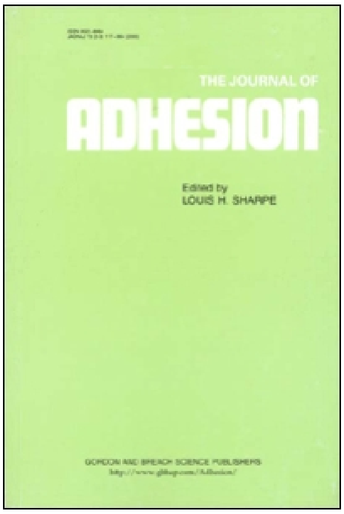

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Improvement of the Durability of Zinc-Coated Steel/Epoxy Bonded Joints*

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The durability properties of bonded lap shear joints made from an epoxy/dicyandiamide adhesive and hot-dipped galvanized (G2F) or electroplated-phosphated (EZ2) steel have been investigated. The degradation mechanisms have been studied after three accelerated ageing tests: the "cataplasme humide" ("C.H.T."), immersion ("I.T."), and salt spray ("S.S.T.") tests. X-ray photoelectron spectroscopy (XPS) analysis of fracture surfaces after ageing have shown that anodic dissolution of the zinc-coating is responsible for debonding in all cases and that intergranular corrosion phenomena account for poorer performances of the hot-dipped galvanized substrate during "C.H.T." and "I.T." Silane coupling agents were successfully used as primers on both substrates to increase the hydrolytic stability of the metal/adhesive interface. XPS results indicate that both the interfacial dissolution of the phosphate coating of EZ2 and intergranular corrosion of G2F are delayed for silane-primed specimens. The observed improvements do not appear to depend on the nature of the silane coupling agents. Alkylsilanes have been found to perform as well as silanes having a group capable of reacting with the epoxy/dicyandiamide system.

Additional tests were carried out in view of the possible application of organosilane reagents as additives in corrosion-protective oils. Good durability properties have been obtained by priming the metal coupons with a standard oil/silane mixture prior to bonding.

When corrosion was the controlling degradation mechanism as is the case during the salt spray test, silane treated specimens did not generally perform better than control specimens.

KEY WORDS adhesion; zinc-coated steel; galvanized steel; epoxy adhesives; durability; corrosion; silane coupling agents; X-ray photoelectron spectroscopy.

1 INTRODUCTION

Galvanized steel has so far proven to be the best choice made by the automotive industry to counteract the detrimental effects of corrosion on car bodies. Currently,

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*One of a Collection of papers honoring A. J. Kinloch, the recipient in February 1992 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M*.

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it is mainly bonded with hot-curing epoxy adhesives which both perform for structural applications and are easy to use on the production line. A systematic study of the degradation mechanisms of bonded parts is complicated by the variety of galvanizing processes, which makes it necessary to consider each surface individually. Foister *et al.* showed, from results obtained with three galvanized substrates and five different one and two-part epoxy adhesives, that the durability properties of galvanized substrates strongly depend on their surface morphology as well as their chemistry.[1,2] Furthermore, besides the differences between hot-dipped galvanized and electroplated steel, the zinc coating is nowadays often phosphated to ease the working of the metal sheets and the painting stage.

Dickie *et al.* demonstrated that the degradation of cold-rolled or electrogalvanized steel/epoxy bonded joints proceeds by anodic dissolution of the metal substrate.[3] In the particular case of hot-dipped galvanized steel, the segregation of elements such as Al and Pb on the surface would be responsible for intergranular corrosion of zinc and facilitate the formation of a weak boundary layer.[4]

The use of organosilane reagents as adhesion promoters for surface coatings and adhesives on glass substrates has proved to be very beneficial. It has been extensively studied and reviewed by Plueddemann.[5] A significant amount of work has also been carried out to determine the role of silane coupling agents in metal/adhesive interfaces.[7] The extent of improvement in durability properties is strongly influenced by the nature of ageing and adhesion tests, and the specifics of the metal/adhesive system. For example, it is impossible to extrapolate results obtained with silane coupling agents on aluminium/cold-cured epoxy bonded joints, using torque shear or direct pull-off tests results, to galvanized steel bonded with hot-curing epoxies and which must fulfill specific durability requirements defined by the automotive industry.

The present paper describes an investigation of the durability and fracture surfaces of bonded joints made from one commercial hot-curing epoxy adhesive and two zinc-coated substrates. The metal/adhesive interfaces were investigated by XPS after immersion, "cataplasme humide," and salt spray tests to determine the mechanisms responsible for debonding.

Attempts to increase the stability of the interfacial adhesion against humidity by mixing organosilanes into the adhesive were unsuccessful. Spectacular improvements were observed by using the silanes as primers. The influence of the functionality of the silane on the durability of the bonded joints was thereafter investigated.

2 EXPERIMENTAL METHODS

2.1 Preparation of the Bonded Joints

The galvanized substrates were supplied by SOLLAC (France) and are referred to as G2F (0.7 mm ultrasmooth hot-dipped glavanized steel, Ra = 1.5 μm) and EZ2 (0.7 mm electroplated-phosphated steel, Ra = 2 μm). A 0.7 mm cold-rolled steel substrate (XES, Ra = 2.2 μm), also supplied by SOLLAC, was used for comparison of durability properties. The metal coupons were degreased in an ultrasonic bath for 15 min. prior to bonding. Lap shear samples were made with a 12.5 mm × 25 mm bond overlap and a 0.2 mm bond thickness. They were cured with a one-component adhesive supplied by CECA (France) and referred to as "1K-A" in the text. After cure (1 hour at 200°C), the samples were either aged following the "cataplasme humide" (70°C) or salt spray (35°C, 5% NaCl) test procedures, or immersed in water in air-tight containers at 90°C. This latter screening test was developed because of the great amount of organofunctional silanes studied and the cost both in time and space of the "cataplasme humide" procedure. The durability tests are respectively abbreviated "C.H.T.," "S.S.T.," and "I.T." in the text. The "cataplasme humide" test is often used in the automotive industry. It simulates the degradation mechanisms likely to take place inside door panels for example. The preparation of the samples is the following: after curing of the adhesive, the bonded joints are wrapped in cotton, soaked with distilled water, sealed in polyethylene bags, and placed in an oven for periods up to 28 days. Before testing, they are transferred to a freezer at −20°C for 2 hours and allowed to rest at room temperature for an additional 4 hours.

Preliminary studies showed, in agreement with earlier work,[1,2] that 1K-A performs better than do most two-part epoxies. The best durability properties among all adhesive systems tested were, however, obtained with toughened acrylic adhesives. For adhesives giving similar shear strengths in the unaged state, strength retentions of G2F/adhesive joints after 8 days of immersion in water at 80°C could be rated: 2 part epoxies (between 5–30%) < 1K-A (60%) < toughened acrylics (100%).

Figure 1 illustrates the great differences in ageing properties of EZ2, G2F, and XES/1K-A bonded joints. The three metals tested displayed similar shear strengths

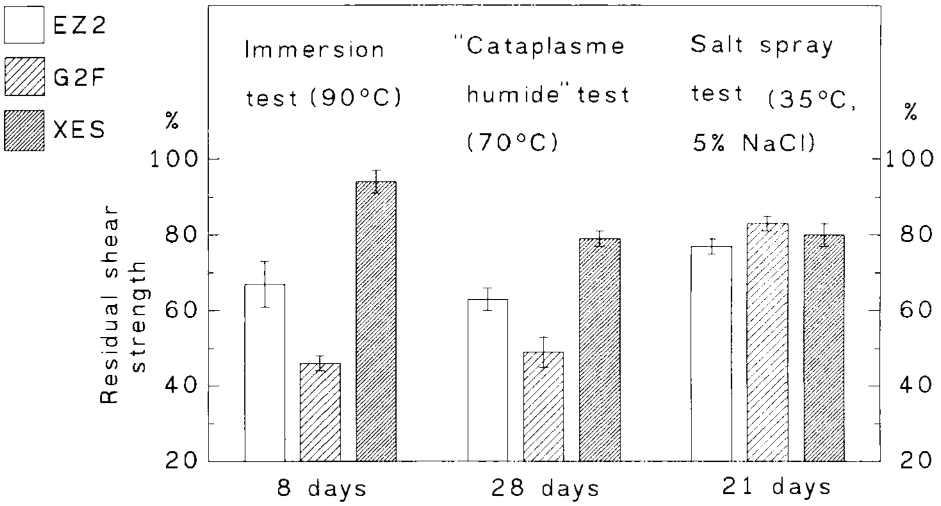


FIGURE 1 Durability of EZ2, G2F, and XES/1K-A bonded joints after "I.T.," "C.H.T.," and "S.S.T."

before durability testing, around, 12, 13, and 14 MPa, respectively, for EZ2, G2F, and XES.

While bonded joints made from cold-rolled steel performed very well during the three ageing tests (strength retentions higher than 75% in all cases), poor results were obtained following immersion or "cataplasme humide" tests for both galvanized substrates. The fracture surfaces also clearly reflected these differences in performance. For cold-rolled steel specimens, the area corroded on the adhesive and metal interfacial sides was restricted to a very small area close to the edges of the bonded joints, whereas both fracture surfaces of electrogalvanized and hot-dipped substrates were widely corroded, the latter substrate being corroded over the whole surface. After salt spray testing, the extent of corrosion was about the same for the three substrates.

These results can readily be understood by considering the ability of zinc to corrode in media deprived of oxygen,[12] and illustrate the importance of taking into account the intrinsic corrosion properties of the adherend in the prediction of the durability of bonded joints.

Foister *et al.* recently demonstrated with the help of activation energies derived from adhesion loss, corrosion, and diffusion measurements in water, that the degradation of cold-rolled steel/epoxy bonded joints is controlled by diffusion of water.[6] For electroplated substrates, corrosion was found to be responsible for debonding.

2.2 Surface Analysis

XPS analyses were performed with a SSI model 301 spectrometer using a focused (diameter of the irradiated area: 600 μm) monochromatic AlKα radiation (10 kV, 10 mA). The residual pressure in the chamber was about 5×10^{-8} Pa. The sample charging effects were minimized with a low energy flood gun (5 eV). The calibration of the spectra was done with the C(1s) (284.8 eV) from the carbonaceous contaminant overlayer. The spectra were recorded in the constant pass energy (50 eV) mode. XPS peaks were decomposed into subcomponents using a Gaussian (80%)-Lorentzian (20%) curve-fitting program with a nonlinear (Shirley)[8] background. Quantitative analyses were performed with the sensitivity factors given by Scofield.[9]

3 RESULTS AND DISCUSSION

3.1 Analysis of the Substrates

XPS analyses of EZ2 and G2F substrates are summarized in Table I. The surface of EZ2 mainly consists of $Zn_3(PO_4)_2.4H_2O$ and mixed alkali phosphate salts such as Na_3PO_4, $Ca_3(PO_4)_2$, and K_3PO_4. SIMS measurements revealed that the phosphate coating is less than 0.2 μm thick for an overall thickness of the zinc coating of *ca.* 7 μm. Such a thin coating is not efficient as a further protection against corrosion. It is suitable for paint and organic finishes and acts as a lubricating agent to facilitate the working of the metal sheets. The hot-dipped galvanized substrate has a thicker (*ca.* 10 μm) coating less evenly distributed on the base metal than the coating of EZ2 (verified by SEM on a cross-section). The high concentration of Al

TABLE I
Atomic composition of the substrates (EZ2, G2F, 1K-A) and unaged interfacial fracture surfaces

				Electroplated steel (EZ2)		Hot-dip. galv. steel (G2F)	
Element (At.%)	EZ2 substrate	G2F substrate	1K-A adhesive Bulk cross-section	Interfacial adhesive side	Interfacial metal side	Interfacial adhesive side	Interfacial metal side
%C	31.4	36.0	63.4	68.3	27.2	59.2	60.3
%O	39.8	41.7	25.1	20.1	38.5	27.3	25.5
%N	0.9	3.2	3.3	4.2	3.4	3.3	3.2
%Zn	11.3	6.1	0.0	0.2	14.3	0.0	0.8
%Al	0.0	12.5	0.0	0.0	0.0	0.0	2.8
%Si	0.0	0.0	7.3	3.5	0.0	6.2	5.2
%P	6.8	0.0	0.0	0.0	7.6	0.0	0.0
%Na	4.3	0.0	0.0	0.0	5.2	0.0	0.0
%Ca	1.5	0.0	0.0	0.0	1.5	0.0	0.0
%K	4.0	0.0	0.0	0.0	2.2	0.0	0.0
%Mg	0.0	0.0	1.0	3.4	0.0	4.0	2.2
%Pb	0.0	0.7	0.0	0.0	0.0	0.0	0.0
%Cl	0.0	0.0	0.0	0.4	0.0	0.0	0.0

near the surface (12.5% against 6.1% of Zn) is due both to its low solubility in the zinc matrix and its high oxidation potential. The same is true for Pb which is also detectable on the surface of the clean substrate (0.7%). Maeda *et al.* showed that the cooling rate of freshly galvanized metal sheets has an important influence on the diffusion of Al to the surface, the quickest cooling rates giving the highest Al contents in the top layers of the zinc coating.[4] SNMS and SIMS depth-profiling measurements carried out on G2F showed that the concentration of Al at 0.2 μm below the surface level is more than 50 times lower than the concentration of zinc.

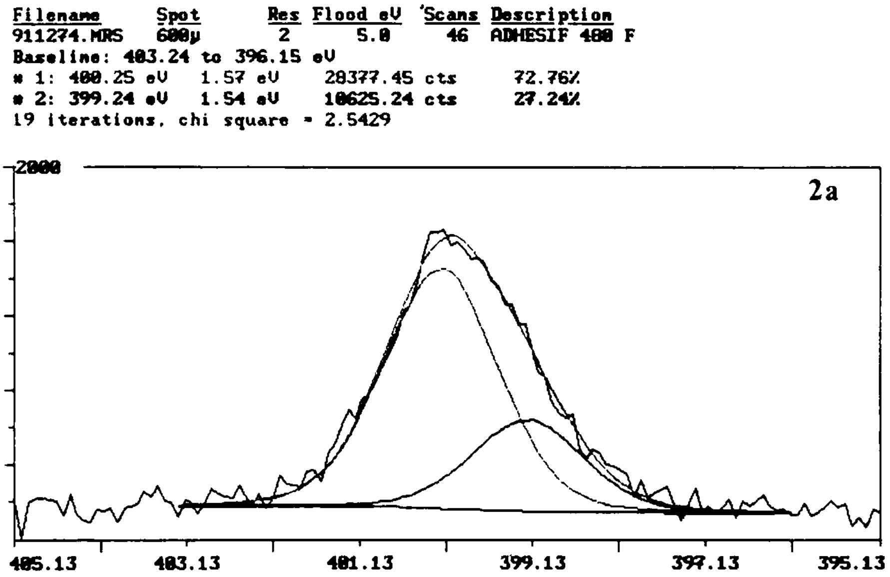
3.2 Fracture Surfaces of Unaged Bonded Joints

EZ2/1K-A fracture surfaces Bonded joints made from non-phosphated electroplated steels and the hot-curing epoxy 1K-A failed within the adhesive, with approximately equal amounts of adhesive on both sides. The initial shear strength of phosphated (EZ2) specimens was about 20% lower than that measured for simply electroplated specimens (both substrates had the same thickness and were electroplated following the same process). XPS analysis of EZ2/1K-A fracture surfaces revealed that the thin phosphate coating deposited on zinc had a detrimental effect on initial adhesion.

The interfacial metal surface of unaged bonded joints had almost the same atomic composition as the clean EZ2 substrate (see Table I). The percentage of the characteristic elements in the phosphate coating was slightly enhanced after curing. This may be attributable to partial absorption or displacement of the contamination layer. No chemical transformation of the coating occurred as a result of curing the adhesive. No characteristic component of the adhesive (fillers) on the metal side or of the phosphate coating on the adhesive side were detectable, giving evidence of a mainly adhesional failure. The only significant difference was the increase of the N/C % ratio on the metal side: 12.5% against 2.9% and 5.2%, respectively, for the clean metal substrate and bulk adhesive. These results suggest that dicyandiamide tends to segregate at the metal/adhesive interface during curing of the adhesive. Hong *et al.* investigated the interfaces of bonded joints made from various metals and a polyamide cured adhesive. They observed a higher adsorption of the curing agent on electrogalvanized steel than on cold-rolled steel or aluminium substrates.[10] These localized concentrations of highly polar materials can increase the hydrophilic character and consequently the degradation rate of the interphase region.

G2F/1K-A fracture surfaces A preliminary examination of the fracture surfaces with a stereomicroscope showed that the failure was within a layer of adhesive. This was later confirmed by XPS measurements. The elemental compositions of a cross-section of the bulk adhesive and both interfacial adhesive and metal sides were very similar (see Table I). 0.8% of Zn and 2.8% of Al were also measured on the metal interfacial side, giving evidence that the failure was cohesive within a layer of adhesive near the metal/adhesive interface. The N/C ratios found on the adhesive and metal sides were nearly identical (respectively, 5.6% and 5.3%). Taking into account the "cohesive nature" of G2F/1K-A failure, this may indicate that the segregation of the curing agent was localized in a region very close to the metal/adhesive interface. After mechanical testing, particles of metal were sometimes visible on the adhesive side, indicating a poor adhesion of the zinc coating to the base metal.

Presence of a "protonated amino species" at the adhesive/metal interface Hong *et al.* reported the formation of a "protonated amino species" on the interfacial metal side of oil-contaminated, cold-rolled steel/epoxy bonded joints cured with an amidoamine curing agent having a low amine number.[11] Later, they could also pinpoint a "protonated amino species" in the interfacial region formed between an epoxy/polyamide adhesive and cold-rolled steel or 2024 aluminium.[10] Surprisingly, no protonation was detected when using an electrogalvanized steel substrate. Figure 2 compares the N(1s) high resolution spectra of EZ2 and G2F/1K-A interfacial



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Filename     Spot       Res Flood eV 'Scans Description
911274.MRS   600μ        2      5.0     46  ADHESIF 400 F
Baseline: 403.24 to 396.15 eV
# 1: 400.25 eV   1.57 eV    28377.45 cts     72.76%
# 2: 399.24 eV   1.54 eV    10625.24 cts     27.24%
19 iterations, chi square = 2.5429
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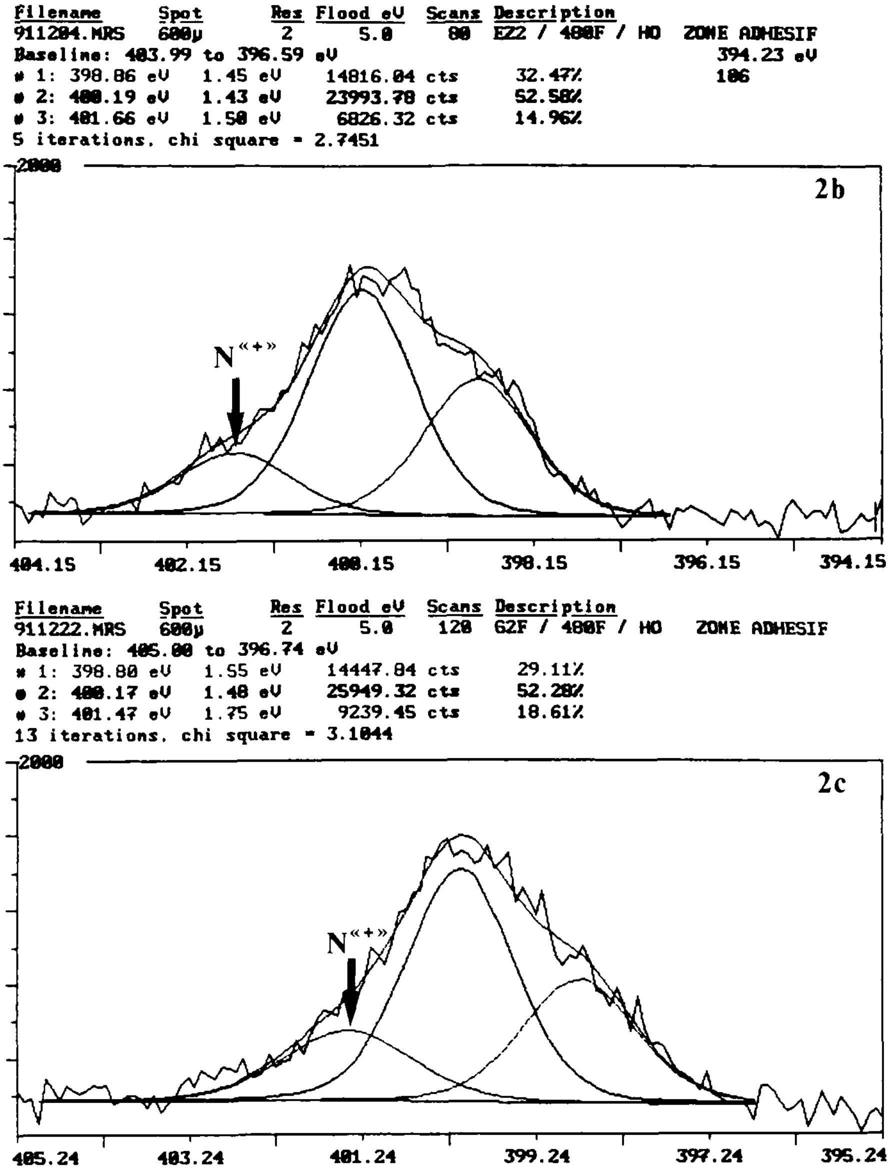

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Filename      Spot      Res  Flood eV  Scans  Description
911204.MRS    600µ       2      5.0      80   EZ2 / 400F / HO  ZONE ADHESIF
Baseline: 403.99 to 396.59 eV                                   394.23 eV
# 1: 398.86 eV   1.45 eV   14816.04 cts     32.47%              106
# 2: 400.19 eV   1.43 eV   23993.78 cts     52.58%
# 3: 401.66 eV   1.50 eV    6826.32 cts     14.96%
5 iterations, chi square = 2.7451
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Filename      Spot      Res  Flood eV  Scans  Description
911222.MRS    600µ       2      5.0     120   G2F / 400F / HO   ZONE ADHESIF
Baseline: 405.00 to 396.74 eV
# 1: 398.80 eV   1.55 eV   14447.84 cts     29.11%
● 2: 400.17 eV   1.48 eV   25949.32 cts     52.28%
# 3: 401.47 eV   1.75 eV    9239.45 cts     18.61%
13 iterations, chi square = 3.1044
```

FIGURE 2 N(1s) spectra obtained from a cross-section of the bulk adhesive (2a) and EZ2 (2b) or G2F/1K-A (2c) interfacial adhesive side.

adhesive side with the N(1s) high resolution spectra of a cross-section of the bulk adhesive. Both interfacial regions display, in addition to the characteristic bands associated with N≡C, N=C (at *ca.* 399 eV) and N – C, N – H (at *ca.* 400 eV), an extra peak shifted 1.5 eV at higher binding energies. This may indicate that an acid/base reaction between dicyandiamide and the hydroxylated surfaces took place for both galvanized substrates. The N(1s) high resolution spectra of specimens primed with an amino coupling agent (DAMO, see Figure 10) did not display this extra band, probably because the aminosilane was coordinated to zinc and prevented further protonation of the adhesive.

3.3 Fracture Surfaces after Ageing Tests

EZ2/1K-A fracture surfaces after "C.H.T." and "I.T." Figures 3a and b present, respectively, a photograph and a schematization of the four distinct zones observed on the fracture surfaces of EZ2/1K-A lap shear joints after "I.T.," "C.H.T.," or "S.S.T." They consist of:

Zone 1: inside the bonded joint, a white metallic zone of the same aspect as the interfacial metal side of the unaged specimen

Zone 2: adjacent to Zone 1, a zone where the adhesive does not seem to have been badly degraded by the ingress of water during ageing tests

Zone 3: a widely corroded black area near the edges of the bonded joint

Zone 4: a zone associated with Zone 3 where the adhesive has the typical "smooth aspect" of an adhesive after delamination.

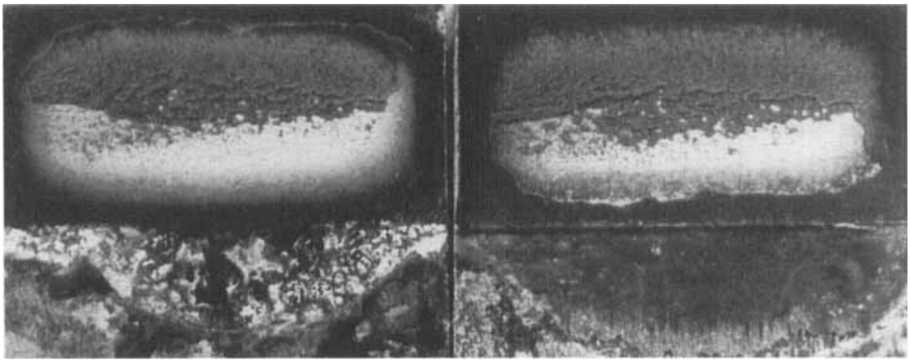


FIGURE 3a EZ2/1K-A fracture surfaces after 28 days of "cataplasme humide" test (70°C).

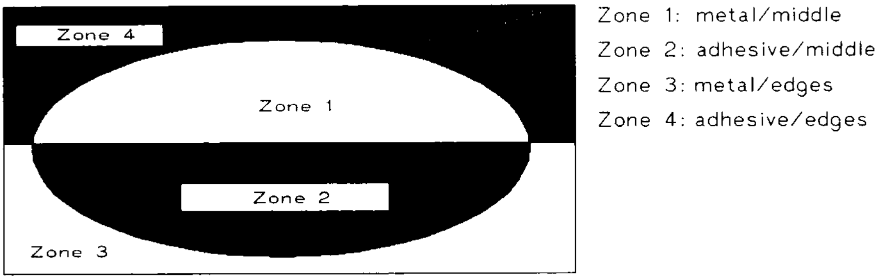


FIGURE 3b Schematization of an EZ2/1K-A fracture surface after "cataplasme humide", immersion, or salt spray test.

At the metal/adhesive interface, which is likely to be deficient in oxygen during immersion or "cataplasme humide" tests, zinc normally corrodes with the evolution of hydrogen.[12] A great amount of small blisters, probably stemming from a high pressure of hydrogen underneath the adhesive coating, was visible around the bonded joints after both durability tests. No blisters were found after the salt spray test. The main corrosion products likely to be formed, zinc oxide, hydroxide, and chloride are normally white and the deep black colour observed near the edges of the aged specimens is probably due to the understochiometry of ZnO (excess of Zn in the ZnO lattice).[13]

It is interesting to note that the concentrations of N and N/C ratios in the four zones remained unchanged after the ageing test. Hence, there is no evidence of any segregation of dicyandiamide to the interface during the ageing process, as was observed, for example, by Devries *et al.* in the case of epoxy-modified-PVC/galvanized steel joints.[14] The concentrations of Zn, and main components of the phosphate coating (P + Na + Ca + K) in the various zones of the fracture surfaces after "C.H.T." or "I.T.," were very similar and are presented in Figure 4. After "C.H.T.," no characteristic component of the phosphate layer was detectable in Zone 3, near the edges of the bonded joint. Further inside the bonded joint, in Zone 1, the concentrations of Na and K were negligible and that of P was 4%, compared with 7.6% for the interfacial metal side of the unaged fracture surface. The same effects were observed after "I.T.," suggesting that the ingress of water inside the bonded joint was responsible for a progressive dissolution of the phosphate coating. This is not surprising if we take into consideration the high solubility of orthophosphate salts in hot water.[15] Nevertheless, a similar strength retention was measured for bonded joints made from non-phosphated substrates analogous

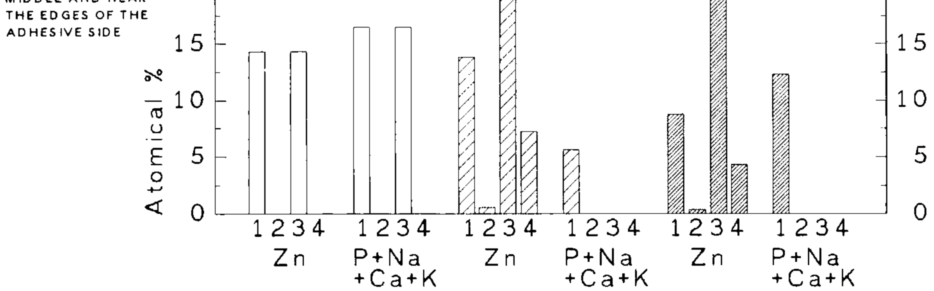


FIGURE 4 Evolution of Zn and P + Na + Ca + K atomic % in the 4 zones of EZ2/1K-A fracture surfaces.

to EZ2 (same base material and electroplating process): 74%, against 75% for EZ2, after 21 days of "C.H.T." This demonstrates that although the phosphate coating is responsible for poor initial adhesion, its dissolution is not a critical factor in the adhesion loss. The important zinc concentrations found in the corroded black area (Zone 3) and on the interfacial adhesive side near the edges of the bonded joint (Zone 4) show that the degradation process is dominated by anodic dissolution of the metal substrate. Samples of pure ZnO, $Zn(OH)_2$, the dicyandiamide and ethylenediamine complexes of $ZnCl_2$, and $ZnCl_2$, were analyzed in order to identify the corrosion products. The Zn(2p) binding energies measured for these five species were respectively 1021.3, 1021.8, 1022.3, 1022.4 and 1023.1 eV. The Zn Auger spectra were also acquired. The Zn(2p) binding energies of Zn in zinc oxide/hydroxide and zinc amino-derivatives are relatively close to each other; it is possible to resolve ZnO and $Zn(OH)_2$ in the presence of amino residues without ambiguity by checking the positions and ratio of the O(1s) bands which are well separated for both species (530.4 and 531.9 eV, respectively). Thus, the black corrosion product near the edges of the interfacial metal side in Zone 3 consisted mainly of ZnO and $Zn(OH)_2$. The $Zn(OH)_2/ZnO$ ratios were equal to 0.6 and 0.5 respectively, after "C.H.T." and "I.T."

G2F/1K-A fracture surfaces after "C.H.T." and "I.T." The failure, which was cohesive within a layer of adhesive for unaged bonded joints, occurred in a layer of zinc corrosion products after "C.H.T." and "I.T." The residual strength measured after 28 days of "C.H.T." was only 45%, compared with 71% for EZ2. The changes of Al and Zn atomic percentages in the various zones of fracture surfaces after "C.H.T." and "I.T." are presented in Figure 5. The progressive decrease in aluminium concentration between Zone 1 and Zone 3 (6% to 2.1%) is associated with a strong increase in zinc concentration (13% to 28.2%) after "C.H.T." Devillers *et*

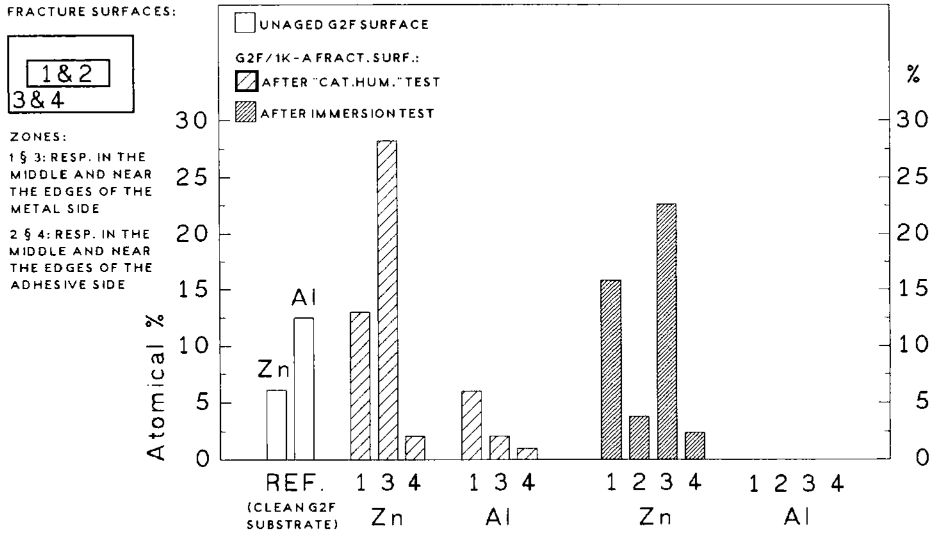


FIGURE 5 Evolution of Zn and Al atomic % in the various zones of G2F/1K-A fracture surfaces.

al. pointed out that passive aluminium is usually more noble than Zn in neutral water.[12] In this case, the large Al/Zn ratio determined on the surface of G2F would be equivalent to a large cathode/anode ratio and would accelerate the dissolution of the zinc substrate. But, in most cases, the electrolyte generated at the metal/adhesive interface is likely to be alkaline (possible reasons: uncured amino residues, dissolutions of hydroxides); Al thus becomes anodic to zinc and is preferentially dissolved.[12] Al and Zn were present on both interfacial adhesive and metal sides after "C.H.T.," whereas only Zn was present at a high level after "I.T." Maeda *et al.* showed that the alloying of Zn with elements such as Al and Pb results in accelerated grain boundary corrosion at galvanized steel/epoxy interfaces.[4] The high temperature at which the "I.T." was carried out (90°C as compared with 70°C for the "C.H.T.") probably contributed to accelerated intergranular corrosion by diffusion at grain boundaries, so that no aluminium residues could be found in Zones 1 and 3 of the fracture surfaces. A SEM picture of Zone 3 after "I.T." (see Fig. 6) shows cracking effects at grain boundaries. The $Zn(OH)_2/ZnO$ ratios in Zone 3 were found to be close to the ones observed for EZ2/1K-A fracture surfaces: 0.4 and 0.5, respectively, after "C.H.T." and "I.T."

We observed in the case of SNMS depth profiling measurements that the concentration of aluminium within the zinc coating of G2F was well above the level necessary to spark off grain boundary corrosion in an Al-Zn alloy, around 0.03 wt.%.[12] The concentration of aluminium in the galvanizing bath itself is 0.15 wt.%.

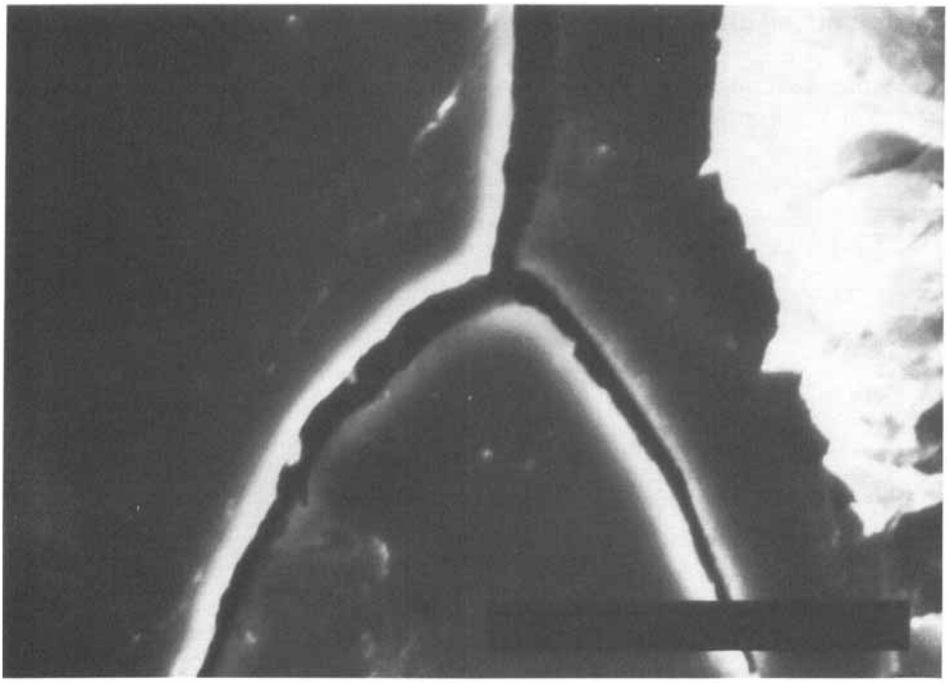


FIGURE 6 Scanning electron micrograph of G2F/1K-A interfacial metal side after immersion test: cracking effects due to intergranular corrosion at grain boundaries (×5000).

In order to assess the influence of Al in the bulk metal on the speed of grain boundary corrosion, electroplated and hot-dipped galvanized metal coupons were sandblasted with a 100–120 μm mesh corundum under a low pressure of air (4 bar). A couple of cross sections of the freshly prepared specimens were then analyzed by SEM to check the residual thickness of the zinc coating, *ca.* 6 μm. After 21 days of "cataplasme humide" testing, bonded joints prepared from both sandblasted substrates had similar residual strengths (75% and 77%, respectively, for EZ2 and G2F) and displayed identical fracture surfaces. Assuming that the sandblasting process modified the morphologies of the substrate surfaces to a comparable extent, this experiment would indicate that a content of aluminium higher than 0.03 wt.% within the zinc coating does not significantly affect the kinetics of the degradation process of hot-dipped galvanized/epoxy bonded joints. The use of a smooth sandblasting process, although difficult to put into practice, could then be a way of levelling the performances of zinc-coated substrates (the performances of sandblasted EZ2 and G2F/1K-A bonded joints were also slightly higher than the ones observed for degreased specimens after salt spray test).

EZ2 and G2F/1K-A fracture surfaces after salt spray test The salt spray test is usually carried out at a relatively low temperature (35°C) so that the diffusion of water is not the main controlling parameter of the degradation mechanism, as is observed during immersion of the joints. The very detrimental effects of grain boundary corrosion previously described on G2F samples were also limited after "S.S.T." For these reasons, the strength retentions for both hot-dipped and electroplated substrates after 6 weeks of testing were close to each other, *ca.* 80% (see Fig. 1).

The main features of the XPS analyses of EZ2 and G2F/1K-A fracture surfaces after "S.S.T." are presented in Figure 7. The concentration of Cl increases from

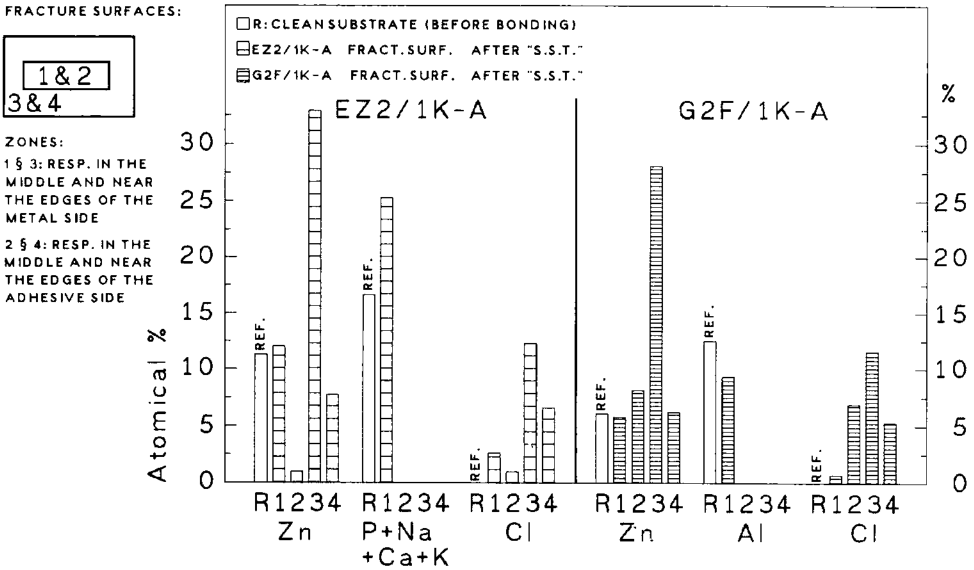


FIGURE 7 XPS analysis of the 4 zones of EZ2 and G2F/1K-A fracture surfaces after salt spray test.

2.6% to 12.3% on the interfacial metal side as we move from the middle (Zone 1) to the edges of EZ2/1K-A bonded joints (Zone 3). The phosphate coating does not display any sign of dissolution in Zone 1. Therefore, contrary to what was observed after "I.T.," the extent of degradation effects merely due to diffusion of water is limited to a small area preceeding the corrosion front. The higher concentrations of alkali metal salts and phosphorus observed on the interfacial metal side, 25.3% against 16.6% for the "clean" metal surface, are likely to be due to partial displacement of the contamination layer (8.6% of C at 284.8 eV against 23.1% for the reference substrate). Figure 8 illustrates the clear transition between Zone 1 and Zone 3. The atomic % of the three corrosion products present in Zone 1, ZnO, $Zn(OH)_2$, and $ZnCl_2$ are, respectively, 5.2%, 15.0%, and 12.7% (overall concentration of Zn: 32.9%).

The same effects are observed on G2F/1K-A fracture surfaces, providing evidence of a degradation mechanism less dominated by diffusion of water. Concentrations of Al and Zn close to the ones found on the clean substrate are measured in Zone 1 (9.3% and 5.3% respectively, against 12.5% and 6.1%). Only C, O, Zn, and Cl are detectable in Zone 3. The same species plus N are detectable in Zone 4. Therefore, the failure, which is cohesive inside a layer of adhesive for unaged specimens, is located in a layer of zinc corrosion products consisting of ZnO, $Zn(OH)_2$, and $ZnCl_2$ after "S.S.T." (respectively, 9%, 14.6% and 4.5% for an overall concentration of 28.1 atomic % Zn in Zone 3). Apart from the characteristic

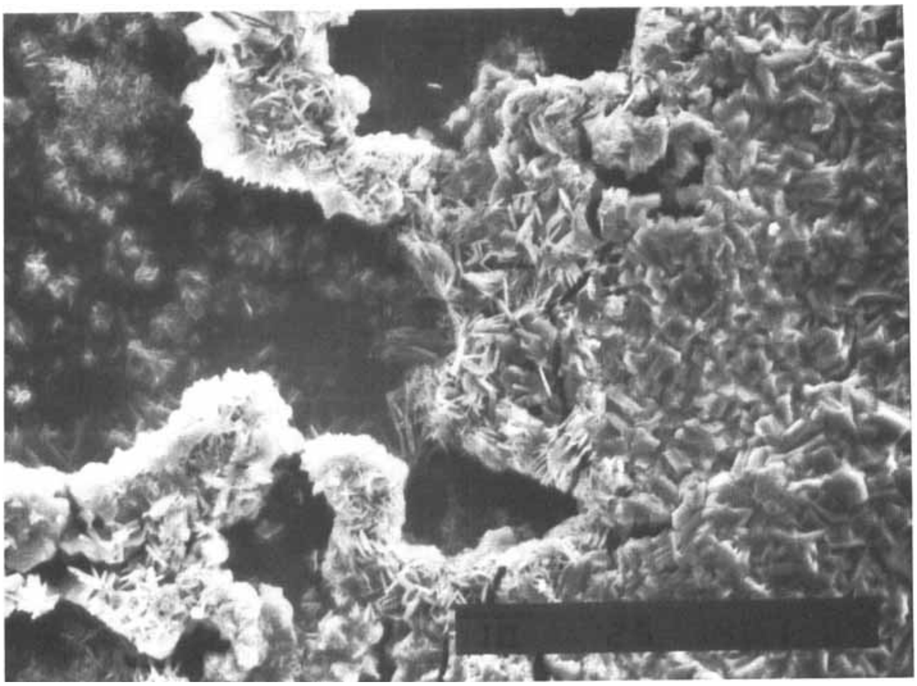
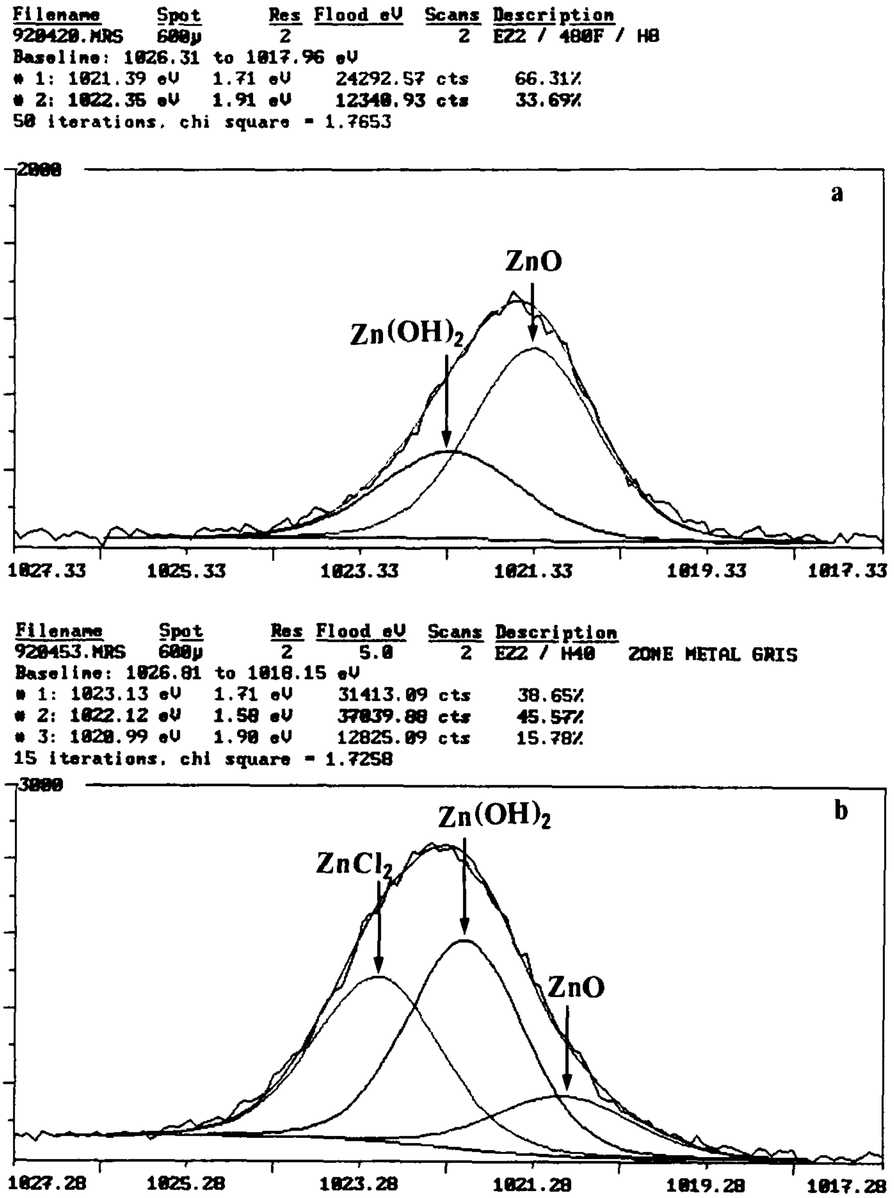


FIGURE 8 Scanning electron micrograph of EZ2/1K-A interfacial metal side after salt spray test (×1500). Note the clear separation between Zones 1 and 3 and the progressive dissolution of the phosphate coating.

binding energy of Zn(2p) in $ZnCl_2$, the well-resolved $Cl(2p^{3/2})$ bands of $ZnCl_2$ and NaCl (respectively, at 198.9 and 200 eV) facilitate the assignment and quantitative analysis of $ZnCl_2$. $Zn(OH)_2$ is preferentially formed after "S.S.T." The $Zn(OH)_2$/ZnO ratios equal 2.9 and 1.6 for EZ2 and G2F/1K-A bonded joints, against *ca.* 0.5 after "C.H.T." or "I.T." Figure 9 compares the distribution of the corrosion prod-



```
Filename      Spot       Res Flood eV  Scans Description
920420.MRS    600µ        2                2  EZ2 / 400F / H0
Baseline: 1026.31 to 1017.96 eV
# 1: 1021.39 eV   1.71 eV    24292.57 cts    66.31%
# 2: 1022.35 eV   1.91 eV    12340.93 cts    33.69%
50 iterations, chi square = 1.7653
```

```
Filename      Spot       Res Flood eV  Scans Description
920453.MRS    600µ        2     5.0        2  EZ2 / H40   ZONE METAL GRIS
Baseline: 1026.81 to 1018.15 eV
# 1: 1023.13 eV   1.71 eV    31413.09 cts    38.65%
# 2: 1022.12 eV   1.58 eV    37039.88 cts    45.57%
# 3: 1020.99 eV   1.90 eV    12825.09 cts    15.78%
15 iterations, chi square = 1.7258
```

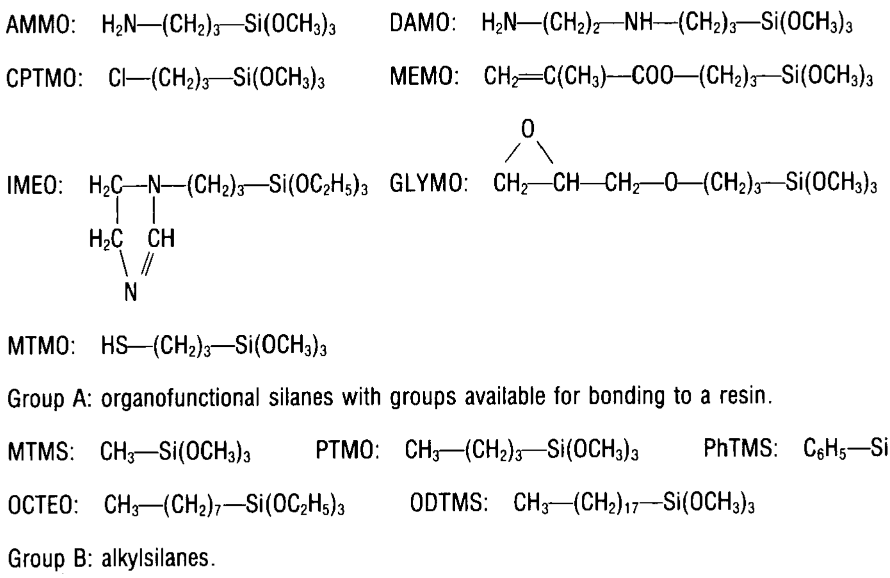
FIGURE 9 Zn(2p) XPS spectra obtained from the interfacial metal side of EZ2/1K-A bonded joints (Zone 3) after immersion test (a) or salt spray test (b).

ucts on the interfacial metal side after "I.T." and "S.S.T." While ZnO is the main corrosion product formed during "I.T.," it is likely that the hydrolysis of $ZnCl_2$ (stemming from the dissolution of Zn, and the migration of Cl^- at the metal/adhesive interface) enables direct formation of $Zn(OH)_2$ during "S.S.T." It should also be borne in mind that the direct production of OH^- by cathodic reduction of oxygen is likely to replace the reduction of water, which is favoured in oxygen-deprived medium during "I.T." or "C.H.T." As can be seen in Figure 1, the greater durability of bonded joints made from cold-rolled steel substrates under "I.T." or "C.H.T." conditions, as compared with zinc-coated steels, is probably partly due to the thermodynamically favoured reduction of water on zinc.[16]

3.4 Improvement of the Durability with Organosilanes Reagents

Experimental conditions A total of 12 organosilanes (courtesy of Hüls) presented in Figure 10 were investigated. All exist as clear liquids and were used as received. "Group A" encompasses organosilanes having a group capable of reacting with the dicyandiamide/epoxy system. "Group B" alkylsilanes were used to assess the usefulness of a "chemical bridge" (if any) for the durability of the metal/adhesive interface.

Primers were prepared in isopropanol. The hydrolysis of neutral silanes was catalyzed by adding 1.5% of DAMO based on total silane.[17] The surface coverage obtained from solutions of silane in isopropanol was not found to strongly depend on the type of silane used. It was also nearly proportional to the concentrations of the solutions: from 90 to 1600 mg/m^2 for concentrations ranging from 0.5 to 10 wt.%. XPS analysis of specimens primed with 5 and 10 wt.% solutions of DAMO



AMMO: $H_2N—(CH_2)_3—Si(OCH_3)_3$

DAMO: $H_2N—(CH_2)_2—NH—(CH_2)_3—Si(OCH_3)_3$

CPTMO: $Cl—(CH_2)_3—Si(OCH_3)_3$

MEMO: $CH_2{=}C(CH_3)—COO—(CH_2)_3—Si(OCH_3)_3$

IMEO: $H_2C—N—(CH_2)_3—Si(OC_2H_5)_3$

GLYMO: $CH_2—CH—CH_2—O—(CH_2)_3—Si(OCH_3)_3$

MTMO: $HS—(CH_2)_3—Si(OCH_3)_3$

Group A: organofunctional silanes with groups available for bonding to a resin.

MTMS: $CH_3—Si(OCH_3)_3$

PTMO: $CH_3—(CH_2)_3—Si(OCH_3)_3$

PhTMS: $C_6H_5—Si(OCH_3)_3$

OCTEO: $CH_3—(CH_2)_7—Si(OC_2H_5)_3$

ODTMS: $CH_3—(CH_2)_{17}—Si(OCH_3)_3$

Group B: alkylsilanes.

FIGURE 10 Organofunctional silanes applied as primers on EZ2 and G2F.

demonstrated that the locus of failure was inside the silane film.[18] Preliminary tests showed that 1 wt.% was a suitable concentration (corresponding thickness of the silane film: *ca.* 0.18 μm). The primed samples were allowed to dry at room temperature for 30 minutes before bonding.

Results and discussion Figure 11 presents the results obtained after "I.T." with electroplated phosphated steel. All the silanes tested at a 1 wt.% level gave very good results, from 85% strength retention for GLYMO to 109% for AMMO (>100%, probably due to plasticization effects), compared with 67% for unprimed specimens. The fracture surfaces were also drastically improved, implying that the ingress of water was reduced when the organosilane was present at the metal/adhesive interface. The extent of the improvement was somewhat lower for the hot-dipped galvanized substrate, see Figure 12. Residual shear strengths ranging from 53% to 69% were measured for silane-treated bonded joints, against 46% for the reference samples.

Among the numerous theories postulated to explain the beneficial effects of silane coupling agents, Plueddemann showed that the chemical bonding theory was the most appropriate to account for the very good results obtained by bonding silane-treated polyester composites to glass.[19] This theory was later supplemented by Pohl and Osterholz who demonstrated the reversible nature of siloxane bonding to glass surfaces.[20] Such a mechanism is also likely to take place on metal surfaces and one does not need to worry about the hydrolyzable nature of metal-oxygen-silicon bonds if these bonds can readily reform. The results presented in Figures 11 and 12 clearly demonstrate that non-functional silanes such as MTMS, PTMO, and OCTEO performed equally well against the silanes having a group able to react with the

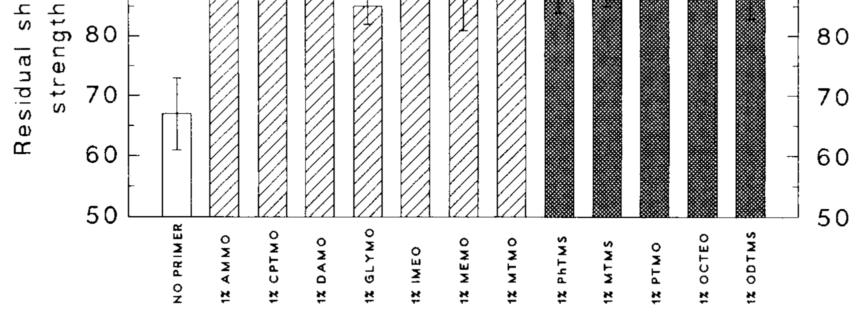


FIGURE 11 EZ2 specimens primed with 1% solutions of silane in isopropanol (dried at RT for 30 min.).

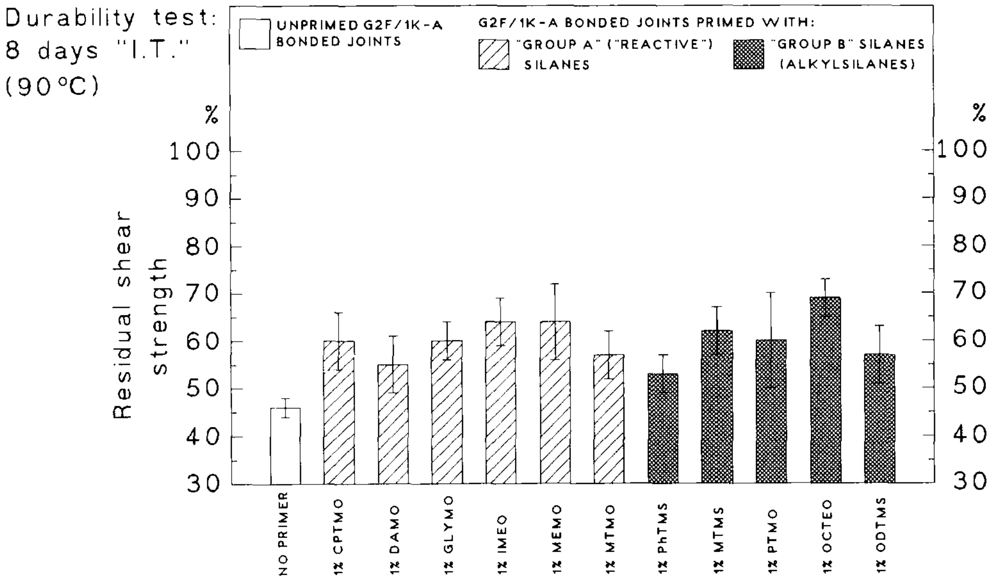


FIGURE 12 G2F specimens primed with 1% solutions of silane in isopropanol (dried at RT for 30 min.).

epoxy/dicy system. OCTEO performed even better than GLYMO which should have provided a good transition between the metal surface and the dicy-cured adhesive. Walker *et al.* also found the chemical bonding theory questionable after having obtained very good durability properties for a polyurethane coating applied on aluminium primed with vinyltris(2-methoxyethoxysilane); the results were even better than the ones observed for AMMO.[7] The aliphatic chain or the phenyl ring borne by Si in MTMS, PTMO, OCTEO, ODTMS, and PhTMS is likely to create a more hydrophobic adhesive/metal interface than the interface of untreated specimens and slow down the diffusion of water.

Furthermore, bonded joints made from EZ2 metal coupons primed with dimethyldimethoxysilane and trimethylmethoxysilane had residual shear strengths of 93% and 95%, respectively. This shows that the siloxane film may not need to be highly cross-linked at the metal/adhesive interface. Fracture surfaces of specimens primed with these silanes are presented in Figure 13. Similar results were obtained with triphenylsilanol which is sterically very hindered and probably fulfills, once dimerised or reacted with the metal surface, the conditions necessary for the building of a "tight hydrophobic roof" on the metal surface. It is, nevertheless, unlikely that a silanetriol molecule reacts with the metal surface with more than one hydroxy group, in view of the average density of hydroxyl groups on most mineral surfaces (1 to 5 per square nanometer).[21] Toulhoat *et al.* studied the silanation of glass surfaces by Atomic Force Spectroscopy.[22] They reported that the average density of trimethylsilane groups adsorbed on the surface was 3 per square nanometer, in agreement with the reported surface densities for —OH groups in the particular case of activated silicas.

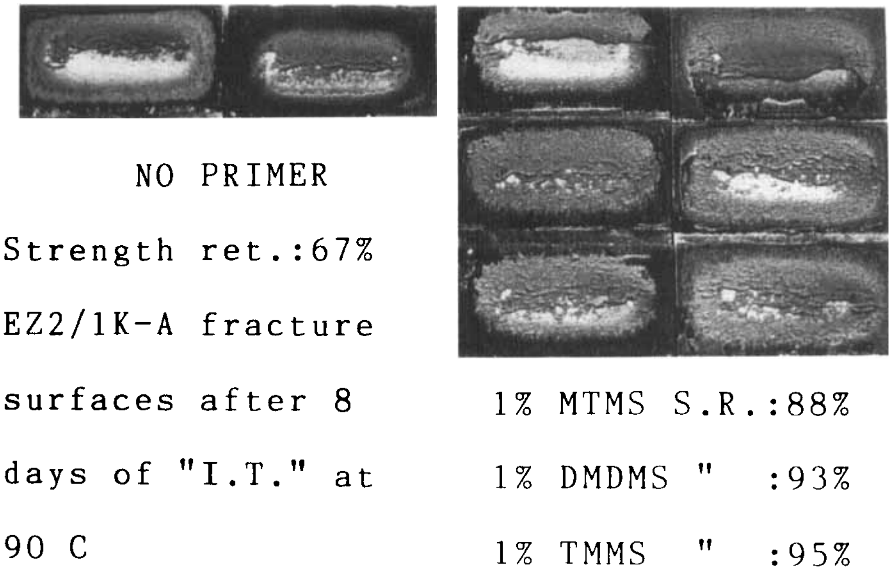


FIGURE 13 Reduction of the ingress of water at EZ2/1K-A metal/adhesive interface by using alkylsilanes (MTMS = methyltrimethoxysilane; DMDMS = dimethyldimethoxysilane; TMMS = trimethylmethoxysilane).

Strength retentions after redrying of aged bonded joints Silane coupling agents were most efficient as far as the wet-strength of the bonded joints was concerned. Upon drying, joints made from silane-primed metal coupons regained strength to a smaller extent than unprimed specimens. After immersion testing, specimens treated with alkylsilanes were dried in an oven for one week at 60°C. Shear strengths of G2F specimens increased by an average of 10% (about 0.5 MPa) as compared with the strengths measured directly after immersion, against 14% for control samples (0.9 MPa). Bonded joints made from EZ2 displayed a lower increase, about 5% (*ca.* 0.3 MPa), against 18% (*ca.* 1.2 MPa) for untreated specimens.

Influence of the drying conditions of the silane film EZ2 and G2F/1K-A bonded joints made from metal coupons primed with DAMO, IMEO, MTMS, or OCTEO at room temperature or 100°C were aged following the "C.H.T." procedure. Although the durability properties of all silane-treated specimens were much better than those of the control specimens, Figure 14 demonstrates that it is often profitable to cure the primer prior to bonding. The average improvement was *ca.* 10% of the residual lap shear strength after "C.H.T." This effect was most pronounced for G2F specimens primed with a 1% solution of DAMO. Badly polymerized DAMO is likely to weaken the silane film and, because of the large excess of unreacted amino groups, increase the hydrophilicity of the metal/adhesive interface. The high natural PH of the solution (*ca.* 11) can also contribute to the dissolution of the "aluminium islands" on the surface of G2F.

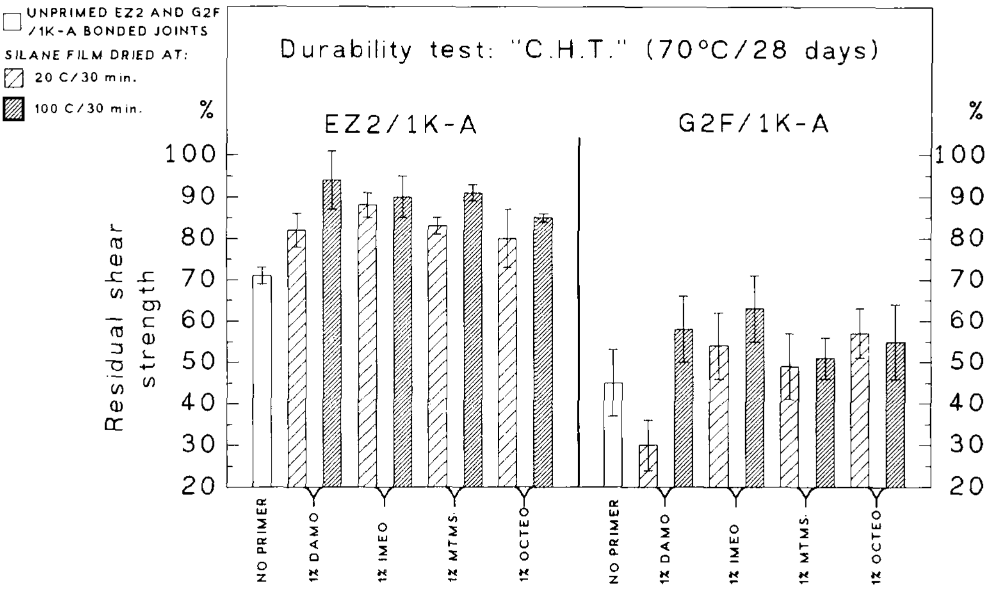


FIGURE 14 Influence of the drying temperature of the silane film on the durability of the bonded joints.

XPS analysis of specimens primed with DAMO Figure 15 illustrates the chemical composition of the surface of EZ2 specimens primed with DAMO in isopropanol (main components of the phosphate layer). The concentrations of Zn and P on samples primed with a 1% DAMO solution in isopropanol were both equal to 1.2%, against 11.3% and 6.8% for the clean metal substrate. Weight measurements gave an average surface coverage of 180 mg/m^2 corresponding to a silane film thickness of *ca.* 180 Å. The overall composition of the interfacial metal side of primed specimens is very close to the composition of the clean metal substrate. It is interesting to see that Si, present at a 5.8 atomic % on the surface of the primed substrate, was not detectable on the unaged interfacial metal side. Furthermore, the Si concentration on the adhesive side increased from 3.5% to 7.8%. This demonstrates that the silane film fully remained on the adhesive side after shear testing and that the failure took place at the silane film/metal interface. Five and 10 atomic % of nitrogen were found, respectively, on the interfacial adhesive side and the primed non-bonded EZ2 substrate, giving additional evidence that the primer was displaced while curing the adhesive.

After ageing tests, the phosphate coating of untreated specimens was nearly entirely dissolved away from the interfacial metal side, whereas its chemical composition remained unmodified for DAMO-treated specimens. This clearly shows that DAMO, and most likely all other tested coupling agents, stabilize the metal/adhesive interface against hydration.

Priming the specimens with mixtures of silanes and oil In the automotive industry, galvanized steel is rarely degreased prior to bonding. It was, therefore, of interest

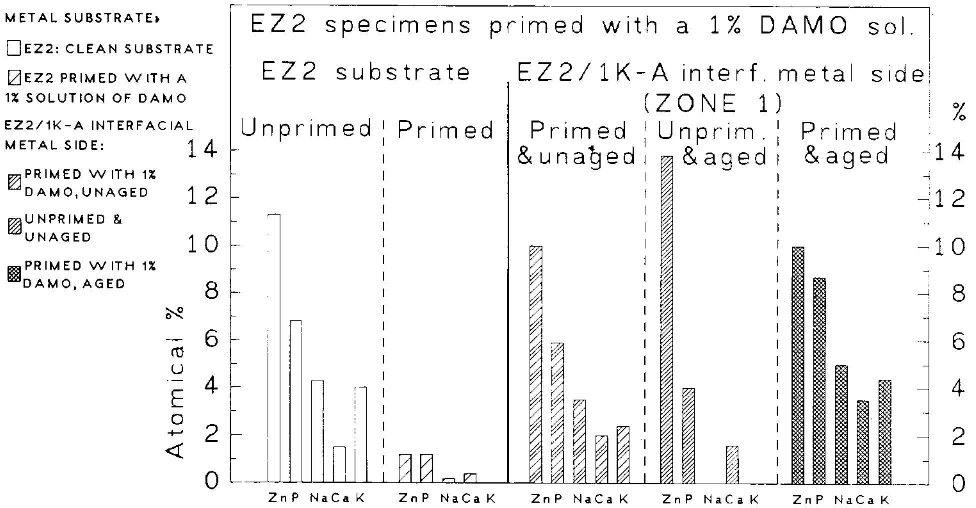


FIGURE 15 Atomic % of Zn, P, Na, Ca, and K on EZ2 surface and EZ2/1K-A interfacial metal side (for primed and unprimed specimens) before and after "cataplasme humide" test (70°C/28 days).

to investigate whether bonded joints made from metal coupons primed with mixtures of silane coupling agents and lubricating oil would retain their good durability properties. The specimens were primed with a mixture of 2 wt.% silane + 8 wt.% oil (ASTM 3 standard regreasing oil) in isopropanol against 10 wt.% for the control specimens in order to maintain an average surface coverage of 3g/m^2. Results obtained after "C.H.T." and "I.T." are presented in Figure 16. Both IMEO and OCTEO gave strength retentions close to 100% with EZ2 after "I.T." against 65% for the control specimens. The results were also very good after the "cataplasme

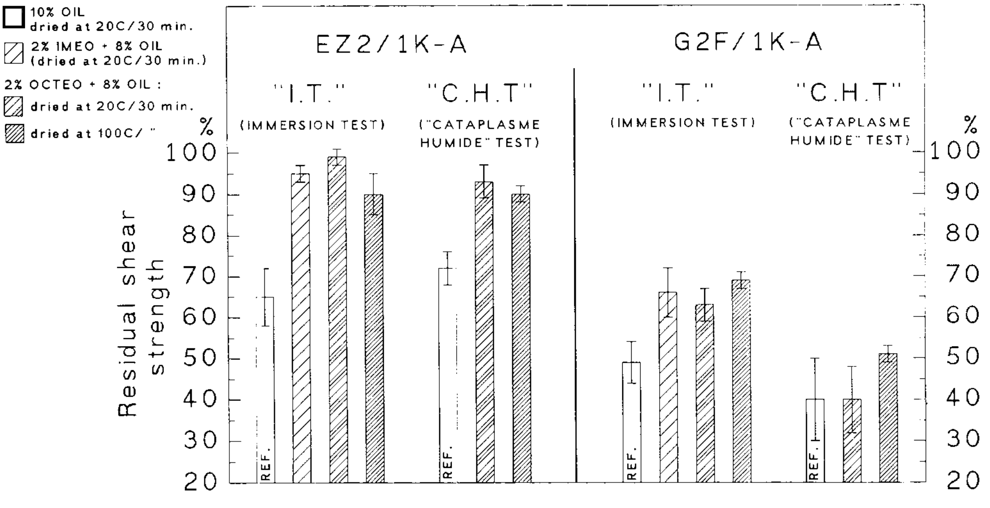


FIGURE 16 Specimens primed with mixtures of silane and standard regreasing oil (ASTM 3).

humide" test on EZ2: *ca.* 90% against 70% for unprimed specimens, but less satisfactorily on G2F. These results can probably be explained by the ability of hot-curing epoxies to displace or absorb most of the oil present at the adhesive/metal interface, as was shown by Debsky *et al.*[23]

Strength retentions after salt spray test The hydrolitic stability of the interface is not as critical during "S.S.T." as it is in the degradation mechanisms associated with the "I.T." and "C.H.T." Silane coupling agents had a slight beneficial effect when applied on electroplated-phosphated steel (EZ2); but they mainly accelerated the degradation of bonded joints made from hot-dipped galvanized steel. G2F silane-treated specimens gave strength retentions between 10 to 20% lower than control samples (on average, −1.5 MPa), in contrast with the 10% improvement (about +1 MPa) observed on electroplated specimens. Bonded joints made from another electroplated substrate (non-phosphated) displayed fracture surfaces slightly more corroded and strength retentions 10% lower than control specimens after 6 weeks under salt spray test exposure.

SUMMARY

Zinc-coated steel/epoxy bonded joints were aged following "cataplasme humide," immersion, and salt spray tests. The durability properties of lap shear joints were evaluated and the fracture surfaces analyzed by XPS.

Anodic dissolution of the zinc-coating was found to be responsible for debonding in all cases and the failure occurred in a layer of $ZnO/Zn(OH)_2$ after "I.T." and "C.H.T.," and in a layer of $ZnO/Zn(OH)_2/ZnCl_2$ after "S.S.T." Intergranular corrosion of the G2F substrate was responsible for a quicker degradation of the bonded joints during "C.H.T." and "I.T."

Alkylsilanes applied as primers from isopropanol or oil/isopropanol solutions proved to be very useful in increasing the hydrolytic stability of the interphase region. They performed as well as functionalized silanes having a group able to react with the epoxy/dicy system. XPS results showed that the hydrophobic character of such organosilane reagents plays an important role in reducing the ingress of water at the metal/adhesive interface. But the results obtained after salt spray test demonstrated that organosilanes do not protect the bonded joints against bondline corrosion.

Hence, the necessity of using several ageing tests before drawing conclusions about the viability of a coupling agent is demonstrated. Specific zinc and aluminium chelating agents which are water insoluble and offer good protection against corrosion are now under study. It should then be possible to design them (adequate functionalization) in order to reach maximum durability on any type of galvanized steel.

Acknowledgements

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