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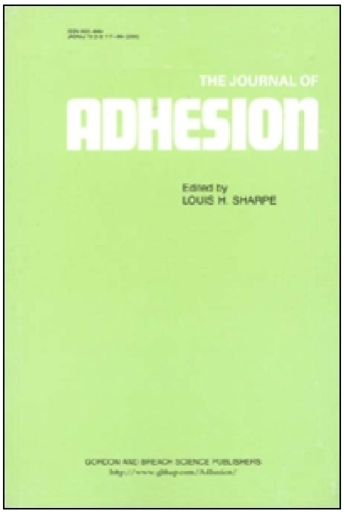

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Adhesive Bonding to Galvanized Steel: II. Substrate Chemistry, Morphology and Bond Failure Analysis

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Adhesive Bonding to Galvanized Steel

II. Substrate Chemistry, Morphology and Bond Failure Analysis

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Galvanized substrate morphology, oxide layer chemistry, bond failure modes, failure loci, and bondline corrosion have been investigated for adhesive bonds to galvanized steel. Significant differences in surface morphology were observed between the relatively smooth surfaces of "hot-dipped" substrates and the considerably rougher texture of "electroplated" substrates. The hot-dipped substrates were also chemically heterogeneous, with significant amounts of Al, Mg, Ca, and Pb, in addition to Zn, constituting the surface layer. For electroplated substrates, on the other hand, Zn was the major constituent. It was concluded that, for a given adhesive, low strengths and poor bond durability generally correlated with the minimum surface roughness and maximum chemical heterogeneity of the hot-dipped substrates. Higher strengths, and better durability, on the other hand, were observed for electroplated substrates, which showed the greater roughness, as well as chemically the more uniform surface.

Significantly, ESCA spectroscopy of fracture surfaces of unaged samples established that failure loci for both one and two-part epoxy adhesives included the oxide layer of the substrate. This was true for both hot-dipped, as well as electroplated substrates. For aged samples, scanning electron microscopy and X-ray diffraction analysis of failure surface identified zinc-based corrosion products present in the original bond area.

KEY WORDS Galvanized substrates; substrate morphology; surface composition; failure analysis; structural adhesives; bondline corrosion.

INTRODUCTION

Replacing sheet steel with galvanized steel in automotive applications has received a good deal of attention as a means of increasing product durability through improved corrosion resistance. However, the compatibility of galvanized steel with production processes such as welding, painting, and adhesive bonding, has yet to be firmly established. In particular, there have been no systematic studies of structural bonding to the range of galvanized steel substrates currently available. With this in mind, our work has been directed toward characterizing some of the fundamental aspects of structural adhesive bonding unique to galvanized steel. A companion paper[1] dealt with the adhesion and durability, as assessed from lap shear specimens, for five epoxy adhesives used to bond three different types of galvanized steel substrates.

As these laboratory lap shear tests for initial adhesion and bond durability progressed, it became increasingly apparent that the particular type of galvanized steel substrate used had a direct bearing on the results obtained. Furthermore, one and two-part epoxy adhesives showed differences in behavior among themselves (for a given type of galvanized substrate), as well as behavior which differed significantly from previous results, using the same adhesives, on cold rolled steel. Thus, we concluded that lap shear strength and durability would not, in themselves, provide sufficient information to assess structural bonding to galvanized steel.

We therefore paralleled the testing efforts with an investigation of those fundamental features of the galvanized substrates, and of adhesive bonds to these substrates, which would most likely have the greatest influence on bond strength and durability. These factors included galvanized substrate morphology and chemistry, bond failure modes, bond failure loci, and corrosion. On the basis of this work it has been possible to identify some common features of bonds to galvanized steel, as well as significant differences arising from adhesive and substrate variables, which control bond performance.

EXPERIMENTAL

Materials

The epoxy adhesives used in this work included one unfilled two-part system, two commercial one-part systems and two commercial two-part systems. A list of these adhesives and comments is given in Table I.

TABLE I
Adhesives

Designation†	Type	Remarks
EA2	Two-Part Epoxy	Imidazole-Cured Modified Epoxy Novolac
H2071	Two-Part Epoxy	Amine-Cured Epoxy; 1:1 (by weight) Catalyst/Resin Mix Ratio
H5188	Two-Part Epoxy	Triethylenetetramine-Cured Epoxy: 1:17 Mix Ratio
H1989	One-Part Epoxy	Latent Catalyst (dicyandiamide)-Cured Epoxy
O1055	One-Part Epoxy	Latent Catalyst (dicyandiamide)-Cured Epoxy

† These are coded designations for the adhesives investigated. The author may be contacted regarding their specific identity.

Three types of galvanized steel were used as bonding substrates. These included two hot-dipped products (ultrasmooth and minimum spangled) and one electrogalvanized product (Table II).

A total of ten different zinc-coated steels, representing a cross-section of available commercial products, were analyzed for surface chemical composition using Auger spectroscopy. A list of these materials is given in Table III (see also Table IV).

Sample preparation, testing and analysis

Standard lap shear samples were prepared and tested essentially in accordance with ASTM D1002. Details of surface preparation, adhesive cure, and results are given in Ref. 1. We have also adopted the same nomenclature used in Ref. 1. Additional designations are as follows: "Initial" samples were tested immediately after curing, "control" samples after aging under ambient conditions for a specified time, "water immersion" samples after 7-day, 60°C water immersion, and "scab corrosion" samples after a standard number of cycles (15 cycles = three weeks, 30 cycles = six weeks.)† Finally, "cleaned" samples were prepared by wiping with acetone prior to bonding, and "oiled" samples were dipped in a light mineral seal oil (Texaco ALMAG 1564) prior to bonding.

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† Details of the scab corrosion cycle may be found in Ref. 1.

TABLE II
Substrate materials

Designation	Thickness: Coating (μm, 0.001 in)	Thickness: Substrate (mm, in)	Coating Wt.	Coating type	Comments
Ultrasmooth A	12.5, 0.492	0.81, 0.032	G60†	Hot-dipped galvanized	Hot-dipped under N_2 atmosphere
Minimum Spangled A	12.5, 0.492	0.81, 0.032	G60	Hot-dipped galvanized	Zinc dust nucleated after hot-dipping
Electropolated A	8.7, 0.344	1.1, 0.042	G60	Electrogalvanized	Electroplated from $ZnSO_4$ solution
Cold Rolled Steel	—	0.94, 0.037	—	—	1010 Steel
Cold Rolled Steel	—	2.7, 0.093	—	—	1010 Steel
Zincrometal	15.5, 0.613	1.0, 0.040	—	Zincrometal	Zn-Cr chemical treatment followed by Zinc-rich (85% by wt.) primer

† G60 designates a coating thickness corresponding to 0.60 oz/ft^2.

TABLE III
Oxide characterization (*via* auger depth profiling) for selected commercial galvanized steels

Sample	Supplier	Coating weight	Oxide thicknesses (Å)	Major oxides	Minor surface constituents
Ultrasmooth A	1	G60†	80	Al, Ca, Zn	P, F, S, Cl, N
Ultrasmooth B	1	G90‡	250	Al, Mg, S, Zn, Pb	Cl, Ba, Ca, N
Ultrasmooth C	2	G90	60	Al	Zn, S
Ultrasmooth D	3	G90	70	Al, Zn	Ca, S, Cl; P(?)
Minimum Spangled A	1	G60	70	Al, Ca, Zn	Pb, S, Cl
Minimum Spangled B	1	G90	150	Al, Mg, P, Zn	Ba, Ca, S, Cl; Si(?)
Minimum Spangled C	4	G90	250	Al, Mg, Zn	Ca, P, Cl, S
Electroplated A	1	G60	50	Zn, Cl§	P, Ca, S; Ba(?)
Electroplated B	5	G60	100	Zn, Cl§	P, Ca, S
Electroplated C	5	G90	150	Zn, Cl§	P, Ca, S; Ba(?)

† 0.60 ounces/ft^2.
‡ 0.90 ounces/ft^2.
§ As chloride.

TABLE IV
Surface composition (in relative atomic %) for selected commercial galvanized steels)†

Sample	Supplier	Al	Ca	Zn	Mg	S	Cl	S	Pb	O
Ultrasmooth A	1	15	5.0	41	—	1.0	1.9	1.9	—	34
Ultrasmooth B	1	8	0.5	24	14	1.5	2.2	6.5	14	29
Ultrasmooth C	2	29	0.2	16	—	—	—	0.5	—	54
Ultrasmooth D	3	25	1.0	27	—	<0.5	0.8	1.1	—	45
Minimum Spangled A	1	19	6.0	28	—	2.5	2.0	1.2	—	32
Minimum Spangled B	1	11	1.0	29	16	3.0	1.1	2.1	—	38
Minimum Spangled C	4	18	3.0	27	7	0.5	1.5	2.4	—	40
Electroplated A	1	—	2.0	61	—	—	7.5	4.0	—	26
Electroplated B	5	—	1.5	61	—	2.0	3.0	0.9	—	32
Electroplated C	5	—	3.0	60	—	2.5	2.0	1.2	—	32

† Surface composition is computed neglecting the carbon signal.

Tensile yield strengths for cold-rolled steel and galvanized bonding substrates were determined according to a modified version of ASTM A370. Instead of the tapered specimens called for in this test method, rectangular samples (1.27 × 191 mm) were used. These samples were instrumented with a strain gage extensometer (#230-009, Instron Co.) and the load/displacement curves were recorded at various strain rates on the Instron Test Machine. Yield points were taken as the load corresponding to the initial onset of zero slope in the load/displacement curves.

Surface analysis by electron spectroscopy Galvanized surfaces were examined using a Physical Electronics Industries Model 549 scanning Auger microprobe. This technique samples the outermost 2 nm of the surface, and is sensitive to all elements except H and He, with detection limits ranging from 0.1 to several atomic percent (depending on elemental sensitivity). Semi-quantitative surface compositions, in terms of relative atomic percents (neglecting the carbon signal) of surface constituents, were calculated from peak-to-peak heights in the Auger spectrum. Auger depth profiles were also obtained for several samples by combining the Auger microprobe with an ion sputtering gun which removes surface layers. Approximate sputter rates from 25 to 75 Å/min (depending on the particular samples) were employed.

The Model 549 spectrometer was also used to obtain ESCA characterization of zinc coatings, as well as the locus of failure in bonded adhesive joints. A Mg anode was used, and resolution of the technique was approximately 0.5 eV. To determine the locus of failure, lap shear samples were pulled in the Instron Testing Machine, the bonded areas cut from the coupons, and these areas put immediately (within ten minutes after testing) into the vacuum chamber of the spectrometer. The locus of failure was then determined by comparing corresponding areas (~2 mm diameter) on matching failure surfaces to reference spectra for the non-bonded coating. In several cases, oxide thicknesses calculated from Auger depth profiles, and percent zinc as oxide, were used to fix the locus of failure. To distinguish Zn as metal *vs.* Zn as oxide, adjacent Zn (LMM) Auger peaks were separated using a curve resolution procedure, and relative peak heights compared. Separation of these peaks is approximately 5.0 eV.

Analysis of corrosion products in bonded area Corrosion products from bonded areas of lap shear coupons exposed to scab corrosion cycling were identified by X-ray diffraction analysis. Data were obtained using a Siemens D-500 automated diffractometer. Identification of the corrosion product was made by using the known chemistry (from electron microprobe analysis) of the material, together with the location and intensity of major peaks in the diffraction spectrum.

RESULTS AND DISCUSSION

Surface morphology of zinc coatings

The processes of hot-dipping and electroplating, currently used to zinc-coat sheet steel, give rise to very different surface morphologies. Ultrasmooth coatings are obtained by a hot-dip process carried out under nitrogen, while minimum spangled coatings (also a hot-dipped product) consist of crystals nucleated from zinc dust which is applied after hot-dipping. Figure 1A (ultrasmooth) and Figure 1B (minimum spangled) are scanning electron micrographs of typical surface regions of these two types of hot-dipped coating.† The ultrasmooth surface is quite free of sharp asperities, but patterns of surface cracks and occasional pits are apparent. Minimum spangled surfaces are somewhat rougher, although this additional roughness takes the form of waves or undulations rather than sharp edges. In contrast to these hot-dipped coatings, electroplated zinc coatings (such as that shown in Figure 1C) are quite rough. For the substrate material ("Electroplated A") we have used, plate-like zinc crystals are grown on the surface during electrodeposition from a $ZnSO_4$ solution. Figure 1C clearly illustrates the difference such crystals make in the surface morphology of electroplated coatings, compared to the smoother hot-dipped coatings.

Surface roughness, as well as the surface chemistry discussed below, is known to influence adhesion.[2] Generally, if the adhesive

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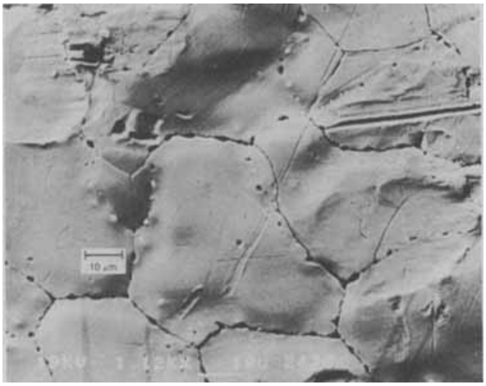
† A survey of the commercial materials listed in Table III revealed no significant differences in morphologies for "ultrasmooth," "minimum spangled," or "electroplated"-type coatings from different suppliers. Our discussion of morphologies in this section is therefore confined to substrate materials listed in Table II.

A. Ultrasmooth



B. Minimum Spangled

C. Electroplated

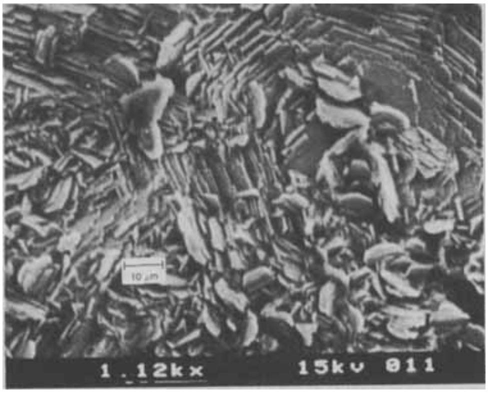


FIGURE 1 Surface morphologies of bonding substrates.

adequately wets the substrate, increasing the surface roughness will result in greater bond strength, particularly as measured by peel tests.[3] There is still some debate on the reasons for this trend, but an important factor appears to be the role surface asperities play in increasing the viscoelastic energy dissipation which accompanies joint loading and failure.[2] A major trend evident from lap shear tests[1] is that for a given adhesive, the lap shear strength of unaged samples generally increases as the substrates are varied in the order ultrasmooth $\leq$ minimum spangled $<$ electroplated. Surface morphology is therefore a major factor in the observed differences in initial (*i.e.*, unaged) bond strength.

Surface chemistry of zinc coatings

Although galvanized coatings are composed primarily of zinc in bulk, the surface composition will reflect other components which are present in the hot-dipping baths and the solutions used for electrodeposition. While surface chemistry may not greatly influence overall corrosion resistance compared to other factors (such as coating thickness), it may well have a deciding influence on adhesive bond durability. For example, trace materials left from surface treatments, as well as trace amounts of contaminant metals in alloys, have been shown to influence bond durability in accelerated adhesion tests.[4,5]

Commercial materials In addition to the bonding substrate surfaces used in lap shear and durability evaluations, the surfaces of seven different commercial galvanized steel products were analyzed. Bulk oxide composition and thickness (Table III) as well as surface composition were obtained.

Referring to Table III, oxide thicknesses varied from ~250 Å (for two of the hot-dipped products) to ~50 Å (an electroplated product). No clear trends in thickness were apparent with galvanized type. However, bulk oxide composition did separate into two distinct categories. For hot-dipped (both ultrasmooth and minimum spangled types) the oxides contained Al, Ca, Mg and, in some cases Pb, in addition to Zn. In fact, for one material ("Ultrasmooth C"), Al was found to be the major surface constituent, with Zn as a relatively minor surface component. The existence of Al-rich surface layers has also been reported by Ziane, *et al.*,[6] in their investigation of adhesion to hot-dipped galvanized substrates.

In distinct contrast, the electroplated coatings are characterized by oxides whose major component is Zn, present in crystal form (Figure 1C). Table IV lists Zn at a relative atomic percent of about sixty for the three electroplated surfaces, while the highest corresponding value for a hot-dipped surface is forty-one ("Ultrasmooth A"), with the other hot-dipped samples showing less than thirty-five percent Zn. In all cases, the hot-dipped surfaces showed amounts of Al and/or Ca, Mg, or Pb comparable to the amount of Zn.

Thus, for the commercial galvanized steels analyzed, the actual bonding surfaces are by no means composed primarily of zinc.

Surface chemistry of bonding substrates The three galvanized substrates used for lap shear strength and durability evaluations were Ultrasmooth A, Minimum Spangled A, and Electroplated A (Table II). Auger depth profiles of these three substrates are shown in Figure 2. As noted above for the commercial materials, the hot-dipping process produces surfaces which contain significant amounts of other elements in addition to Zn, while electroplating gives primarily Zn oxide, with only traces of other elements. The same is true in general for the three bonding substrates. The ultrasmooth substrate (Figure 2A) has significant amounts of Al,

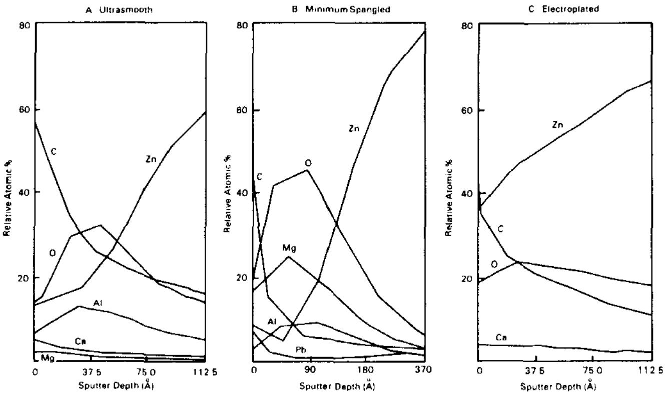


FIGURE 2 Auger depth profiles of bonding substrates.

Ca, and Mg in the surface, but Zn is still the major constituent. In contrast Figure 2B indicates that the minimum spangled substrate contains Mg as a major constituent, followed by Zn, Al, and Pb. Although in both cases the relative atomic percent of Zn in the hot-dipped coating increases with sputter depth, the actual bonding surface is chemically heterogeneous. Finally, and in contrast, the surface of the electroplated substrate (Figure 2C) contains primarily Zn, with small amounts of Ca.

Thus, to the significant differences already noted in morphology between the galvanized coating types, we may add the different surface chemistries discussed above. Just as surface roughness influences bond strength through viscoelastic energy dissipation, surface chemistry also influences strength and, probably to a greater degree, the environmental durability of the bond. A body of empirical evidence exists[4,5,7] which suggests, for example, that trace amounts of Mg in alloys of Al are detrimental to adhesive bond durability, measured as strength loss in water immersion environments. The mechanism is believed to be preferential corrosion of MgO-rich portions of the oxide film.[7] Likewise, surface treatments which modify the chemistry of the oxide layers by adding phosphates[8] can improve bond durability by retarding moisture degradation. Initial (unaged) adhesion seems to be less affected than durability, as demonstrated by the results of Ziane, *et al.*[6]

In general it is difficult to separate effects due solely to surface roughness from those due solely to surface chemistry. Consequently, it is difficult to establish unambiguous, fundamental cause/effect relationships between lap shear strengths and durabilities, on the one hand, and surface characteristics of the bonding substrates on the other. However, we can make the empirical observation that bond strengths and durabilities increase as surface roughness of the substrate increases, and that the bonded surface which is primarily composed of Zn (electroplated) is less susceptible to environmental degradation (in water-immersion and scab-corrosion environments[1]) than those hot-dipped (ultrasmooth, minimum spangled) surfaces characterized by chemical heterogeneity.

Classification of failure modes

Having established the nature of substrate morphology as well as bonding surface chemistry, we now turn to a classification of the

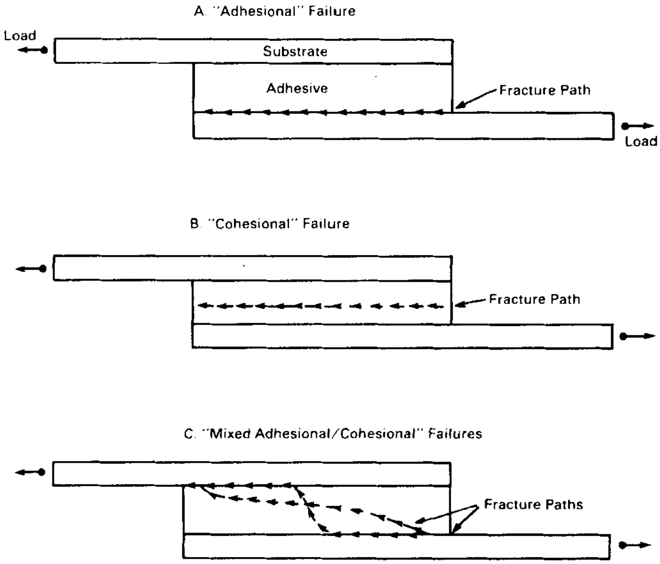


FIGURE 3 Schematic illustration of fracture paths producing (a) adhesional, (b) cohesional, and (c) mixed adhesional/cohesional failures in lap shear samples.

various failure modes evident in lap shear testing of the adhesive bonds.

Nomenclature and general features For classification purposes it is convenient to adopt the nomenclature defined below and illustrated in Figure 3. In addition to strengths obtained in lap shear testing, it is customary to report failure modes as being of "adhesional" or "cohesional" character. True "adhesional" failure occurs when a crack propagates at the material interface between the adhesive and the substrate. Likewise "cohesional" failure occurs when a crack propagates entirely within the adhesive itself. In practice one rarely, if ever, encounters examples of true adhesional failure, particularly with lap shear test samples. What may appear to be a bare metal surface resulting from adhesional failure may in reality be covered with patches or a very thin film of adhesive. Alternately, as we show below, failure can actually occur within the oxide layer itself, rather than at the material interface or within the adhesive. Nonetheless, it is still useful to adopt a scheme whereby we classify failures as "adhesional" if little visible adhesive remains on exposed metal surfaces, and "cohesional" if there is little visible evidence of bare metal on the surfaces of matching lap shear coupons.

Figure 3 illustrates, in schematic form, the terminology for adhesional, cohesional and mixed adhesional/cohesional failures. Within the mixed adhesional/cohesional category, a crack may propagate initially at the adhesive/substrate interface, but may be diverted into the adhesive after it has travelled some distance along its initial path. Various degrees of mixed failure result from different distances of initial propagation, as shown in Figure 3C.

It is well known and documented[9] that considerable normal stresses, with resulting rotation of the bonded area, can occur in stressed single lap shear joints. The magnitude of these normal stresses depends primarily on substrate stiffness. It is essential to keep in mind the actual nature of the stress distribution in the single lap shear configuration when attempting to correlate strengths and failure modes. Figure 4 illustrates schematically the essential features of this stress distribution. These are (1) normal (or "peel") stress distributions accompanying bond rotation, and (2) normal and shear stress concentrations at the indicated bond edges. Recalling Figure 3C, which illustrates a mixed adhesional/cohesional failure mode, these areas of shear and normal stress concentration will act as likely initiation sites for bond failure.

Review of trends from lap shear results With reference to Table I, three two-part and two one-part epoxy adhesives were used in assessing lap shear strengths and bond durabilities. It is important for the following discussion to review the general performance

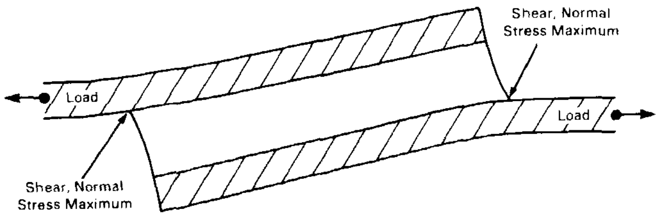


FIGURE 4 Schematic of lap shear sample exhibiting rotation (bending) and associated normal stress concentrations.

trends for these adhesives.[1] These trends can be summarized as follows:

1) For a given galvanized substrate type, the one-part epoxies evaluated generally give higher strengths than do two-part epoxies.

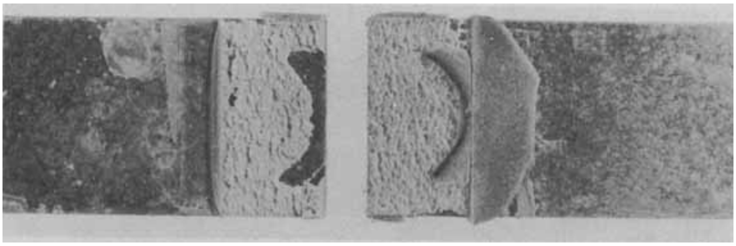
2) For a given galvanized substrate type, the one-part epoxies evaluated generally give higher strength retention values in water immersion at 60°C, and six-week scab-corrosion cycling, than do the two-part systems.

Illustration of failure modes in lap shear testing

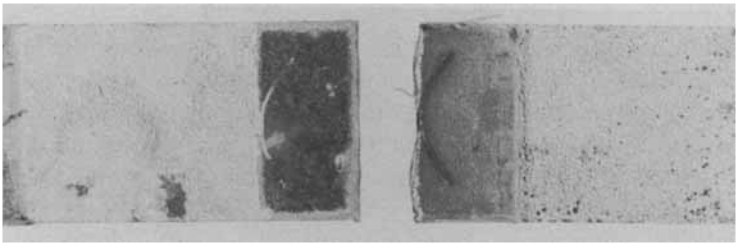
In this section, for each adhesive, we have classified the failure modes for initial or control samples, then for water immersion and scab corrosion samples. Following this, we discuss failure mode variation with substrate coating type, for a given test condition. The discussion of adhesives is arranged in the order of increasing strength and durability. Since under the present test conditions no significant differences were apparent in strength, durability, or failure modes between cleaned and oiled samples,[1] illustration of the failure modes includes both cleaned and oiled samples. Designations of "cleaned" or "oiled" are therefore omitted in the following discussion.

H2071 two-part epoxy Of all the adhesives tested, H2071 gave the clearest indication of cohesional failure under initial and control testing conditions. Figure 5A illustrates that matching failure surfaces (minimum spangled substrate) each contain large, uniform layers of adhesive. However, upon water immersion (Figure 5B) and scab corrosion cycling (Figure 5C), the failure mode changed to adhesional. For this adhesive, failure occurred either at very low load levels, or substrate/adhesive delamination occurred during environmental exposure. A general feature of all failure surfaces for samples exposed to accelerated tests involving moisture is evidence of moisture ingress into the bond area *via* diffusion, and subsequent substrate corrosion. This can be seen in Figure 5B (water immersion) as a light-colored rectangular ring on the bond area of the left-hand (metal) failure surface. On the left hand surface shown in Figure 5C (scab corrosion), premature bond failure has occurred,

A. Unaged "Initial Strength"



B. One Week Water Immersion



C. Six Week Scab Corrosion

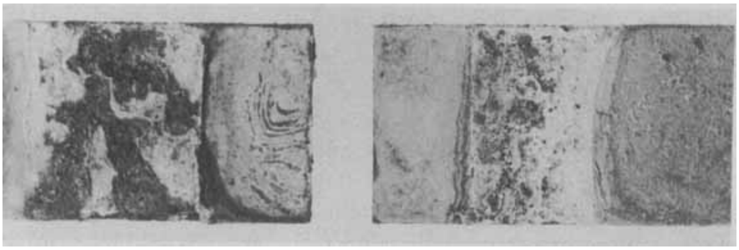


FIGURE 5 Matching lap shear failure surfaces for two-part Epoxy H2071 on minimum spangled galvanized steel.

and the rings now cover the majority of the metal side of the failure surface.

Initial and control sample failure modes for H2071 showed little variation with substrate type. Figures 6A (ultrasmooth) and 7A (electroplated), together with 5A (minimum spangled), all show primarily a cohesional failure of the adhesive. Very clear evidence of substrate corrosion following moisture and (in the case of scab-corrosion environments) salt solution ingress is evident in Figures 5C, 6B, and 7B. Note again, in all cases, the characteristic

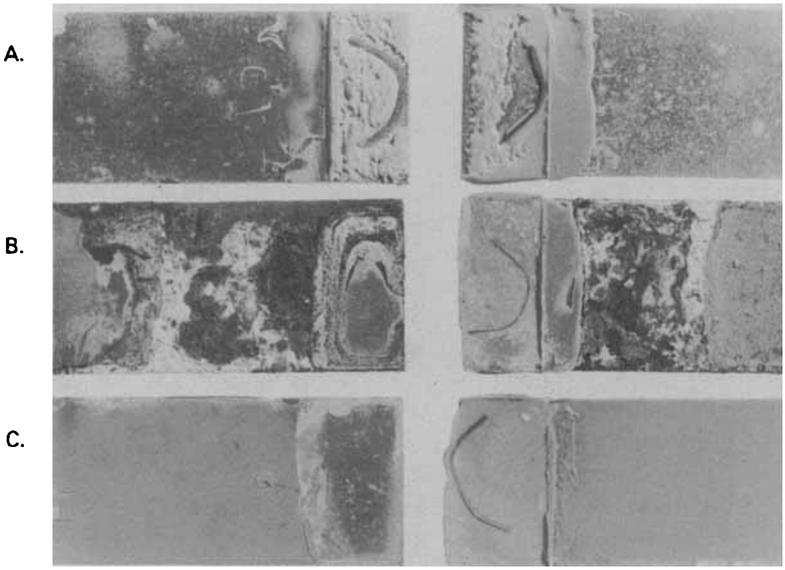


FIGURE 6 Matching lap shear failure surfaces for two-part Epoxy H2071 on ultrasmooth galvanized steel. (a) initial, (b) six-week scab corrosion, (c) one-week water immersion (sample ELPO-primed before exposure).

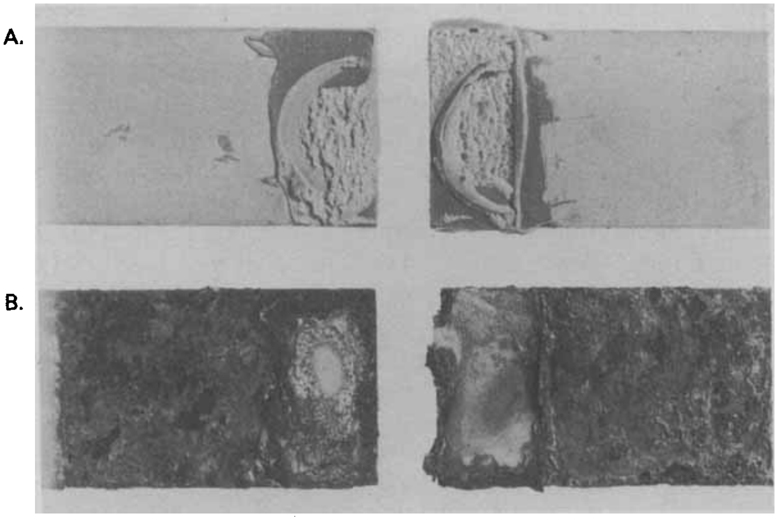


FIGURE 7 Matching lap shear failure surfaces for two-part Epoxy H2071 on electroplated galvanized steel. (a) initial, (b) six-week scab corrosion.

annular areas of corrosion. Bond deterioration was sufficient on ultrasmooth substrates to give total loss of adhesion after six weeks in scab corrosion.[1] However, small residual strengths were found in some cases for minimum spangled and electroplated substrates. No qualitative differences in failure surfaces for these substrates could be found to correlate with the observed variation in strength retention. When bonded samples were electrodeposition-primed prior to exposure, deterioration was sufficiently retarded to give a mean bond strength retention of around thirty percent, compared to zero on average for non-primed samples.[1] Figure 6C shows a typical primed sample after six-week scab-corrosion cycling. Bond corrosion as well as adhesional failure have evidently occurred. The extent of corrosion, however, is much less than for the unprotected sample (Figure 6B) above, since the primer coating has retarded (but not entirely eliminated) moisture ingress into the bond.

EA2 two-part epoxy Similar results were obtained for the EA2 adhesive as were obtained for the H2071 system on ultrasmooth and minimum spangled substrates, *i.e.*, low strengths (4000–8000 kPa) and poor to non-existent strength retention after environmental exposures. There was some improvement for EA2 on the electroplated substrate, however. In terms of failure modes, the most obvious difference between H2071 and EA2 is that EA2 failed adhesionally under initial and control testing conditions, rather than cohesionally. One reason for this is that EA2 is a brittle, unfilled, high modulus adhesive, while H2071 is considerably less brittle and is highly filled. Figure 8A (EA2 on ultrasmooth), and Figure 9A (EA2 on minimum spangled) can be contrasted with Figure 6A (H2071 on ultrasmooth) to illustrate this difference. Since the mean strength for EA2 was somewhat less than that measured for H2071 (for initial and control samples), H2071 showed slightly better adhesion to the ultrasmooth substrate. However, the effects of water immersion and scab corrosion cycling were more evident for H2071 than for EA2, as can be seen by comparing six week scab corrosion failure surfaces for H2071 on minimum spangled (Figure 5C) to those for EA2 on minimum spangled (Figure 9B). For EA2, the area of corrosion occupies a smaller portion of the total bond surface than is the case for H2071 after the same exposure time.

Since, as discussed previously, intrinsic adhesion is quite difficult

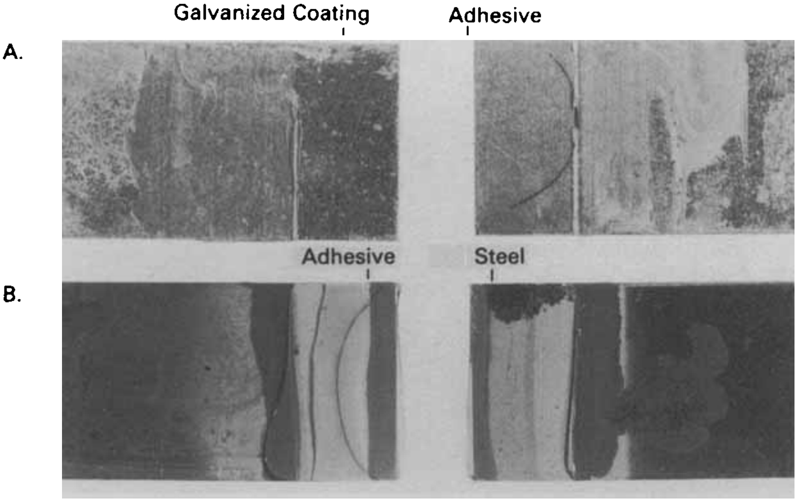


FIGURE 8 Matching lap shear failure surfaces for two-part Epoxy-EA2 on (a) ultrasmooth galvanized steel (initial) and (b) cold-rolled steel (initial).

to achieve on the ultrasmooth surface, adhesive strengths for EA2 on cleaned steel (of the same substrate thickness) are approximately twice as high as those recorded for the ultrasmooth galvanized surface. Corresponding differences in failure mode can be seen in Figures 8A (ultrasmooth) and 8B (cleaned steel). Adhesional

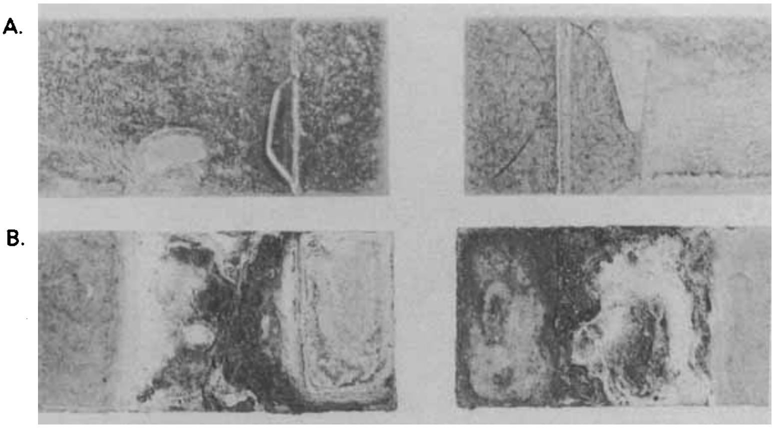


FIGURE 9 Matching lap shear failure surfaces for two-part Epoxy EA2 on minimum spangled galvanized steel. (a) initial, (b) six-week scab corrosion.

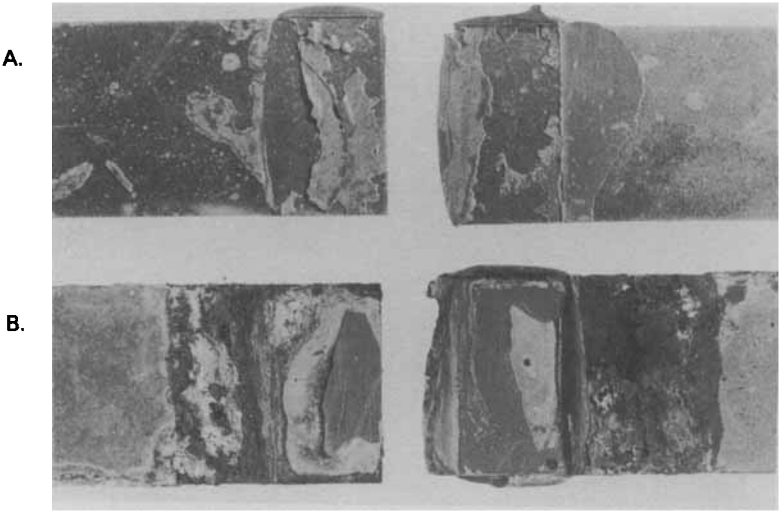


FIGURE 10 Matching lap shear failure surfaces for two-part Epoxy H5188 on ultrasmooth galvanized steel. (a) initial, (b) six-week scab corrosion.

failure is evident for ultrasmooth galvanized, while a mixed-mode failure is the case for cleaned steel (note the difference between these two modes illustrated schematically in Figure 3).

H5188 two-part epoxy In marked contrast to the low lap shear strengths and poor durabilities found for the other two-part epoxies, H5188 gave a mean strength and durability similar to those of the one-part epoxies, which consistently gave the best performance of all systems tested.

In addition to differences in strength and durability, the failure modes for H5188 also differed from those for EA2 and H2071. Figure 10A shows mixed adhesional/cohesional failure on ultrasmooth substrates, but failure of the adhesive appears to be brittle. This type of failure is illustrated by the crack path in Figure 3C. While also showing a mixed-mode failure, Figure 11A, on the other hand, shows that for H5188 on electroplated galvanized, the crack proceeded in large part through the adhesive itself. This corresponds to the more gradual path illustrated in Figure 3C. Also, cohesional failure of H5188 was observed on the 2.7 mm thick

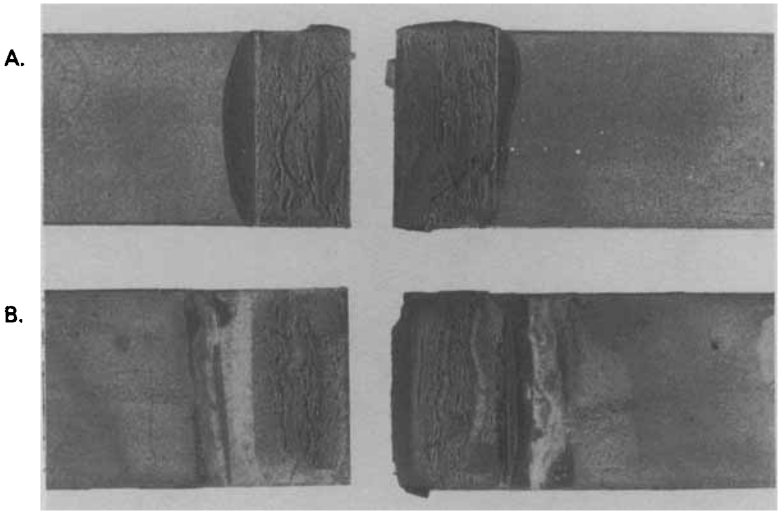


FIGURE 11 Matching lap shear failure surfaces for two-part Epoxy H5188 on electroplated galvanized steel. (a) initial, (b) one-week water immersion.

cleaned steel substrates (Figure 12). Thus, it appears that the failure mode for H5188 is quite specific to substrate type for initial and control testing conditions. This specificity persists in accelerated testing environments as well. Figure 11B shows the mixed-mode failure after water immersion for electroplated galvanized, and Figure 10B shows the more brittle mixed mode for ultrasmooth substrates after scab-corrosion cycling.

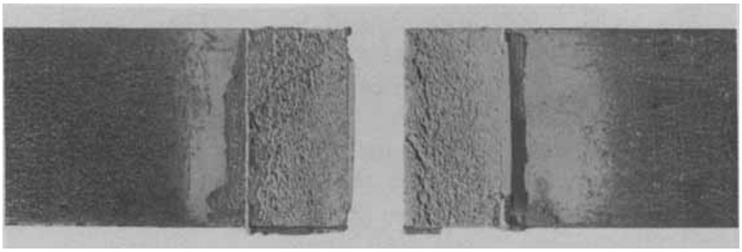


FIGURE 12 Matching lap shear failure surfaces for two-part Epoxy H5188 on cleaned cold rolled steel (coupon thickness is 2.7 mm).

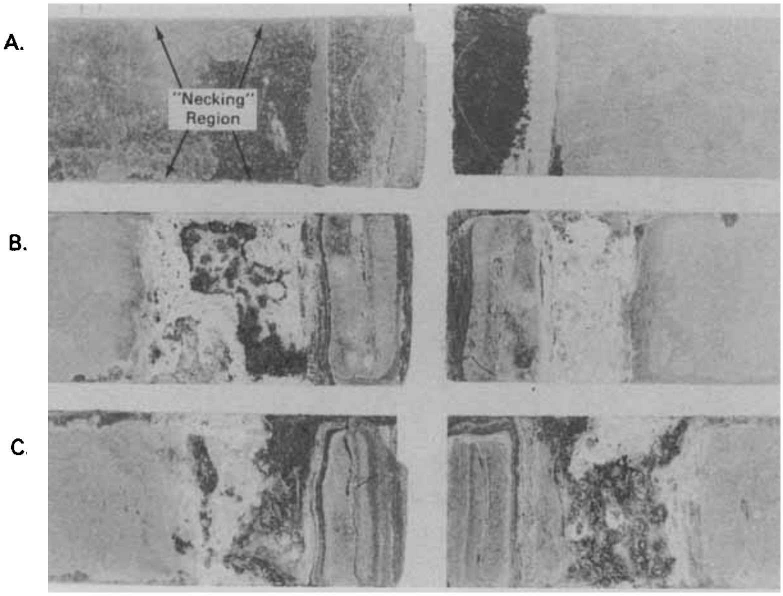


FIGURE 13 Matching lap shear failure surfaces for one-part Epoxy H1989 on ultrasmooth galvanized steel. (a) initial, (b) three-week scab corrosion, (c) six-week scab corrosion.

H1989 one-part-epoxy Both one-part epoxies, H1989 and O1055, gave similar lap shear strengths, trends in strengths, and durabilities, so discussion of failure modes is confined to the H1989 system. Generally, the failure mode for initial and control test conditions was mixed, with considerable amounts of adhesive left on both failure surfaces. As was the case for H5188 on electroplated substrates above, close inspection of Figures 13A, 14A and 15A reveals that failure involved crack propagation primarily through the adhesive itself when the bonds were to minimum spangled and electroplated substrates. A slightly more brittle failure (the shorter path through the adhesive in Figure 3C) is apparent for ultrasmooth substrates. Although there is a slight difference in failure mode between ultrasmooth and minimum spangled substrates, no corresponding differences in lap shear strength were observed.[1]

There was a difference in lap shear strength between the two hot-dipped galvanized substrates and the electroplated substrate,

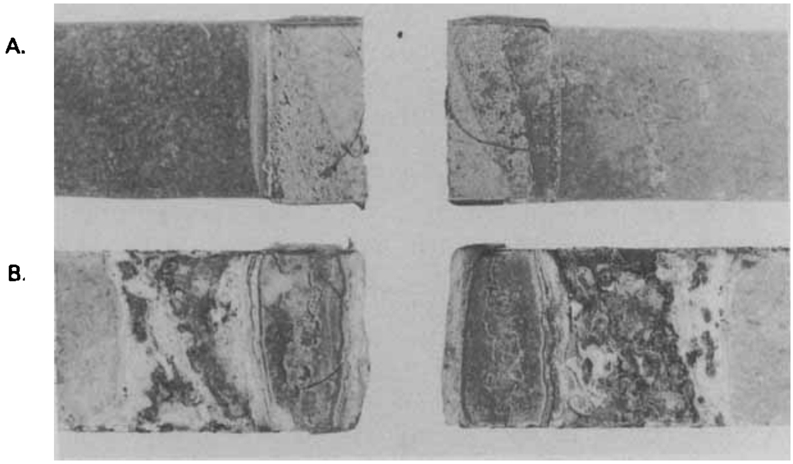


FIGURE 14 Matching lap shear failure surfaces for one-part Epoxy H1989 on minimum spangled galvanized steel (a) initial, (b) six-week scab corrosion.

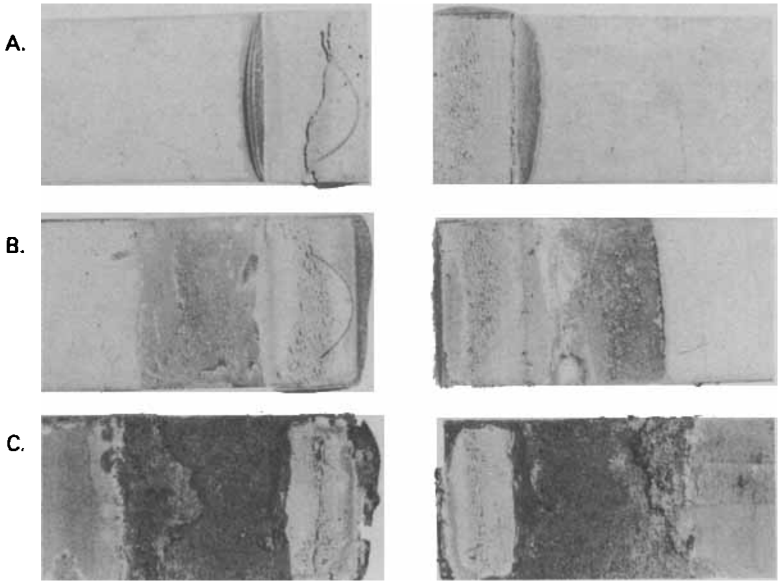


FIGURE 15 Matching lap shear failure surfaces for one-part Epoxy H1989 on electroplated galvanized steel. (a) initial, (b) one-week water immersion, (c) six-week scab corrosion.

however, with improvements of some 25% recorded for the electroplated samples. The fact that the failure mode is the same for minimum spangled and for electroplated substrates suggests that the higher strength of H1989 on electroplated may be attributable to differences in substrate thickness (1.1 mm for electroplated *versus* 0.091 mm for minimum spangled and ultrasmooth). For a given load level, the stress distribution in the bond will vary with substrate thickness, with thicker coupons giving a more uniform stress distribution.[9]

Characteristics of the failure modes for H1989 remained constant for a given substrate as test conditions ranged from initial and control, to water-immersion and to scab-corrosion exposures. The progressive influence of corrosion with increasing exposure time (increasing cycles in scab corrosion) can be seen by comparing Figures 13B (three weeks, or fifteen cycles) and 13C (six weeks, or thirty cycles). For the three-week exposure, corrosion has occurred primarily at the two edges of the bond overlap, while for six-weeks exposure, corrosion has occurred around the entire perimeter.

Since the mean lap shear strength for H1989 on ultrasmooth after six weeks in the scab-corrosion environment is almost half that for the electroplated substrate, it is instructive to compare three and six week failure surfaces for the two substrates. Figure 16 shows three (16A) and six (16B) week failure surfaces for electroplated substrates, which have distinctly less corrosion than do the corresponding surfaces for ultrasmooth substrate (Figure 13B, C). This evidence, together with the difference in mixed mode failure, suggests that the two cases may have qualitatively different underlying adhesion. It is likely that the different type or quality of adhesion is, as we noted in the discussion above, a function of vastly different surface morphologies, and surface chemistries, for the two substrates.

As one final point in our discussion of lap shear testing and associated failure modes, if adhesion to the substrate and mechanical strength of the adhesive itself were sufficient, yielding of the substrates, occurred prior to bond rupture. Thus, the lap shear coupon would show "necking" below the bonded area (see Figures 13A, 14A, and 15A, for example), and the load/displacement curve recorded during the testing would flatten out prior to break. Substrate yielding is a function of sample thickness, as can be seen in Table V, where the yield strengths for cold rolled steel

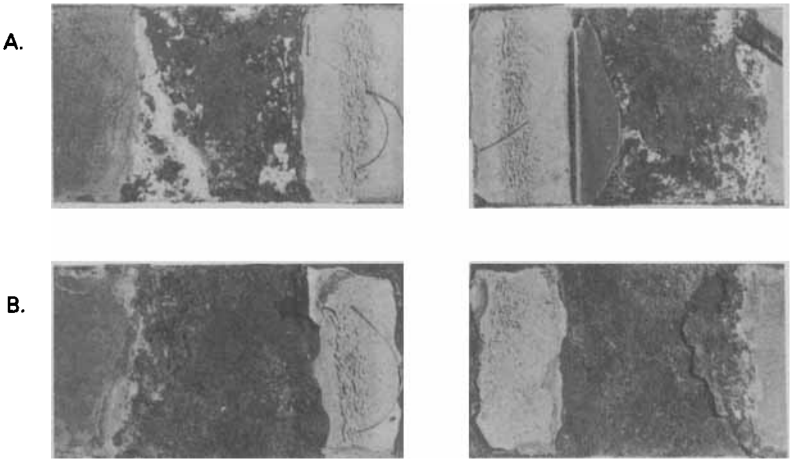


FIGURE 16 Matching lap shear failure surfaces for one-part Epoxy H1989 on electroplated galvanized steel (a) three-week scab corrosion, (b) six-week scab corrosion.

(0.94 mm), ultrasmooth (0.81 mm) and electroplated (1.1 mm) galvanized steels are compared. No significant variation of yield strength with strain rate was found. However, the load levels (in kN) listed in Table V fell within the range of loads (1–10 kN) recorded in lap shear testing.[1] Thus, we recall the comment above that the type of stress distribution within the adhesive bond is hardly one of pure shear, but will have significant normal stress components.

TABLE V
Yield strength (kN) for cold rolled steel and selected galvanized steel substrates

		Strain rate (mm/min)			
Sample	Thickness (mm)	0.51	1.3	2.5	5.0
Cold Rolled Steel	0.94	3.50	3.79	3.70	3.90
Ultrasmooth Galvanized	0.81	1.40	1.45	1.45	1.10
Electroplated Galvanized	1.1	2.25	2.34	2.20	2.20

Nature of the corrosion product

A powder X-ray diffraction study of the corrosion products on lap shear failure surfaces after scab-corrosion cycling revealed that moisture and electrolyte at the zinc surface produce basic zinc chloride: $ZnCl_2 \cdot 4Zn(OH)_2$. No differences in the X-ray diffraction spectra were detected as the galvanized substrate type was varied, suggesting that surface composition, although markedly different (recall Tables III, IV), did not influence the bulk of the corrosion product. Thus, although trace amounts may have been present, no Mg, Al, Pb, or Ca salts were detected in the analyses.

A likely sequence of events leading to the observed corrosion products is as follows. During exposure of the bonds to 49°C, 85% relative humidity in the initial part of the cycle, water diffuses into the bond a certain characteristic distance, which is a function of humidity level and the moisture diffusivity of the adhesive. As is well known and documented,[10] bonds are susceptible to degradation in the presence of moisture. Subsequent soaking of the samples in 5% NaCl at room temperature (the second step of the cycle) provides the opportunity for formation of the corrosion product. Every subsequent cycle introduces a new annular ring of corrosion products (see Figure 14B, for example).

Figure 17A is a scanning electron micrograph of a portion of adhesive remaining on the failure surface after scab corrosion. This illustrates that the basic zinc salt collects on the adhesive surface, as well as on the metal surface, since the adhesive no longer adheres to the substrate. Figure 17B shows the boundary between electrodeposited zinc crystals (upper portion of micrograph) and the corrosion product (lower portion). Note especially the different morphologies of the two regions. An X-ray map of the distribution of chlorine confirmed that the lower portion was high in chlorine, as we would expect from the presence of the basic zinc chloride salt.

Locus of bond failure *Via* ESCA analysis

For all of its practical utility as a classification tool, visual and/or microscopic examination of bond failure cannot determine the precise locus of bond failure. The ESCA technique offers a chemical means of accomplishing this task, by comparing the

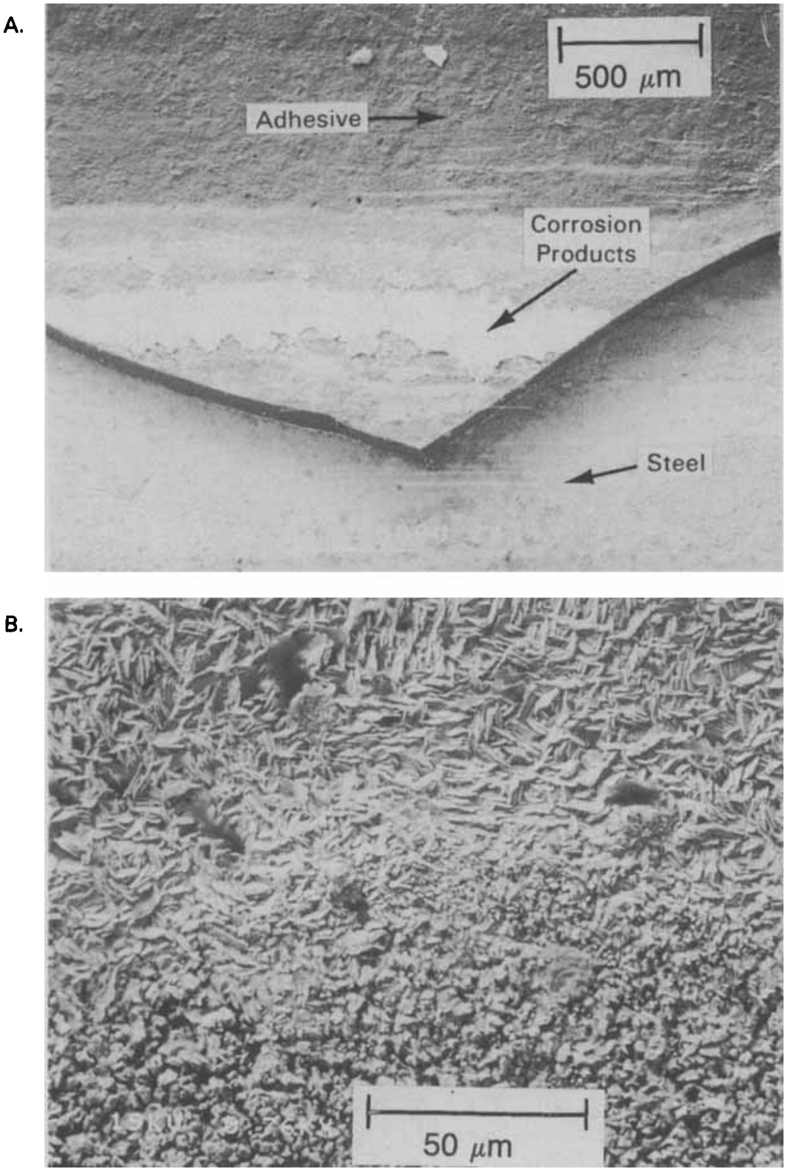


FIGURE 17 Scanning electron micrographs of corrosion product on (a) adhesive surface and (b) substrate surface after bond failure.

non-bonded metal substrate chemistry with the chemistry of the failure surfaces. We have used this technique to establish the locus of failure in unaged (*i.e.*, "initial strength") lap shear samples, which were bonded with the EA2 two-part epoxy (ultrasmooth, minimum spangled, and electroplated) and the one-part epoxy H1989 (ultrasmooth only). In interpreting the results below we have used as a general guideline that the presence of metallic elements (such as Zn, Pb, Al, Mg) on the adhesive material after fracture is an indication that failure has occurred (at least in part) in the substrate. The spectra and surface compositions given are considered typical of the sampled areas, since several spots (~2 mm diameter) on each surface were sampled and compared for reproducibility.

The EA2/ultrasmooth system Recalling the earlier discussion (see also Figure 8), EA2 on ultrasmooth substrates gave strong evidence of failure at the adhesive/substrate interface ("adhesional" failure). ESCA analysis was therefore directed toward the matching sides of failure surfaces: an "adhesive" side, and a "metal" side. For the sample fractured for ESCA analysis two such pairs of matching areas on the failure surfaces were examined. Visual examination of the adhesive revealed what have been termed a "light" area and a "dark" area (see Figure 8B, right side micrograph). Portions of the ESCA spectra for these areas, the corresponding areas on the matching surfaces, and the spectrum for the control (non-bonded) surface are shown in Figures 18 and 19.

It is immediately obvious from Figures 18 and 19 that both "adhesive" areas contain residual Zn, so that the fracture path has included portions of the galvanized surface. However, Figures 18 and 19 also indicate that the fracture is much nearer the oxide/adhesive interface for the "light" area, than the "dark" area. Note that the intensities of Zn, Pb, Al and Mg peaks for the metal side of the light area (Figure 18B) more closely approximate those for the control surface (Figure 18A) than do those for the metal side of the dark area (Figure 19B). In fact, the adhesive side of the dark area (Figure 19C) more closely resembles the control non-bonded surface (compare Figure 18C, where there is little evidence of metals other than Zn). Table VI, which gives a breakdown of

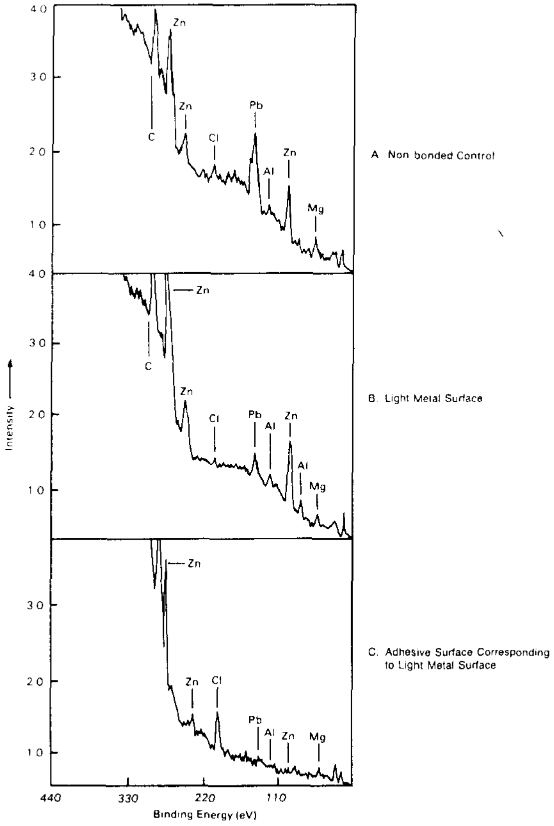
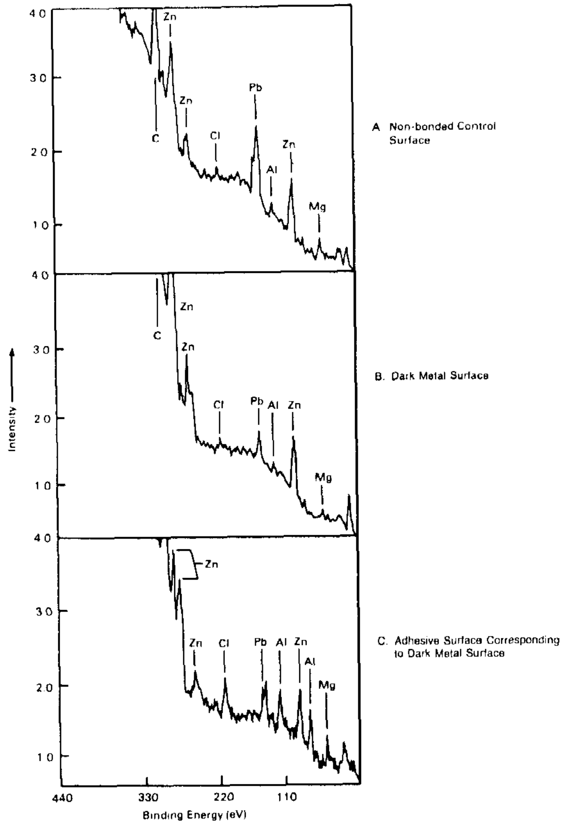


FIGURE 18 ESCA spectra for determination of EA2/ultrasmooth galvanized failure locus: "light" adhesive area.

surface compositions, also shows that the light metal surface is closer in composition, particularly in Zn present as metal *versus* oxide, to the control surface than the dark metal surface. Higher percentages of Zn as metal would presumably indicate that the failure locus was within the oxide layer, since a larger amount of the underlying coating would be sampled.

Based on the ESCA analysis, Figure 20 shows the probable locus of failure for the EA2/ultrasmooth sample. The path obviously included significant portions of the oxide layer before being diverted


A Non-bonded Control Surface

B. Dark Metal Surface

C. Adhesive Surface Corresponding to Dark Metal Surface

FIGURE 19 ESCA spectra for determination of EA2/ultrasmooth galvanized failure locus: "dark" adhesive area.

into the adhesive. This accords with the conclusions reached by Commerçon and Wightman.[11] It is therefore obvious that the mechanical strength of the galvanized surface can influence bond integrity. Similar conclusions have been reached for other systems.[2]

EA2/minimum spangled and EA2/electroplated systems ESCA spectra of matching sides of failure surfaces for minimum spangled and for electroplated bonding substrates were very similar to those shown in Figures 18 and 19. In both cases strong peaks for the

TABLE VI
Surface chemistry (*via* ESCA analysis) of lap shear failure: EA2/cleaned ultrasmooth galvanized

	Atomic % surface composition								% Zn As	
Surface	Zn	Mg	Al	Pb	O	C	Cl	N	Metal	Oxide
Adhesive Surface (Dark Area)	1	3	4	0.2	31	58	1	1	<10	>90
Adhesive Surface (Light Area)	≤0.1	1	<1	<1	27	69	1	2	—	—
Dark Metal Surface	5	4	4	<1	30	56	1	<1	40	60
Light Metal Surface	5	7	6	<1	35	47	1	<1	20	80
Non-Bonded Control Surface	3	8	4	1	32	53	<1	<1	10	90

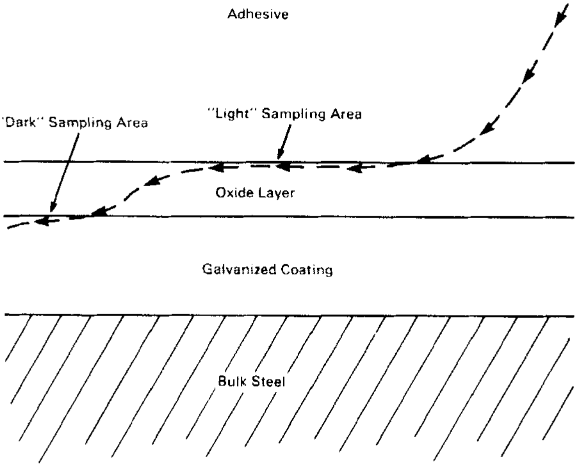


FIGURE 20 Schematic interpretation of failure locus from ESCA spectra. Arrows denote failure path.

metals which constitute the surfaces of the non-bonded control substrates were found in spectra taken from the adhesive surfaces. "Adhesional" failure, the general descriptive term given these examples in the classification scheme above, should therefore be understood to include the possibility of failure within the oxide layer as well as at the adhesive/substrate interface.

H1989/ultrasmooth system From our previous discussion of lap shear failures in the H1989/ultrasmooth system, it will be recalled that the failure mode was "mixed", with the metal areas showing in the inner regions near the back edges, and adhesive at the front edges (see Figure 13A). ESCA sampling was directed to matching sides of the inner region (a metal side and adhesive side opposite).

Figure 21 confirms that again the locus of bond failure has included the substrate oxide layer, since the spectrum for the adhesive portion (Figure 21C) contains peaks for Zn, as well as Pb and Mg. The Si peaks in Figure 21C are most likely due to filler in the adhesive.

Thus the lower strengths for the two-part epoxy (EA2) (~6400 kPa) as well as the higher strengths for the one-part epoxy (H1989) (~15,100 kPa) both reflect failure initiation in the oxide region. In the case of EA2, however, the stress in the bond was

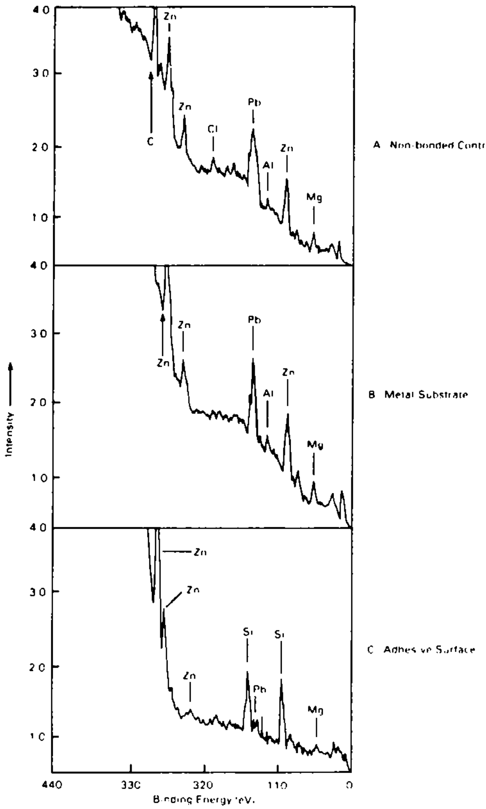


FIGURE 21 ESCA spectra for determination of H1989/ultrasmooth galvanized failure locus.

primarily shear, since no significant substrate deformation occurred prior to bond rupture. In contrast, high normal stress was a contributing factor to rupture in the H1989 system, particularly in those areas of shear and normal stress concentrations shown in Figure 4.

SUMMARY AND CONCLUSIONS

Galvanized substrate morphology, oxide layer chemistry, bond failure modes, failure loci, and bond corrosion have been investigated in the context of structural adhesive bonding to galvanized steel. The work detailed in this paper complements an investigation of lap shear strengths and environmental durability.[1]

Specific conclusions of this work are as follows:

1) Significant differences in surface morphology were observed between hot-dipped substrates (such as ultrasmooth and minimum spangled) and electroplated substrates. The hot-dipped substrates were free of large scale roughness, although shallow waves and surface cracks were apparent. Electroplated substrates, in contrast, were very rough due to the growth of a dense layer of sharp, plate-like zinc crystals in the electrodeposition process.

2) Just as surface morphology varied with the type of process used to galvanize the bonding substrate, so did the chemistry of the surface and of the oxide layer. For example, Zn was not the major constituent at the surface of the hot-dipped substrates. Significant amounts of Al, Mg, Ca, and Pb were also present. For electroplated substrates, on the other hand, Zn was the major constituent, and no measurable amounts of other metals were present.

3) Lap-shear failure modes, ranging from "cohesional" (failure in the adhesive) to "adhesional" (apparent failure at the adhesive/substrate interface) were observed. Furthermore, changes occurred in failure mode from cohesional (for "initial" and "control" samples) to adhesional (for samples aged in water-immersion or scab-corrosion accelerated-testing environments) for both one-part and two-part epoxies.

4) For samples exposed to scab-corrosion cycling, progressive growth of annular corrosion rings in the bonded area suggested a mechanism for bond strength deterioration: moisture diffusion through the adhesive is followed by sorption of aqueous electrolyte into the debonded areas. The resultant corrosion product was identified by X-ray diffraction analysis as the basic zinc chloride salt $ZnCl_2 \cdot 4Zn(OH)_2$. The bulk of the corrosion product was constant with galvanized substrate type, and no evidence of other metallic salts was found.

5) ESCA spectroscopy of fracture surfaces of unaged samples established that failure loci for both a two-part and a one-part adhesive included the oxide layer of the substrate. This was true for ultrasmooth and minimum spangled hot-dipped, as well as electroplated substrates; and for low as well as high lap shear strengths.

On the basis of this work we have concluded that surface morphology exerts a major influence on bond strength for initial and control samples, while variations in surface chemistry can influence bond durability in samples exposed to accelerated environmental tests. Thus, for a given adhesive, low strengths and poor durability correlated with the minimum surface roughness and maximum chemical heterogeneity of hot-dipped substrates. Higher strengths, and better durability, on the other hand, were observed for the electroplated substrates, which showed the greatest roughness, as well as chemically the most uniform surface and oxide layer.

Acknowledgments

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