker Chemical Co.).

EGS substrate were cut into small coupons (1 cm × 2 cm), and were cleaned first in a 20.4 g/l Parco 1500 aqueous solution at 40 °C for 3 minutes, ultrasonically cleaned in the same solution for 5 minutes, and finally rinsed with deionized water and blown dry with nitrogen gas. In some specimens, oil was wiped onto the cleaned surfaces. The thickness of the applied oil was about 2 microns. Then the epoxy adhesives were applied to both the clean and the oiled EGS surfaces, and cured at room temperature for 18 hours and postcured at 50 °C for 5 hours. The epoxy and curing agents were mixed stoichiometrically. The curing agent V-15 was added as 120 parts per hundred resin (phr) and the adhesive was referred to as Adhesive A. V-25 was added as 90 phr (referred to as Adhesive B) and V-40 added as 75 phr (referred to as Adhesive C). Silanes were added to these epoxy adhesives as 2, 5, and 10 wt.%. In some formulations, different amounts of the wetting agent were added to the adhesives.

In order to assess rapidly the durability of different bonding systems in the humid environment, an accelerated screening test was used. In the test, the cured specimens were immersed in boiling water for various times. Samples were then removed from the water and examined periodically to determine if any delamination had occurred. If delamination happened, the "failure surfaces" were analyzed by XPS. For comparison purposes, two types of "fracture surfaces" (adhesive and substrate sides), obtained from immersing the as-prepared specimens in liquid nitrogen, were also analyzed to obtain original information about the adhesive/steel interface regions from the as-prepared joints.

XPS analyses were performed with a Perkin-Elmer Model 5300 ESCA system. Mg(K_α) X-rays, with a photon energy of 1253.6 eV, were selected to generate spectra. In survey spectra, from which compositional information on the surface was obtained, 44.75 eV pass energy and 0.5 eV/step were chosen to scan the region from 0 to 1100 eV. In angle-resolved multiplex spectra, 17.9 eV pass energy and 0.05 eV/step were applied to obtain more detailed information on each element of interest at 15°, 45°, and 75° take-off angles. In curve-fitting the spectrum, the full width at half maximum of constituent peaks in the multiplex spectrum was kept the same and the shape of fitting curves was determined by 90% Gaussian distribution (10% Lorentzian). The correct binding energy shifts of different C(1s) spectra were determined by analyzing the epoxy resin and the curing agent alone.

Reflection absorption infrared (RAIR) spectra were taken at an incident angle of 78° on an external reflection accessory from Harrick Scientific Co. with single reflection. One hundred scans were averaged at a resolution of 4 cm^{-1} from 4000 cm^{-1} to 450 cm^{-1} on a Perkin-Elmer 1800 Fourier Transform Infrared Spectrophotometer. Difference spectra were obtained by subtracting the baseline spectrum of a clean EGS surface. For comparison purposes, the specimen prepared with the cold-rolled steel substrate (CRS) was also analyzed. Similar to EGS, CRS was also obtained from Armco.

Lap shear strength (L.S.S.) measurements were performed according to ASTM D-1002. EGS coupons were cut into strips (10.2 × 2.5 cm), cleaned, and then oiled. Different adhesive formulations were used to bond the adherends with a 1.3 cm overlap to form single lap shear joints. A 0.1 mm spacer was applied to keep the bond-line thickness constant. After curing, the residual epoxy adhesive along the bondline was trimmed using a razor blade. Some of the specimens were tested to failure on an Instron using a crosshead rate of 1.3 mm/min. Other specimens were put in an environmental chamber at 60 °C and 85% R.H. for two weeks and then vacuum-dried overnight before testing. Five specimens were tested for each measurement.

III. RESULTS AND DISCUSSION

Screening Tests

The durability of bonds formed by curing Adhesives *A*, *B*, and *C* on oiled EGS substrates is shown in Figure 1. Without the addition of silanes, Adhesive *A*, *B*, and *C*

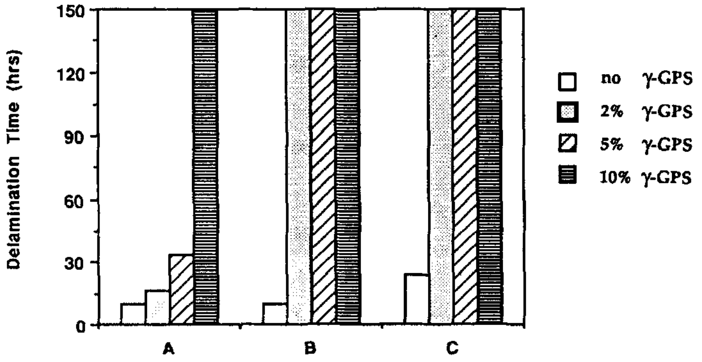

FIGURE 1 Effect of curing agents and amounts of silanes added on the time to failure of bonds between epoxy/amidoamine adhesives and oiled EGS substrates. The curing agents were (1) V-40, (2) V-25, and (3) V-15.

delaminated from the substrates after about 24, 10, and 9 hours exposure to boiling water, respectively. As found on oiled CRS substrates, the durability of Adhesive *A* was the greatest, while that of Adhesive *C* was the least on oiled EGS substrates.[20]

Results of screening tests from cured adhesives containing different amounts of γ-GPS on oiled EGS substrates are also shown in Figure 1. As the amount of silane added to the adhesives was increased, the delamination time increased. With 10 wt.% γ-GPS, all the adhesives remained intact on the substrates after 160 hours. The increase in delamination times by adding 2 wt.% silane was significant for Adhesive *B* and Adhesive *A*. With addition of only 2 wt.% γ-GPS, these two adhesives showed no sign of delamination even after 160 hours in boiling water.

More effort was expended in testing Adhesive *A* because of its better performance than Adhesives *B* and *C*. The durability of bonds formed by curing Adhesive *A* containing different amounts of wetting agent on oiled EGS substrates is shown in Figure 2. Addition of 5 phr wetting agent to Adhesive *A* resulted in an increase in the

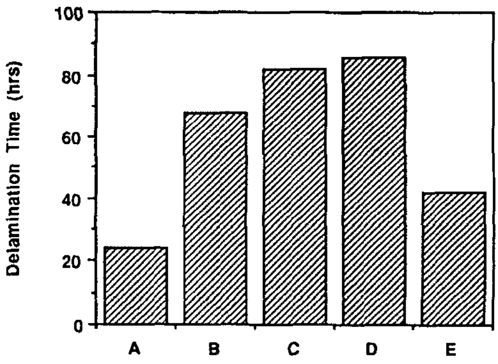

FIGURE 2 Effect of wetting agent on the time to failure of bonds between Adhesive *A* and oiled EGS substrates. The amounts of wetting agent added were (1) 0, (2) 5, (3) 10, (4) 15, and (5) 20 phr.

delamination time from 24 hours to 66 hours. The delamination time increased to 86 hours in the presence of 15 phr wetting agent. However, the delamination time decreased with 20 phr wetting agent. Since the wetting agent is a low molecular weight diluent with hydrophilic polar groups, excess amounts not only can plasticize the adhesive, but also can increase the water absorption.

γ-AEAS and γ-MPMS are also effective in improving the durability of adhesive bonds to oil-contaminated EGS substrates. With the addition of 2 wt.% γ-AEAS or γ-MPMS to Adhesive *A*, no delamination occurred after 160 hours exposure in boiling water. This result was also similar to that obtained previously on oiled CRS substrates.[20]

Although it was recognized that the accelerated test, such as the screening test, may introduce unnatural effects into the materials tested, it is a rapid and easy method to differentiate the relative performance of different bonding systems. Plueddemann used a similar test condition to assess the durability of various silanes as primers for bonding metal and plastic substrates.[22,23] In this study, the screening test results have been proven to be consistent with the XPS results shown below.

Lap Shear Strength Measurement

The lap shear strengths of joints prepared using Adhesive *A* cured against clean and oil-contaminated EGS substrates are shown in Figure 3. The initial lap shear strength of joints prepared using Adhesive *A* on clean EGS surfaces was 1233 psi (8.5 MPa) (standard deviation $\sigma = 187$ psi (1.3 MPa)). When the same adhesive was cured on oiled EGS surfaces, the initial lap shear strength decreased to 1022 psi (7.0 MPa) ($\sigma = 23$ psi (0.16 MPa)).

The addition of wetting agents and silanes to Adhesive *A* increased the lap shear strength of the joints. For specimens prepared with Adhesive *A* with 15 phr wetting agent on oiled EGS substrates, the initial lap shear strength was 1346 psi (9.3 MPa) ($\sigma = 36$ psi (0.25 MPa)) (see Figure 3). The greatest lap shear strength, 1518 psi (10.5

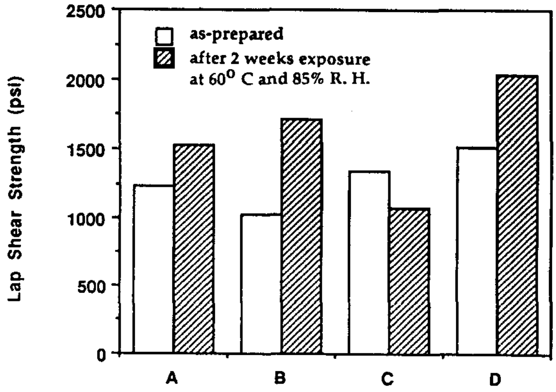

FIGURE 3 Initial strength and durability of lap shear joints prepared using Adhesive *A* on (1) clean EGS, (2) oiled EGS, (3) oiled EGS but with addition of 15 phr wetting agent to the adhesive, and (4) oiled EGS but with addition of 2 wt.% γ-GPS to the adhesive.

MPa) ($\sigma = 76$ psi (0.52 MPa)), was observed in joints based on Adhesive *A* with the addition of 2 wt.% γ-GPS on oiled EGS surfaces, showing almost a 50% increase in lap shear strength on oiled EGS compared with that of joints prepared with Adhesive *A* alone.

It is also shown in Figure 3 that after two weeks exposure at 60 °C and 85% R.H., the lap shear strengths of all joints, except that of the joints prepared using Adhesive *A* with 15 phr wetting agent, increase. The lap shear strength of joints prepared using Adhesive *A* on clean and oiled EGS substrates increased to 1525 psi (10.5 MPa) ($\sigma = 88$ psi (0.61 MPa)) and 1722 psi (11.9 MPa)) ($\sigma = 108$ psi (0.74 MPa)) after environmental exposure, respectively. The greater strength and strength retention of joints prepared with oiled substrates over those prepared with clean substrates was also observed by Foister.[9] For joints prepared using Adhesive *A* with the addition of 2 wt.% γ-GPS, the lap shear strength increased from 1518 psi (10.5 MPa) to 2042 psi (14.1 MPa) ($\sigma = 81$ psi (0.56 MPa)) after two weeks exposure.

The lap shear strength of joints prepared using Adhesive *A* with wetting agent on oiled EGS substrates decreased from 1346 psi (9.4 MPa) to 1071 psi (7.4 MPa) ($\sigma = 620$ psi (4.3 MPa)) after two weeks exposure. The large standard deviation obtained, 620 psi (4.3 MPa), indicated the presence of significant differences among specimens. The specimens with large decrease in strength showed corrosion products along the bondline. This observation was consistent with those from the screening test. The presence of the hydrophilic functional groups, and the possible formation of a weak boundary layer resulting from the wetting agent in the bonding interface, would likely be responsible for such deterioration in strength.

The lap shear strengths of joints prepared with Adhesive *A* containing different silanes on oiled EGS are shown in Figure 4. The lap shear strengths were 1332 psi (9.2 MPa) ($\sigma = 55$ psi (0.38 MPa)) and 1311 psi (9.0 MPa) ($\sigma = 56$ psi (0.39 MPa)) for specimens prepared with Adhesive *A* containing 2 wt.% γ-AEAS and 2 wt.% γ-MPMS, respectively. It seems that γ-GPS is the best coupling agent for the studied bonding systems.

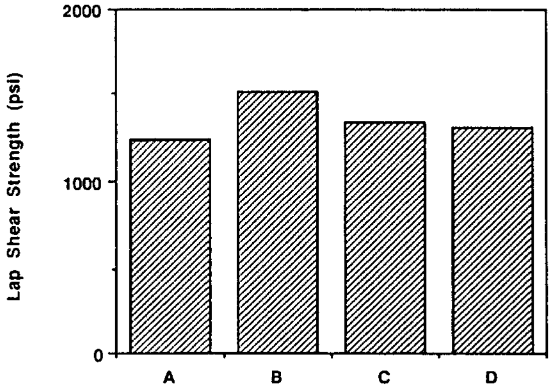

FIGURE 4 Effect of silanes on the initial strength of lap shear joints prepared using (1) Adhesive *A*, and Adhesive *A* with 2 wt.% (2) γ-GPS, (3) γ-AEAS, and (4) γ-MPMS cured against oiled EGS adherends.

XPS Analysis

The differences in performance of the adhesives in displacing the oil from the oiled EGS substrates were analyzed using XPS. The XPS survey spectra obtained from the substrate fracture surfaces of specimens prepared with Adhesives *A*, *B*, and *C* on oiled EGS substrates are shown in Figures 5A, 5B, and 5C, respectively. The spectrum shown in Figure 5A consists of peaks near 285 and 530 eV that are characteristic of *C*(1s) and O(1s) electrons. An additional peak characteristic of zinc is near 1022 eV. The zinc peak from the EGS substrate indicated that the locus of fracture was near the EGS surface. The spectra shown in Figures 5B and 5C consist mostly of the peaks near 285 eV and small peaks near 530 eV that are characteristic of *C*(1s) and *O*(1s) electrons from the oil. The loci of fracture were in the oil abundant layer. No Zn peak from the substrate was observed.

The reasons for the differences in oil-displacing behavior of three adhesives were more clear from the atomic concentrations obtained from the fracture surfaces of specimens prepared using oiled EGS substrates (see Table I). For Adhesive *A* specimen,

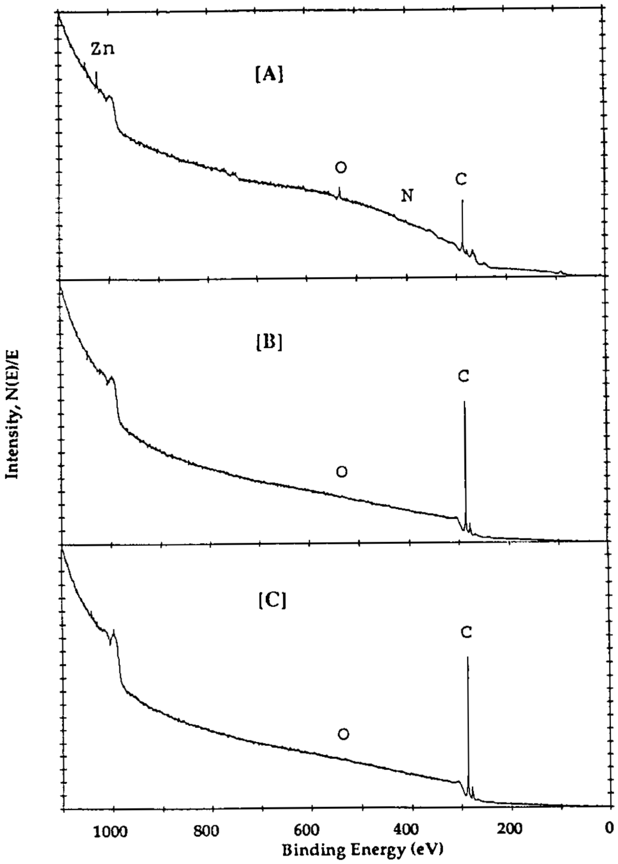

FIGURE 5 XPS survey spectra obtained from the substrate fracture surfaces of specimens prepared using Adhesive (A) *A*, (B) *B*, and (C) *C* cured against oiled EGS adherends. The take-off angle was 45° in all cases.

TABLE I
XPS atomic concentrations detected on fracture surfaces of specimens prepared using different adhesives cured against oiled EGS surfaces. The take-off angle was 45° in all cases

Adhesive	Fracture surface	Atomic concentration (%)						
		C	O	N	Zn	Si	Ca	N/C
A	substrate	87.9	8.8	1.5	1.8			1.7
B	substrate	98.6	1.0	0.4				
C	substrate	99.3	0.7	–				
A	adhesive	88.8	7.3	3.3		Bal.	0.1	3.7
B	adhesive	94.3	4.1	1.4		Bal.		1.5
C	adhesive	94.9	3.6	0.7		Bal.		0.7

(Bal.: Balance obtained by difference)

87.9% C, 8.8% O, 1.5% N and 1.8% Zn were detected on the substrate fracture surface; 88.8% C, 7.3% O and 3.3% N were detected on the adhesive fracture surface. Nitrogen was from the adhesive, which implied that the adhesive absorbed part of the oil from the EGS surface. For Adhesive *C* specimen, there were 99.3% C and 0.7% O on the substrate fracture surface and 94.9% C, 3.6% O, and 0.7% N on the adhesive fracture surface. Little nitrogen was detected on both fracture surfaces, indicating that Adhesive C did not effectively absorb or displace the oil and that the locus of failure was in a layer of oil between the substrate and the adhesive.

The performance of Adhesive *B* was intermediate between those of Adhesive *A* and Adhesive *C*. There were 98.6% C, 1.0% O, and 0.4% N detected on the substrate fracture surface; 94.3% C, 4.1% O, and 1.4% N on the adhesive fracture surface. The nitrogen concentration was greater than that from the Adhesive *C* specimen but smaller than that from the Adhesive *A* specimen, indicating that the performance of Adhesive *B* in displacing the oil was intermediate between those of Adhesive *A* and Adhesive *C*. This result is consistent with the screening test result shown previously.

More adhesive resin in contact with the metal substrate not only can provide more attraction forces between the adhesive and the substrate, but also can provide more bonded surface area and possible mechanical interlocks because of the surface roughness of the EGS. As a result, the durability and the adhesion strength of the bonds prepared with Adhesive *A* were superior to those from Adhesives *B* and *C*.

The results obtained from the oiled EGS substrates were similar to those obtained from the oiled CRS substrates.[20] However, the N/C ratio obtained from the substrate fracture surfaces of the specimens prepared using Adhesive *A* on oiled EGS substrates was smaller than those from the specimens prepared with oiled CRS substrates (8.2%) and the bulk of Adhesive *A* (6.3%), indicating that there were lesser amounts of adhesive, but with some oil left on the substrate fracture surface of oiled EGS specimens.

The substrate fracture surfaces of specimens prepared with clean EGS substrates were also analyzed using XPS. From the atomic concentrations listed in Table II, it is apparent that the N/C ratios obtained from the substrate fracture surfaces of specimens prepared with clean EGS substrates become greater as the take-off angle increases. These results imply that the adhesive closest to the surface contained more nitrogen

TABLE II
XPS atomic concentrations detected on fracture surfaces of specimens prepared using different adhesives cured against clean EGS surfaces

Adhesive	Fracture surface	TOA (degree)	Atomic concentration (%)						
			C	O	N	Zn	Cl	Si	N/C
A	substrate	15	48.9	30.7	9.0	7.6	1.8	Bal.	18.4
		45	41.4	36.5	8.8	9.2	1.8		21.1
		75	29.8	40.1	7.3	18.6	1.4		24.4
B	substrate	15	50.0	27.4	11.9	7.0	1.5	Bal.	23.8
		45	36.3	37.0	9.8	12.4	2.2		27.0
		75	29.2	39.8	9.1	16.8	2.2		31.0
C	substrate	15	65.9	16.4	12.5	3.6	0.9	Bal.	18.9
		45	50.3	28.2	10.9	8.3	1.1		21.7
		75	43.4	31.1	11.3	12.3	1.0		25.8
A	adhesive	45	82.6	10.8	6.0	0.3	0.3		7.2
B	adhesive	45	81.1	11.9	6.2	0.4	0.1	Bal.	7.7
C	adhesive	45	81.3	11.5	6.5	0.4	0.3		8.0

(TOA: take-off angle)

than that farther away. Similar results were also obtained on the substrate fracture surfaces of specimens prepared with clean CRS substrates.[20]

It was also observed that the N/C ratios were higher on the substrate fracture surfaces of specimens prepared with Adhesive *B* and Adhesive *C* than those from specimens prepared with Adhesive *A* on clean EGS substrates (Table II). These results were also similar to those obtained from the substrate fracture surfaces of specimens prepared with clean CRS substrates.[20] V-25 and V-40 have shorter chains, lower viscosities, and higher amine values than V-15. It was reported that the selective adsorption of chemicals with similar chemical structures on solid surfaces was easier for short chain molecules than for long chain molecules.[24] Therefore, amines in V-25 and V-40 should be more easily adsorbed onto EGS surfaces than those in V-15 because of their shorter chain lengths.

However, the N/C ratios detected from the substrate fracture surfaces of specimens prepared with clean EGS substrates were greater than 0.20 at 45° take-off angle (see Table II), and were much higher than those detected from bulk adhesives and substrate fracture surfaces of specimens prepared with clean CRS substrates. The N/C ratios obtained from bulk adhesives are shown in Table III. The N/C ratios obtained from the substrate fracture surfaces of specimens prepared with clean CRS substrates and Adhesives *A*, *B* and *C* were 0.063, 0.081, and 0.114 at 45° take-off angle, respectively.[20] Much greater N/C ratios on EGS surfaces indicated the preferential adsorption of nitrogen-containing species on EGS surfaces.

Different carbon species were also identified by curve-fitting techniques. The $C(1s)$ spectrum obtained from the substrate fracture surface of the specimen prepared with a clean EGS substrate shown in Figure 6 consists of five components. As described previously, the peaks with binding energies near 284.6 eV, 285.7 eV, 286.2 eV, and 287.7 eV are related to C-H, C-N, C-O, and amide groups, respectively.[20] The component with binding energy near 289.1 eV is probably related to carbon in amine bicarbonate.

TABLE III
Relative concentrations of components found in C(1s) spectra that were obtained from theoretical calculations, bulk adhesives, and substrate fracture surfaces of as- prepared screening specimens. The take-off angle was 45° in all cases

Adhesive	Fracture surface	C—H	C—N	C—O(%)	—CON—	N/C
A	before cure	74.4	7.2	16.6	1.8	4.5
(Theory)	after cure	74.4	11.0	12.8	1.8	4.5
B	before cure	71.3	7.4	19.5	1.8	5.1
(Theory)	after cure	71.3	11.9	15.0	1.8	5.1
C	before cure	69.7	7.1	21.4	1.8	5.2
(Theory)	after cure	69.7	12.0	16.5	1.8	5.2
A	bulk	74.8	11.1	12.8	1.3	6.3
B (exp.)	bulk	72.1	12.0	14.6	1.3	6.5
C	bulk	70.2	12.2	16.0	1.5	6.5
A	clean CRS	74.0	11.6	8.4	6.0	6.3
B (exp.)	clean CRS	73.9	15.0	5.9	5.1	8.1
C	clean CRS	68.4	17.0	9.4	5.2	11.4
A	clean EGS	52.2	27.0	12.5	4.1	21.1
B (exp.)	clean EGS	42.0	40.1	9.5	4.1	27.0
C	clean EGS	44.8	36.9	10.1	2.5	21.7

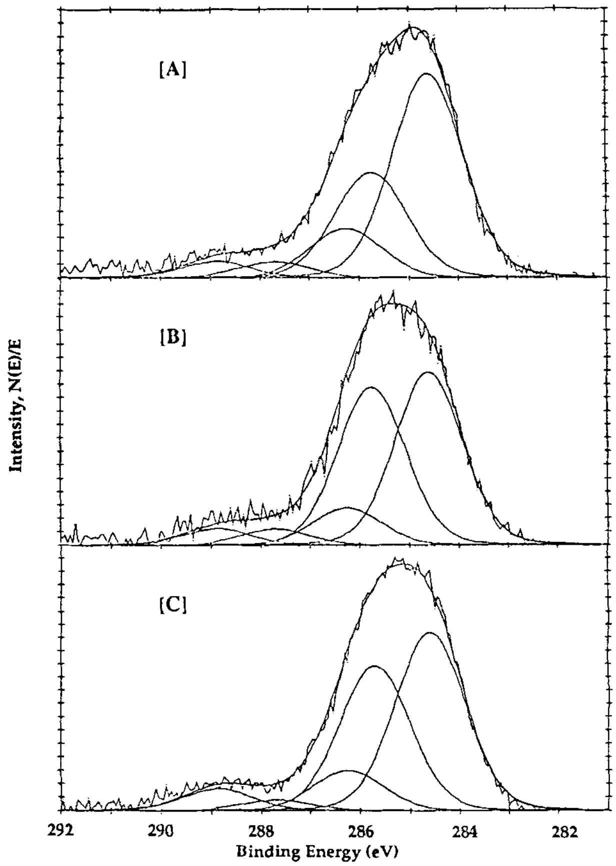

FIGURE 6 C(1s) spectra obtained from the substrate fracture surfaces of specimens prepared using Adhesive (A) *A*, (B) *B*, and (C) *C* cured against clean EGS adherends. The take-off angle was 45° in all cases.

The relative concentrations of the different carbon species on EGS surfaces varied depending on the curing agents and the substrates used. Table III also lists the curve-fitting results from the different fracture surfaces. The areas under the C-N peaks are much greater in spectra obtained from the substrate fracture surfaces of specimens prepared with clean EGS substrates than those in spectra from other surfaces analyzed. Only amino and amide groups in the adhesives contain nitrogen atoms. As a result, much greater intensities of C-N peaks than those of amide peaks indicated that the nitrogen detected was mainly from amino groups and partly from amide groups in the curing agents.

The abundance of amide groups and amino groups on the substrate fracture surfaces was also confirmed by RAIR. The RAIR spectra taken from the substrate fracture surfaces of specimens prepared using Adhesive *A* cured against clean CRS and EGS substrates are shown in Figures 7A and 7B, respectively. The band near 1645 cm^{-1}, characteristic of amide groups, is observed clearly in Figure 7A but almost disappears in Figure 7B. This result is consistent with the XPS results shown in Table IV, which indicates that more amide groups are detected on the substrate fracture surfaces of specimens prepared using Adhesive *A* with clean CRS substrates than with clean EGS substrates. As explained previously, the large amounts of nitrogen detected on the

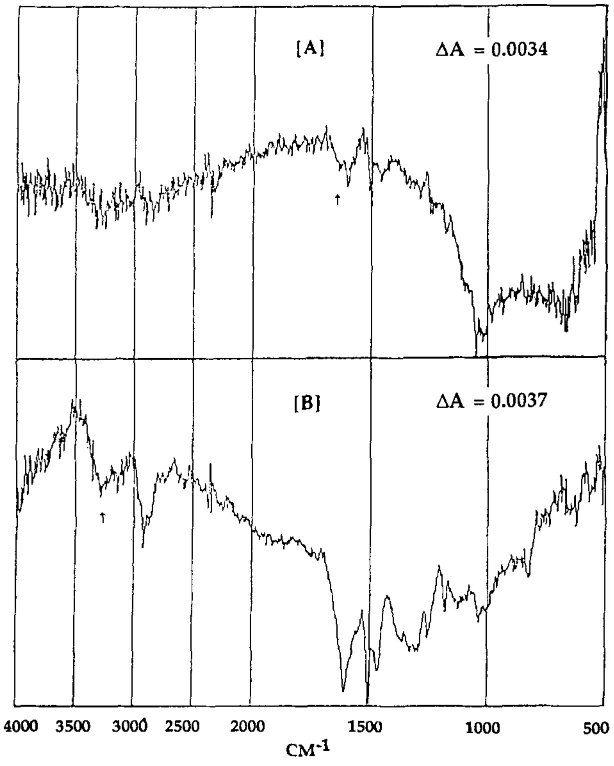

FIGURE 7 RAIR difference spectra obtained from the substrate fracture surfaces of specimens prepared using Adhesive *A* cured against clean (A) CRS, and (B) EGS substrates.

TABLE IV
XPS atomic concentrations detected on substrate failure surfaces obtained from specimens prepared using different adhesives cured against clean EGS surfaces. The take-off angle was 45° in all cases

Adhesive	Atomic concentration (%)						
	C	O	N	Zn	Cl	Si	N/C
A	22.7	43.8	4.9	23.0	1.1	Bal.	21.6
B	24.9	54.2	2.1	16.3	0.7	Bal.	8.4
C	36.4	45.8	2.6	13.2	0.4	Bal.	7.1

(Bal.: Balance obtained by difference)

substrate fracture surfaces by XPS were from either amino or amide groups in the curing agent. Accordingly, the relatively broad band near 1600 cm^{-1} in Figure 7B is due to both the aromatic ring in the epoxy resin and the deformation vibration of NH_2 groups in the curing agent because of the observed small amide absorption band. The small broad band near 3300 cm^{-1} in Figure 7B is mostly related to the N-H stretching of the amino groups.

Preferential adsorption of constituents in adhesives on solid surfaces was also observed by other investigators. Horie *et al.* found that competitive adsorption between epoxy resin and curing agent on a solid surface could occur during cure.[23] Curing agent which was preferentially adsorbed on the surface would result in a layer with composition different from the bulk.[25] Racich *et al.* also showed that amine curing agents were preferentially adsorbed on copper surfaces.[26]

The N/C ratios obtained from the "adhesive" fracture surfaces of specimens prepared by curing adhesives against clean EGS substrates were much lower than those obtained from the "substrate" fracture surfaces (see Table II). It is possible that the amino-containing molecules adsorbed on the EGS surfaces from an adjacent layer which is deficient in amidoamine curing agent near the bonding interface. Such a layer was observed by Racich and Koutsky.[26] It was also pointed out by Van Ooij that the specific adsorption or reaction of the curing agents with the metal oxide surface would reduce the concentration of the curing agents in the adhesive.[27]

The adjacent epoxy-rich layer which resulted from the preferential adsorption of the curing agents on the EGS surface could create a barrier layer that inhibited the oil from penetrating into the adhesive and, thus, inhibited the adhesive from displacing the oil, because the Epon-828 was not miscible with the oil. This probably explains why Adhesive *A* does not displace the oil from oiled EGS surfaces as effectively as from oiled CRS surfaces.

The curing reaction of an epoxy resin was determined by comparing the relative intensities of the C-O and C-N peaks in the *C*(1s) spectra. The reaction of one epoxide with -NH- would form one C-N bond but eliminate one C-O bond. The theoretical values of relative areas under C-O and C-N peaks from epoxy adhesives before and after cure are listed in Table III. The C-N peaks increased in intensity while the C-O peaks decreased in intensity after cure, and theoretical values from cured adhesives correlated well with experimental values obtained from the bulk of cured adhesives. As a result, the correctness of the curve-fitting method applied was also justified. The only small difference was in the N/C ratios. Since V-15, V-25, and V-40 curing agents are not pure compounds and have imidazoline end groups, it is possible that the presence of these nitrogen-rich species resulted in the small differences.[28]

The curing of adhesive near the EGS surface could be affected by the preferential adsorption of curing agents on the EGS surface. Less crosslinking density than in the bulk was observed for adhesives near EGS surfaces. It is shown in Table III that the relative area under the C-O peak is 12.5% on the substrate fracture surface of the specimen prepared with Adhesive *A* and the clean EGS substrate, which is close to the theoretical value of 12.8%. However, the values for Adhesive *B* and Adhesive *C* specimens were only 9.5% and 10.1%, respectively, and were much smaller than the theoretical values (15.0% and 16.5% for Adhesives *B* and *C*, respectively). In spite of this, all three of these adhesives showed many more C-N bonds on the substrate fracture surfaces of specimens prepared with clean EGS substrates than from bulk adhesives, indicating that much more curing agent, but less cured resin, were present on EGS substrates. (C-O intensity calculated was mostly from the reacted epoxides because the absence of a significant absorption band near 910 cm^{-1} in Figure 7, which is characteristic of epoxide groups, indicating considerable reaction of epoxide groups.)

Van Ooij pointed out that preferential adsorption was metal-dependent and could result in a thin polymer layer that had reduced crosslinking density adjacent to the metal surface.[27] Damico also indicated that the chemistry of the galvanized steel surface often interfered with the curing process of the adhesive.[29] Brockmann showed that the polymer near the boundary layer was influenced by the surface state of the metal substrate through selective adsorption by the metallic surface.[30] It was also shown that selective adsorption can result in different curing mechanisms inside the polymer boundary zone.[30]

Relatively small nitrogen contents obtained from the substrate failure surfaces of the specimens prepared with Adhesives *B* and *C* on clean EGS substrates after screening tests also indicated that unreacted adhesives were present near the EGS surfaces (see Table IV). From a comparison of N/C ratios shown in Tables I and IV, it was evident that the N/C ratios of Adhesive *B* and Adhesive *C* specimens decreased significantly during the screening test, implying that some nitrogen-containing molecules were lost from the adhesive/EGS interfaces in the boiling water.

The loss of amino groups in boiling water could be observed more clearly by comparing the intensities of C-N peaks in the *C*(1s) spectra obtained from specimens before and after screening tests. Figures 8A and 8B are *C*(1s) spectra from the substrate failure surfaces of specimens prepared with Adhesive *B* and Adhesive *C*, respectively, on clean EGS substrates after screening tests. By comparing the intensities of C-N peaks in these spectra with those in Figures 6B and 6C, it is evident that many amino groups are lost in the boiling water, indicating that significant decreases of the N/C ratios after the screening test were due to the loss of the unreacted excess amino groups.

Large amounts of unreacted hydrophilic amino groups present at the adhesive/EGS interface could affect the durability of the bonds in the boiling water. The delamination time for Adhesive *C* on clean EGS substrates in boiling water was only 4 hours while that for Adhesive *B* was 9 hours. Carfagna *et al.* indicated that unreacted amino groups were detrimental to adhesive bonds because they could increase the water solubility of the adhesive layer and plasticize the resins.[31] As a result, the bonding durability was deteriorated.

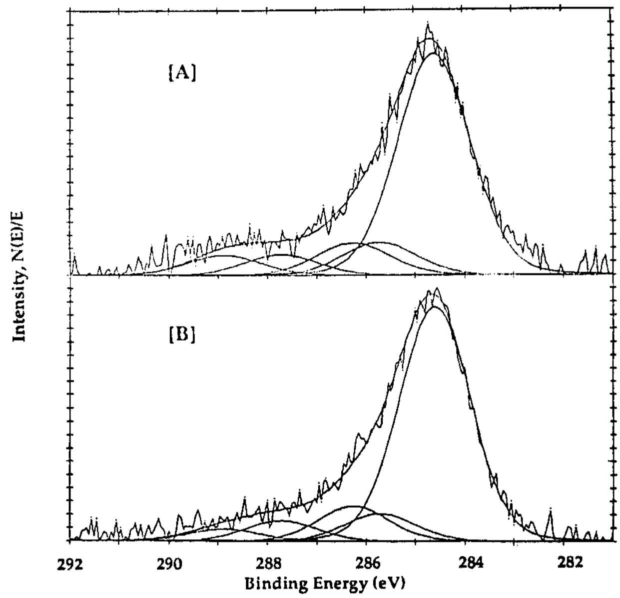

FIGURE 8 C(1s) spectra obtained from the substrate failure surfaces of specimens prepared using Adhesive (A) *B*, and (B) *C* cured against clean EGS adherends. The take-off angle was 45°.

In spite of the short delamination time observed for screening specimens prepared with Adhesive *B* and Adhesive *C* on clean EGS substrates, the delamination time of specimens prepared with Adhesive *A* on clean EGS surfaces in boiling water was nearly 40 hours. Adhesive *A* contained more C-O bonds but fewer C-N bonds on the substrate fracture surface of the specimen prepared with clean EGS substrate than Adhesive *B* and Adhesive *C*, implying more cured epoxy resin near the EGS surface for Adhesive *A*. As a result, the presence of fewer unreacted amino groups and more cured adhesive resin for Adhesive *A* on the clean EGS surface than for Adhesive *B* and Adhesive *C* was responsible for the increase in durability.

Another indication of substrate-dependent reaction could be observed from the reaction of amino groups in the curing agents with the clean EGS surface. The protonation of amino groups, which was observed on the substrate fracture surfaces of specimens prepared with clean CRS substrates,[20] was not detected on the substrate fracture surfaces of specimens prepared with clean EGS substrates. The *N*(ls) spectra obtained from the EGS substrates consist of only one component with binding energy near 399.8 eV, which is characteristic of nitrogen singly-bonded to carbon.

It is thought that the acidity of the hydrolyzed metal oxide surface and, more importantly, the possible complex formation between amino groups and EGS surfaces are related to the lack of protonation. The hydrous Fe_2O_3 or FeOOH (geothite or lepidocrocite) has a lower IEPS (isoelectric point of surface) than that of hydrous zinc oxide surface. Hence, these surfaces are more acidic than the $Zn(OH)_2$ surface.[32] There would be a stronger ionic interaction between the hydrous iron oxide surface and amino curing agent than between the hydrous zinc oxide surface and amino curing agent, so that the protonation of amino groups occurred on CRS surfaces but not on the EGS surfaces. Moreover, it is easy for zinc to react with ligands, such as amines, and form a complex.[33,34] It is possible that the large number of amino groups adsorbed on EGS surfaces resulted from complex formation between zinc and amine. Accordingly, the protonation of amino groups was not detected on EGS surface.

IV. CONCLUSIONS

The durability of adhesive joints prepared by curing epoxy adhesives against clean and oil-contaminated EGS substrates using amidoamine curing agents was influenced by the amine value of the curing agents. The epoxy adhesives cured with amidoamines having high amine value delaminated from the clean and oil-contaminated EGS surfaces after exposure to boiling water before those cured with amidoamines having low amine value. Results obtained from XPS showed that adhesives prepared using curing agents having high amine value were unable to displace the oil from the substrates. However, the addition of silanes or proper amounts of wetting agent to the epoxy/amidoamine adhesives improved the lap shear strength and durability of adhesive bonds on oiled EGS substrates.

A much greater number of amino groups were detected on the substrate fracture surfaces of specimens prepared with clean EGS substrates than in the bulk of the adhesives, indicating that the preferential adsorption of amino curing agents occurred on the EGS surface. Preferential adsorption of amino curing agents not only decreased the durability of the adhesive, presumably bonds because of the presence of hydrophilic amino groups in the bonding interface, but also changed the stoichiometric balance of adhesive functional groups and affected the curing reaction of adhesives in the interfacial region.

No protonated amino group was detected on EGS surfaces because of possible complex formation between curing agents and zinc.

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