



Analysis of

# **PAINTED ALUMINUM HOOD AND ASSOCIATED CORROSION AT HEM**

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# ALUMINUM HOOD CORROSION

## Analysis of Painted Aluminum Hood and Associated Corrosion at Hem

**T**o examine a painted aluminum hood sample taken from a vehicle, it's important to consider key characteristics of aluminum closure alloys, automotive paint systems, as well as types of corrosion and their causes.

### BACKGROUND

Aluminum closure panels for automobile exterior panel components, such as hoods and deck doors, are frequently used for their weight savings potential. Aluminum closures can achieve 35-50 percent weight savings as compared to steel or polymer panels and provide excellent dent resistance due to their considerable strength. Most of the aluminum alloys used for closure panels are designed to precipitation harden during the paint bake/cure cycles, which doubles the alloy's strength from the time of its initial stamping.

Aluminum is naturally corrosion resistant due to the tenacious, but very thin, oxide layer that forms on the surface. Since this surface reaction is rapid and self-healing, bare or uncoated aluminum can be used for many general use applications. This surface may not provide an attractive uniform appearance or corrosion durability in the harsh environments vehicles are typically exposed to. For more severe corrosive environments, the alloy surface is pretreated, anodized and/or painted.

As the aluminum is alloyed to increase its strength, the potential for corrosion to occur increases. The alloying additions of Cu, Mg, Zn, Si, for example, are not uniformly distributed in the aluminum matrix. This variation in composition can create electro-chemical differences, which leads to several types of corrosion. The insoluble intermetallics (Fe) can also be sites for local pitting or corrosion due to their electro-chemical differences.

Today's aluminum closure panels are made from 6xxx series alloys, which contain additions of Mg, Si and Cu for strength with the addition of Mn and Fe to control grain size. These alloys are supplied in a relatively soft T4 temper for good forming behavior and age harden during the paint bake/cure process. Although they age harden significantly, the paint cures are insufficient to provide for maximum strength.

### AUTOMOTIVE PAINT SYSTEMS FOR ALUMINUM

While aluminum is naturally corrosion resistant, it is painted for automotive applications to enhance its appearance and to provide increased corrosion resistance from pitting, scratches and crevice corrosion. Special attention must be given to the hem joints, where the outer surface is hemmed over the inner panel, since this forms a natural collection crevice for salt or other debris. The hinge reinforcements are frequently bolted and can also develop crevices.

During the hood assembly process, an adhesive (a one or two-part epoxy) is used to secure the outer hood to the inner panel. For cosmetic reasons, it is not typically possible to resistance spot weld or rivet the outer to the inner panel. The adhesive is applied by robot to the outer hood when it is inverted (bottom surface), the inner panel is inserted, and the outer flange is hemmed over, capturing the inner panel. The hem adhesive tends to squeeze into the cavity formed by the hemming process, but generally doesn't completely fill the cavity. If too much adhesive is used, it tends to squeeze out from the joint, which causes downstream problems.

The cured adhesive joint is a very stiff and structurally efficient joint. A very small amount of movement has been observed in some hood samples, where the inner

panel can “pull out” from the hem by a very small amount. If the movement occurs during the painting process, this can expose the aluminum surface. Movement like this generally occurs prior to the adhesive curing.

Alternatively, down standing flanges for both the inner and outer panel may be mechanically joined by a variety of methods, or a structural joint could be added with a resistance spot or laser welding. This joint does not allow for relative movement during the painting process, but may be difficult to package, as it requires extra space under the hood. As adhesives, even cured adhesives, are hydroscopic, which require special attention to see that the adhesives don't absorb moisture that can degrade the adhesive or the adhesive to metal interface.

After forming, and prior to paint, the hoods are assembled via mechanical or adhesive joining. In most processes the individual components are not cleaned of the forming lubricant. Because of this, the adhesive, mechanical or other joining methods must be compatible with a small amount of residual lubricant.

If a two-part epoxy is used, the green strength may be improved with a rapid induction cure. Induction curing is not routinely applied, as the volume of closure panels has increased to high volume applications.

To ensure color uniformity between the body and closure panels, the closure panels are attached to the body structure for painting. The doors are removed so that the glass, glass movement mechanisms, electronics and trim may be applied and reattached to the vehicle in final assembly.

The body of the vehicle, including the closure panels, is typically sanded or panel corrected to improve overall appearance and panel alignment. The body of the vehicle is then cleaned, typically in an alkali cleaner, to remove incidental dirt or lubricants. Most paint cleaning and pre-treating takes place in immersion or dip systems, but some spray systems are still used. Dip systems are typically favored due to the uniformity of coverage of the applied chemical. A rapid turn-over of the bath is required to ensure a fresh, non-contaminated bath.

After cleaning, the metal is pretreated. The pretreatment chemicals must be compatible to all the metals used in the vehicle's construction. Polymer panels are not considered here. Zn-phosphate pretreatment systems are used in many original equipment manufacturer (OEM) paint applications and newer Zr-based pretreatment systems are becoming more common.

The pretreatment systems are designed to provide for a very stable oxide surface, much more stable than a naturally occurring oxide, to provide the interface between the applied e-coat and the metal surface. The pretreatments are designed to completely replace the naturally occurring oxides and have etching and nucleate abilities to grow on the metal surface depositing typically plate like Zn-P crystals in a uniform manner. These pretreatments are very thin in the order of 2  $\mu\text{M}$  or less.

The next layer is the cathodic e-coat, which is applied while the vehicle is immersed. An electric current is applied between the external anodic plates and the body structure, which becomes the cathode (negative charge). The positively charged particles in the bath (cations) are attracted to the negatively charged body struc-

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ture. In general, a uniform coating of approximately 20  $\mu\text{M}$ , is applied, but thicker or thinner regions may occur depending on the geometry of the field and the electrical surface characteristics of the pretreated surfaces. The electric field allows for penetration into the nooks and crannies, but not into shielded regions. The e-coat is then cured at a temperature of 160-180C.

Both the pretreatment systems and the subsequent e-coat systems are effectively line of sight and have limited ability to penetrate crevices or between surfaces, including under reinforcements and various hem geometries. Some OEMs purchase coil applied pretreatments, on the aluminum sheet that provide protection in the regions that are otherwise blocked—most steel products have coil applied Zn coatings. In theory, coil applied pretreatments could replace OEM pretreatments, the many trimmed or pierced edges that are created during the forming and metal finishing processes would require local pretreatment to ensure complete coverage. Even when using a pretreated aluminum coil, the finished components are still subjected to a traditional pretreatment to complete the coverage.

The next layer applied is the primer. The primer is spray applied, typically 30-40  $\mu\text{M}$ , and designed to protect the e-coat from UV radiation to provide for a levelling/smoothing of the surface. Typical primers are greyish in color, and as a result, the term “body in white” (BIW) was coined. This coat is also cured but at a lower temperature of 140-160 C.

The next layer is the base or color layer. This layer is spray applied and is typically the thinnest of the layers at 10-20  $\mu\text{M}$  and cured at a temp near 120 C. This layer can also contain the metal flake or an equivalent to enhance its appearance.

The last layer is the clear or top coat to protect the color layer and add depth to the appearance of paint system.

### **HEM SEALANTS**

A variety of sealers that can be based on PVC, modified acrylics or other formulations, are applied to vehicles to close gaps or provide sound deadening. The hem edge in the painted-only condition represents a potential crevice. Almost universally, door hems have a sealant applied to close out this crevice. Hoods may or may not have a hem sealant applied since the hood is generally in a benign corrosion location.

The hood hem sealant may be applied prior to the painting process after the primer coat, or in final vehicle assembly. Where and when in the overall assembly process the sealer is applied has several trade-offs. If the sealant is visible or must color match, then it must be applied prior to the base coat. Some OEMs apply a hem sealer after the primer, and prior to the color coat, but it is difficult for the robots to get access to all regions of the hem. The design of the paint line may not easily accommodate the addition of robots to apply the sealant. As a result, hem sealants are typically applied prior to paint process as the hood is assembled, typically as the last step. For context, hem structural adhesive is applied first to the bottom of the hood outer, along with anti-flutter mastics, the inner inserted, the hemming operation of the outer over the inner completed, followed by the hem sealer.

The difference in the two approaches is the degree of metal preparation under the hem sealer. While it's not always practical, the advantage of applying the hem sealer after the primer is that the metal is already pretreated and e-coated. The alternative, which is more typical, is to apply the sealant during the hood assembly pro-

cess. The sealer is then applied to the stamped metal surface, which typically has some residual oil. Modern sealants are compatible with this approach and have a good service track record, but the quality of the application must ensure the joint is impervious to any water ingress.

As previously mentioned, a coil applied pretreatment has the advantage that the metal under the hem is always protected. Most coil applied pretreatments in exposed regions of the hood are removed, usually not completely, in the etching process step.

#### **FILIFORM CORROSION**

As mentioned, aluminum, and most aluminum alloys, exhibit very good general corrosion resistance but can be prone to filiform or crevice corrosion in automotive service conditions, particularly in wet and salty environments typical of the east coast of Canada or the USA.

Filiform corrosion, named for the observed fine filaments or worm-like tracks, is a form of corrosion that propagates along the metal surface under the paint layer or under the coating that provides for an oxygen barrier. Sometimes the individual filaments may join and present a broader front. The corrosion front is usually at the very surface of the aluminum sheet, under the pretreated surface. Once the initial defect is generated, which may be from a stone chip or a paint defect such as a hole or crack in the paint, the corrosion defect begins to tunnel under the paint surface. This is driven by the difference in oxygen between the head of the filament and the starting initiation defect. This leads to a pH difference within or along the length of the filament. The filiform tunnel exists as an electrolyte rich fluid tunnel. At the very front of the corrosion, the details of the progressing front may be determined. Additional forms of corrosion

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All modern vehicles are extensively tested for durability with accelerated proving ground tests, including paint and corrosion preventative measures. No known examples of filiform corrosion have been observed from these tests.

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may progress as corrosion grows laterally from the electrolyte rich tunnel, which makes a clear determination of cause and effect more difficult.

While many paint defects are typically present to serve as potential nucleation sites, many remain as very small pits or grow so slowly they are of no practical concern. However, if the environment is conducive, and the pretreatment, adhesive or sealer interface is poor, filiform corrosion can progress surprisingly rapidly. This filiform corrosion takes 3-4 years of service in a conducive environment for the filiform corrosion to grow to a size that it is visible. Since this type of corrosion is effectively a "paint blemish" it typically doesn't manifest itself as a structural or safety concern, but it is certainly understandable why the customer would object to such a blemish in a modern vehicle.



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The hem joint is a region that is prone to generating paint defects and gaps in the paint coverage are often observed. The tightness of the outer wrapping around the inner may also display some gaps or non-uniformities.

Certain alloys, particularly those that contain Cu, are more prone to filiform corrosion since the Cu can be leached or corroded out of the aluminum alloy and exists as a Cu ion in the electrolyte solution, which increases the potential difference between the head and tail. This has been observed in aggressive laboratory-accelerated corrosion tests, but may or may not be present in field surface depending on the quality of the paint system. With a quality paint system, virtually all alloys used for automotive applications don't exhibit filiform corrosion. With poor paint preparation, virtually all alloys, including pure aluminum can exhibit filiform corrosion. For example, in the early 1980's the original aluminum Ford Town Car hood was made from a Cu rich aluminum alloy, following the concept of aircraft sheet alloys, and even after 20+ years of service, almost no examples of field filiform corrosion were found on still drivable or parted out vehicles in scrap or parts yards.

It should be noted that all modern vehicles are extensively tested for durability with accelerated proving ground tests, including paint and corrosion preventative measures. No known examples of filiform corrosion have been observed from these tests. It is rationalized that many of the test conditions that were developed for steel bodied vehicles remain in place since the majority of the body structures contain significant amounts of steel, and because of this, these tests are simply not the conditions needed to promote this particular type of corrosion. Test conditions that are able to better promote, and better quantify effective preventative measures

are under development. Care must be taken to promote accelerated conditions that are realistic predictors of service life and service life conditions. Filiform corrosion is particularly difficult to predict through accelerated conditions since the corrosion filament only grows within a narrow range of experimental conditions and at a finite rate. The conditions required to promote filiform corrosion are difficult to promote during typical proving ground tests.

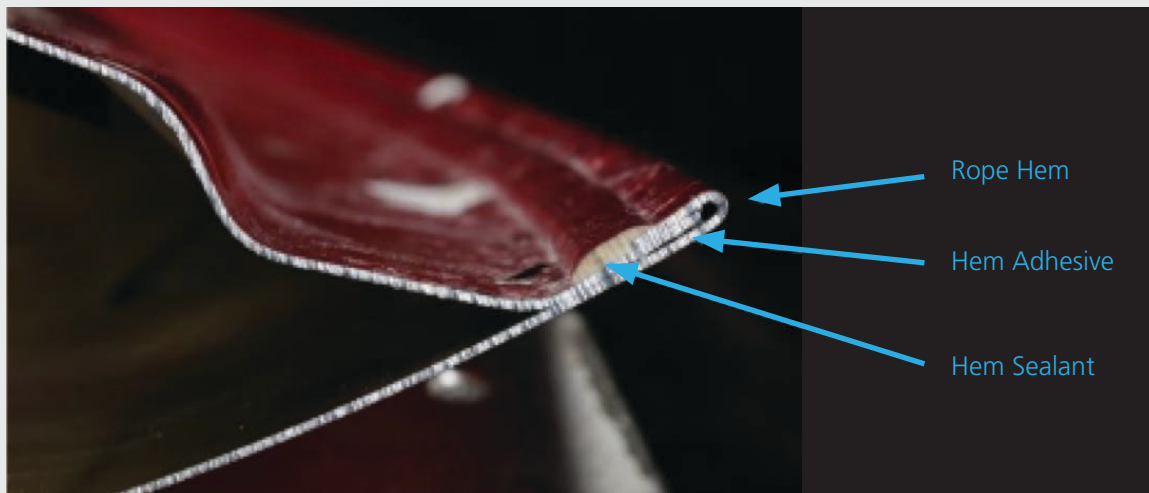
Over the last 5 years or so, the aluminum alloys used to make closure panels have had minimal amounts of Cu, levels so low that even using accelerated laboratory testing, the Cu is not a contributing factor.

Newer alloys have almost equivalent strengths to their predecessors but with improved forming characteristics. The improved forming characteristics result in a virtually flat closed hem which is structurally more efficient and more resistant to the ingress of salt laden water into the hem.

Sanding or abrading the aluminum surface prior to paint has the potential to make the surface more prone to filiform corrosion since the abrasion process effectively thickens the oxide surface which must be removed prior to the pretreatment. If the etch conditions associated with the pretreatment are set up for the nominal un-sanded surface, the thicker regions of oxide associated with the sanded region may not be completely removed, and as a result, may have non-uniform Zn-phosphate crystal growth, or areas of sparse coverage. For after-market repair where parts have been abraded, particular care must be taken to prepare the surface for paint.

**FIG. 1: CROSS SECTION THROUGH HEM**

Cross section depicting the hem sealant, hem adhesive and rope hem.



#### HOOD SAMPLE FROM SERVICE VIA REPAIR FACILITY

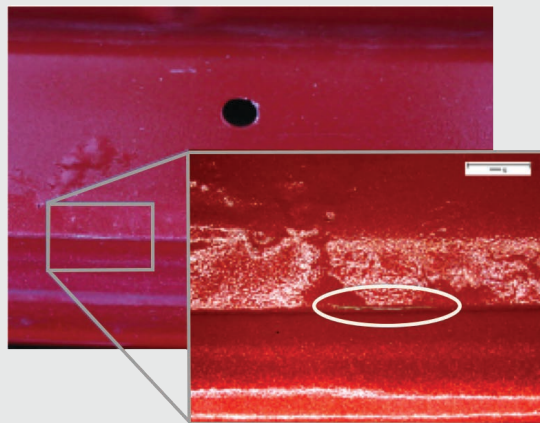
A sample from the front of a hood containing the hem, with extensive paint blistering near the hem was received for examination. The hood was an original OEM hood, which had not been repaired. The vehicle (2012 Model Year) had been in service for approximately four years in the northeastern United States, with proximity to the ocean. The repair facility obtained the sample with the intent of getting a better understanding of the corrosion mechanism.

The hood inner and outer were determined by chemical analysis to be AA6111. This alloy was in wide spread use at this time and was supplied to many OEMs. Alloy AA6111 is a mid-Cu level (0.7 wt%) alloy, with exceptional strength and good forming characteristics. Hence the hem is a rope hem and the outer panel does not completely flatten against the inner along the entire hem. (Section approximately 12-15mm in length perpendicular to hood outer edge.) This alloy is no longer used as a closure alloy, having been replaced by slightly less strong, much lower to Cu free alloys that are flat hemmable.

The hood appears to have been “painted” in a traditional manner with a Zn-Phosphate layer,

**FIG. 2: PAINT BLISTER**

General observations of “paint blister” at front edge of hem, hood underside.



#### Observation:

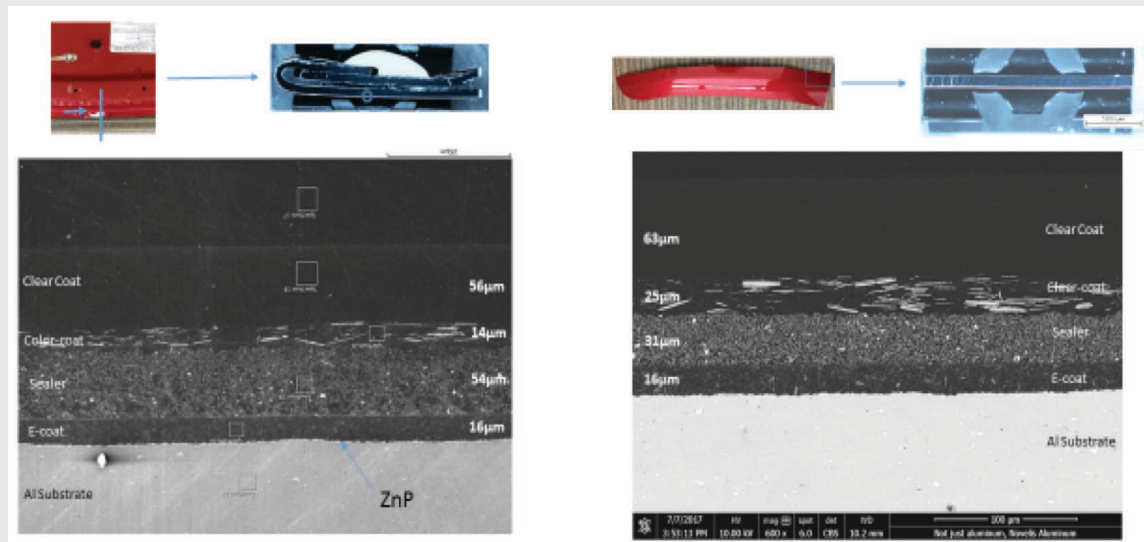
- Evidence of cracks in paint/sealant are observed in regions where corrosion is apparent under paint
- Cracks seem to appear along edge of sealant bead

an e-coat layer, a primer coat, a color or base coat including some metal flake, and the clear top coat. The clear coat appears to have been sprayed with 2 applications in some regions (See Figure 3). All paint layer thicknesses appear to



### FIG. 3: PAINT STACK COMPARISON

Paint system layers away from hem surface.



Paint stack in affected region.

Paint stack in region away from affected region shows a slightly thinner sealer and a thicker top coat.

be typical, and some non-uniformity in paint thicknesses is to be expected. However, as depicted in Figure 4, the Zn-Phosphate coverage close to the hem edge is less complete with gaps in the surface coverage.

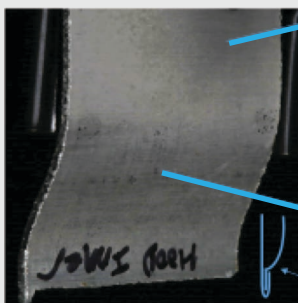
As shown in Figure 4, the general coverage of the ZnP applied coating is uniform and quite compact in areas away from the local hem geometry. This layer of coverage should provide

excellent corrosion protection. Closer to hem detail itself, the ZnP coating becomes less uniform with gaps in the coverage. This has been previously observed on other hood samples, but the exact reason for this lack of coverage is not known. It might be difficult to get the ZnP to adequately etch and to nucleate in these regions, or the local metal working operations, leave a region with a “smeared” oxide that requires an additional degree of metal cleaning.

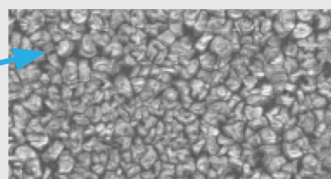
### FIG. 4: ZnP UNIFORMITY

Regions of complete vs. incomplete phosphate coverage.

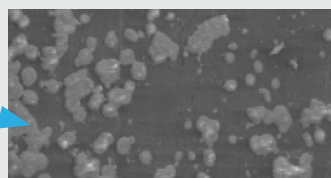
Good



Poor



Further away from hem ZnP response is acceptable.

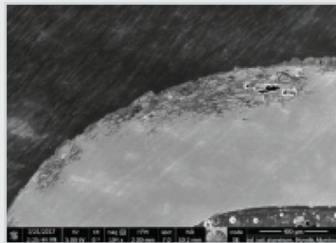


Discontinuities in the ZnP layer are found closer to the hem.

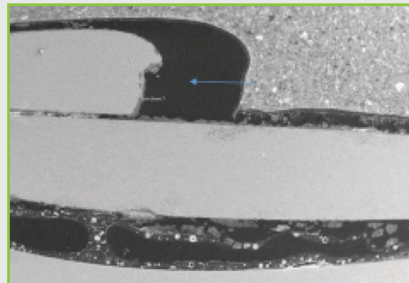
A section of the hood was removed and the paint stripped off using Bonderite S-ST 301, this has been shown to not affect the ZnP layer in the past.

**FIG. 5: CROSS SECTIONS THROUGH HEM**

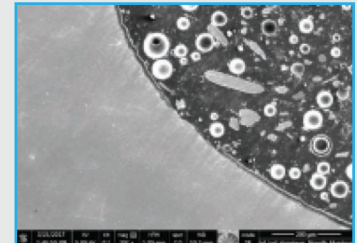
Cross section depicting the hem sealant, hem adhesive and rope hem.



Significant IGC observed in region where paint has been removed due to corrosion.



- Hem sealant bead is observed to have pulled away from the Hem
- Voids in hem adhesive are indicative of excessive moisture in the adhesion
- Delamination of hem sealant bead as well as adhesive within the hem is observed.



Poor adhesion of Adhesive to Hem outer is observed.

Figure 5 depicts several features that are likely to contribute to the formation of the paint blisters. In some regions the hem sealer appears to have pulled away from the edge of the outer material (center photo). Additionally, the hem adhesive appears to contain a high void content which moisture entered the adhesive prior to the cure. There are regions where the adhesive bonding did not adhere well to the aluminum surface. The LH photo depicts a region of intergranular corrosion which is a secondary corrosion product after the filiform corrosion front had passed "over" this region.

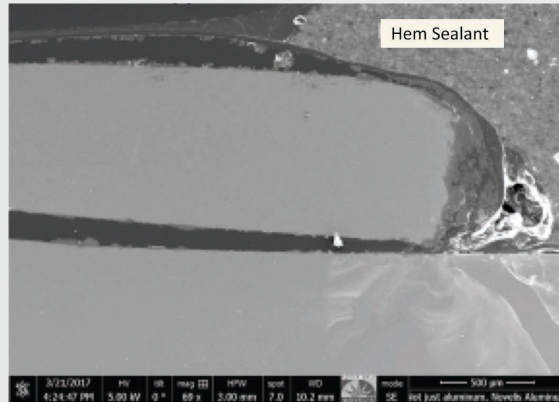
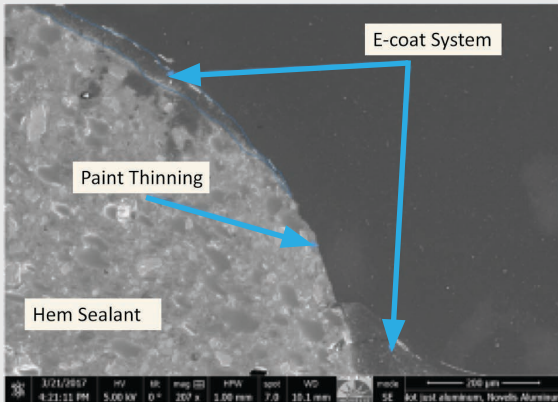
The hem adhesive appears to be more porous, containing more voids than typically observed. This could be a result of the adhesive absorbing moisture prior to the application, or a sign that the level of residual oil on the formed part exceeded the adhesive's ability to absorb. All epoxy adhesives contain fillers and toughening particles, and to a certain degree voids, but a large number of voids accelerates the rate of in-service moisture uptake. Eventually, this moisture migrates to the metal adhesive interface, which

may initiate filiform corrosion. If the metal surface is well pretreated, filiform corrosion is mitigated.

A bead of hem sealer was applied. This sealer appears to have been applied during the hood assembly. Extensive corrosion has been observed under the sealer and as a result, some of the underlying layers are difficult to observe. The layers on top of the sealer suggest it was applied at the assembly stage. As previously shown, there are regions where the sealer pulled away from the metal surface, and filiform corrosion is observed at the edges of the sealer. It should be noted that once filiform corrosion has been initiated at the various defects, such as under the hem sealer, it may grow away from this initiation site and under the paint layers. The lack of ZnP or e-coat under the hem sealer, places all corrosion preventative measures to be provided by: the quality of the hem sealer, the cleanliness of the underlying metal, and the uniformity and integrity of the sealer application. This particular example appears to suggest the sealer was unable to provide the necessary level of protection to the underlying metal.

### FIG. 6: CORROSION ONSET

Section through the hem sealant indicating presence of e-coat and delamination and onset of corrosion.

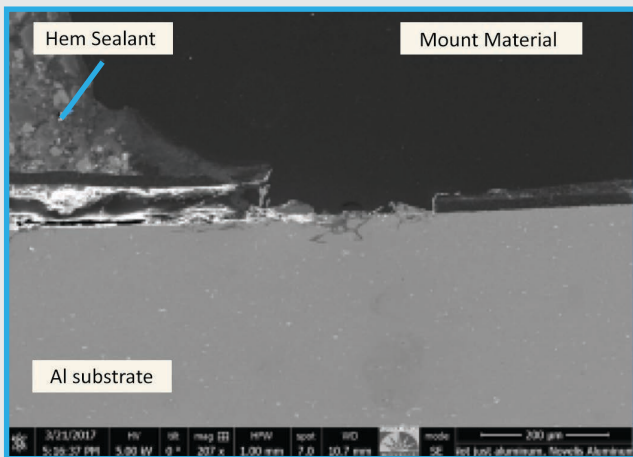


Edge of hem bead reveals thinning of paint system which may compromise the paint system integrity leading to breaches and environment ingress.

Under-film corrosion is observed undercutting the paint system and the Hem Bead is delaminated due to corrosion

### FIG. 7: CORROSION PROPAGATION

Depicts corrosion propagating under the hem sealant, with associated secondary corrosion.

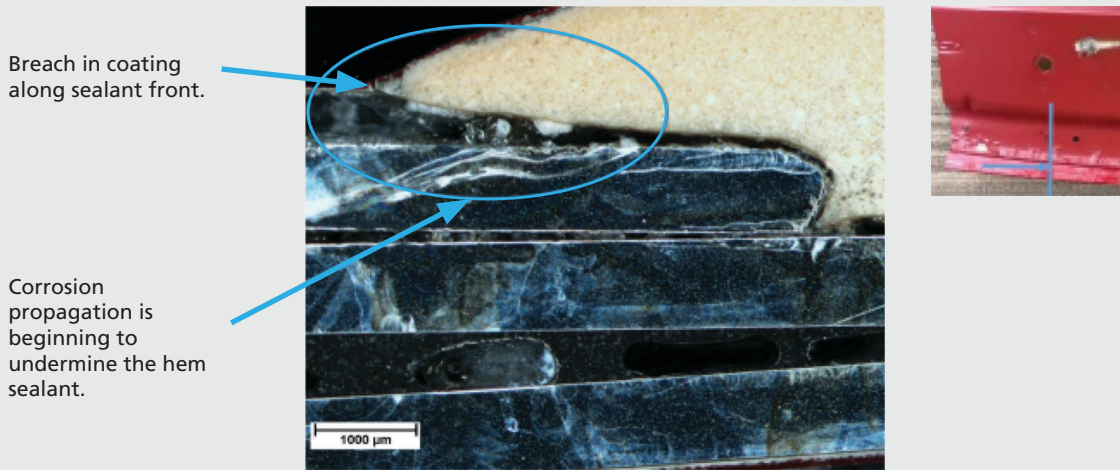


Breach in paint system and under hem sealant leads to undercutting, IGC, as well as delamination due to corrosion is seen.



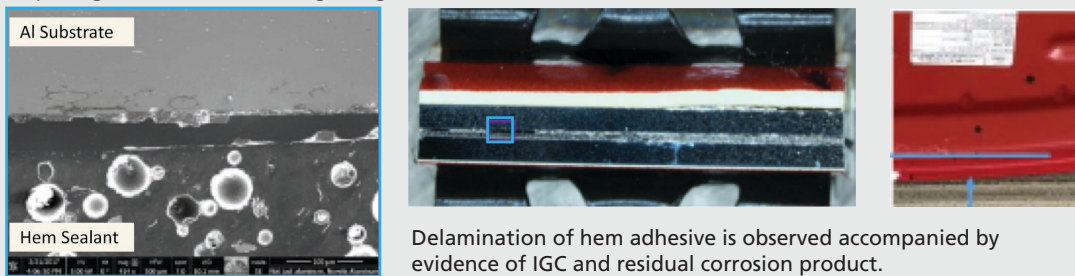
**FIG. 8: OPTICAL CROSS SECTION ANALYSIS**

Initiation of corrosion at hem sealant "front edge."



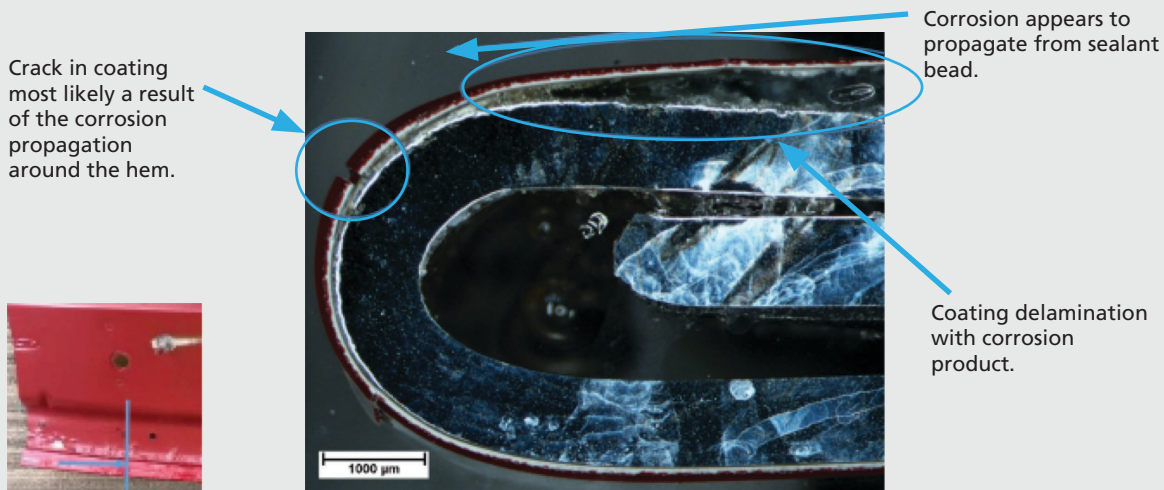
**FIG. 9: PARALLEL SECTION**

Depicting filiform corrosion migrating under the hem adhesive.



**FIG. 10: OPTICAL CROSS SECTION ANALYSIS**

Advanced stages of filiform corrosion migrating to hood outer surface.



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## SUMMARY

Filiform corrosion is observed under the hem sealant and at the adhesive interface, propagating away from these initiation sites under the adjacent paint layers. Gaps in the hem sealant, porosity in the hem adhesive, and non-uniform coverage in the ZnP layer adjacent to the hem have been observed. Various forms of secondary corrosion have also been observed that are a result of corrosion occurring after the filiform "front" has passed over the metal surface at the interface between the ZnP to metal surface.

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OEMs have recognized that the overall hem conditions need to be more robust with regards to corrosion. Newer, more appropriate alloys have been introduced and the hem geometry has been significantly tightened to reduce movement and water ingress. Newer pretreatments have also been introduced and improved testing conditions are under development.

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The source of the paint blisters, which are a manifestation of the filiform corrosion, likely started first at the hem sealant "edge" and then migrated into the hem. Once the filiform corrosion was initiated and allowed for the ingress of water/electrolyte additional filiform corrosion events likely began. It is certainly possible that many of these filiform corrosion events began almost simultaneously as the water ingress proceeded under the hem sealant. The porosity of the adhesive and the non-coherent ZnP layer adjacent to the hem probably contributed to the rapid "spread" of the filiform corrosion event(s).

Corrosion, once initiated from a paint defect or hem sealant edge, can either be arrested by the pretreatment layers or, if the pretreatment and surface conditions are not robust, transition to filiform corrosion and migrate under the paint layers. Effective prevention usually requires that the corrosion initiation events are minimized or delayed; though in practical terms, it is very difficult to eliminate all initiation sites. The rate of filiform corrosion is mitigated with a strong paint to surface interface which causes the growth rate to become insignificant.

OEMs have recognized that the overall hem conditions need to be more robust with regards to corrosion. Newer, more appropriate alloys have been introduced and the hem geometry has been significantly tightened to reduce movement and water ingress. Newer pretreatments have also been introduced and improved testing conditions are under development, which should improve the overall susceptibility. With such a multifaceted engineering problem, additional samples should be obtained to quantify the effectiveness of the corrosion preventative measures.







