Biography

Name: Daniel B. Arnold

Present Affiliation: Boeing Commercial Airplane Company

Title: Technology Supervisor

Field of Interest/Responsibilities:

Composites, Adhesive Bonding, Finishes, and Sealants

Previous Affiliations/Titles:

Academic Background:

B.S. Chemical Engineering- University of Washington B.A. Business Adminstration- University of Washington

Society Activities/Offices:

Publications/Papers:



Improvements in Corrosion Resistance of Adhesive Bonded Structure

Daniel B. Arnold

Boeing Commercial Airplane Company

November 5-7, 1980

Tri-service Conference on Corrosion

United States Air Force Academy, Colorado

BMT80-203

IMPROVEMENTS IN CORROSION RESISTANCE OF ADHESIVE-BONDED STRUCTURE

SLIDE 1

This paper will report the improvements in corrosion resistance of adhesive-bonded structure and be a compendium of the technical changes that have taken place to advance adhesive-bonding technology. It is appropriate that this particular paper will be presented at a corrosion conference, because adhesive bonding has been one of the most serious corrosion problems for Air Force as well as commercial vehicles.

SLIDE 2

This slide portrays the historical flow chart of the paper, as well as the progress that has been made with adhesive bonding over the past 15 years. The paper will trace each of the eight steps as we go through the presentation.

SLIDE 3

Adhesive bonding has long been used as a low-cost fabrication procedure for aerospace structure; however, it has not been without problems, as we will see in the future slides here. The process was originally used by Hawker DeHavilland and Fokker to bond metal to wood structure in the late 1940s. This was done to increase the thicknesses and strengths of wooden structure and aircraft wings. Fokker initially used the process to laminate thin sheets of aluminum together during periods of shortage when thicker sectioned extrusions or plate were not available to make the wing skins on Fokker aircraft.

SLIDE 4

The extent of usage of adhesive bonding has not grown precipitously, but has been a gradual increase starting with the Boeing fleet of aircraft in the mid-1950s. Initially, metal-to-metal and honeycomb bonding were used relatively sparingly on the B-52 and KC-135 types of aircraft. However, as the demand for lower cost fabrication techniques and lighter weight aircraft evolved, with the 727, 737, and 747 adhesive bonding became a more popular means of fabrication of structure. Most recently, the amount of adhesivebonded structure has actually declined in the 757 and 767. That structure has been replaced with composite and hybrid types of components.

SLIDE 5

This slide shows the extent of usage of adhesive bonding on the Model 747. As you can see, there is quite extensive use on the fuselage, empennage, and wings. In the fuselage area, adhesive bonding is used to bond metal-tometal doublers, tear straps, and reinforcements around windows and door areas. In the wing structure, adhesive bonding is used for control surfaces, particularly the spoilers, flaps, and ailerons. In each of these cases, multiple suppliers were used to supply the various components of the aircraft. Thus, it became necessary to have uniform bonding specifications for each of the Model 747 suppliers.

SLIDE 6

Extensive usage of adhesive-bonded structure on the 747, as well as on other aircraft that were emerging in the late 1960s, was not without problems. Specifically, there were delamination and corrosion on a large variety of components, including both metal-to-metal and honeycomb types of structure. The experience in the commercial industry was similar to the experience with military aircraft. The following four photographs detail the types of problems that were typical of service failures.

SLIDE 7

This photograph shows the delamination of an inner skin of a honeycomb panel. Notice that there is lifting of this skin along the edges of the honeycomb. In addition, there is both doubler and skin separation on the external surface.

SLIDE 8

Slide 8 shows the delamination area along the edge of a honeycomb panel in which the face sheet has been peeled off, revealing the areas of corrosion and delamination. Notice that the delamination starts from the edge of the panel as well as from the fastener holes and radiates away from those exposed edges into the center of the bonded area.

SLIDE 9

This slide shows a delaminated body skin doubler leaving behind the external skin on the surface of the airplane. Notice again that the delamination initiates at the fastener holes and propagates radially from these holes. This is due to the ingression of moisture through the fastener holes.

SLIDE 10

This slide shows a severe case of corrosion in which the waffle pattern doubler has completely peeled away from the external skin, leaving behind serious corrosion. Notice also that the delamination occurs from both the doubler and the external skin, indicating that the problem exists with both of these pieces of the bonded assembly. Also, this type of delamination was accelerated by the environment. In this case, the panel was exposed in the bilge of an aircraft, and the fluids that existed in the area accelerated the corrosion.

SLIDE 11

This quotation is typical of the industry mood toward the usage of bonded structure. What is most critical here is that the quote says that the current technology is not satisfying the requirements of the Air Force. The error with this particular quotation is that the technology used was not the up-to-date, proven technology that could be used to solve the corrosion problems. In other words, the problems that exist today are a result of implementation of the incorrect materials and processes in prior designs and in the fabrication of parts in the late 1950s and early 1960s.

SLIDE 12

Thus far, we have shown the problems with adhesive-bonded structure; we are now going to talk about how we should define those particular problems. It must be understood that it is not possible to solve any technology problem unless you really understand the mechanisms of the failure itself. Thus, an in-depth study of the failure mechanisms occurring in adhesive-bonded structure was necessary.

SLIDE 13

Crevice-cell corrosion is one of the most prevalent mechanisms that occur with adhesive-bonding delamination failures. What happens is that a galvanic cell is set up between the clad material and the base metal. This electromotive difference is supposed to exist because the cladding is placed on the external surface of the base metal as a sacrificial barrier that will corrode away, leaving behind the structural base material. However, when cladding is placed in a bondline, this particular mechanism is not desirable. In other words, it is not desirable to have this sacrificial layer in the interface between the two adherents. What occurs chemically during a crevice corrosion attack is that once a crack is initiated through dissolution of the cladding at the edge of a panel, the crack actually propagates and is accelerated by the crevice itself. In the lower sketch, there is a pH gradient from one end of the crack to the other. The tip of the crack is very acidic, and the tail of the crack is basic because of its oxygen enrichment. The crack tip with the increased acidity has a higher etch rate and actually accelerates crack growth as it grows into the structure. The acidic solution dissolves not only the cladding, but also the aluminum oxide as it progresses through the part. This is the most classic and prevalent type of adhesive-bonding failure.

SLIDE 14

The characteristics of delamination are typified in the photograph and sketch shown in this slide. With the crevice corrosion delamination, the initial failure is an interfacial separation of the adhesive from the substrate. The second step is progressive delamination continuing across the panel, accelerated by the pH gradient in the crevice. It is also accelerated by low stresses acting on the adhesive bond, peeling the adherends apart. As noted previously, the cracks start at a free surface and propagate inward toward the panel center.

SLIDE 15

Crevice corrosion that exists in metal-to-metal bonding also exists in honeycomb bonding. In this photograph, delamination has occurred in the edgeband area of a honeycomb panel, exposing the honeycomb itself to further corrosion.

SLIDE 16

A second classical type of failure is shown here. Once water has progressed into the honeycomb area, the honeycomb foil itself is corroded and separation of the adhesive occurs from the foil itself. Thus, we have a lifting of the face sheet from the core, leaving behind a corroded surface of the cells. For this mechanism to occur, there must be water and relatively low stresses present. The water ingresses either through fasteners or through the hydroscopic adhesive that bonds the face sheet to the honeycomb core. The stresses exist due to air loads or fitup stresses.

SLIDE 17

With the establishment of these failure mechanisms, it became necessary to develop new adhesive test methods that would define the materials and processes necessary to improve the technology. It had become obvious that the traditional static test had not provided the discriminating evaluations necessary to select the proper processes and adhesives.

SLIDE 18

This slide shows a 737 body skin doubler that was returned from service, severely delaminated in certain sections of the adhesive-bonded area, but undamaged and still bonded in other areas. The traditional lap-shear and peel tests on the bonded area of the panel showed that the residual strength was on the order of 5100 psi lap shear and some 72 in.-lb of peel. However, if instead of testing the panel or the coupons using a static type of test, we use dynamic tests coupled with an environmental exposure, we can detect the type of failure that occurred in the delaminated section. As shown in the upper photograph, we fabricated a wedge test specimen and exposed it to a low cleavage type of stress and to an environment of humidity or salt spray. With this combined stress and environmental exposure, the specimen delaminated rapidly; as a matter of fact, it took only a matter of hours for the crack to propagate several inches down the length of the specimen. The crack grew interfacially, which is the same type of failure as occurred in the delaminated area of the panel. In the lower photograph, the peel test specimen had a room-temperature peel strength of 72 in.-1b; however, when we added moisture to the crevice of the peel specimen, the peel strength essentially went to zero and failure mode shifted from being cohesive within the adhesive layer to adhesive between the primer and the adherend, again typifying the type of failure that was seen in the delaminated zone of the panel.

SLIDE 19

If we now compare a good panel with a poor panel (i.e., a panel that has gone through service and not delaminated versus a panel that has gone through service and delaminated), we can see in the upper two comparisons of lap-shear portashear that there is no difference in the shear strength of the good and the bad panel. However, in the third comparison, the wedge test shows that the good panel had essentially no crack growth, whereas the delaminated panel had a precipitous crack growth that occurred in a matter of hours. In the fourth comparison, the toughness of the adhesives was measured; the good adhesive maintained its toughness until it was plasticized by the moisture, and then the toughness dropped off. With the poor adhesive that delaminated in service, the toughness of the adhesive, but instead were seeing an interfacial failure, again typical of the type of failure seen in the panel.

SLIDE 20

Because of the large amount of honeycomb bonding, it became necessary to develop a honeycomb specimen that could be a self-contained static or dynamic test specimen and that could be exposed to an environment at the same time it was being loaded. In this photograph, such a specimen was fabricated by bonding a honeycomb specimen and then clamping this specimen in a fulc rum fixture to impart a bending load to the specimen. This specimen is self contained and can be exposed in the environmental chamber.

SLIDE 21

This slide shows the same type of specimen, only instead of a static load, it has been fitted with a bellows and the same fulcrum arrangement and cyclic stress can be applied. A 1-hour cure cycle was chosen because it represents the Webber chamber simulation of a ground-air-ground airplane flight cycle.

SLIDE 22

This slide shows the ground-air-ground environmental cycle. In the upper left, the humidity is varied from 100% to 0% and back to 100%, while at the same time the temperature is cycled from 140° F to -60° F and back to 140° F. The pressure in the chamber is also changed from sea level to a simulated altitude of 40,000 feet. In the right center, you can see a photograph of the inside of the chamber with a number of these different types of coupons sitting on the racks. The lower part of the slide shows a comparison of old and new-technology adhesive-bonded structure. Reading across, we can see that with no stress there were approximately 100 cells filled with water after 4000 cycles with the old-technology alkaline system, and no water was absorbed even up to 8000 cycles with the newer technology. If a static stress was applied, 50 or more cells filled with water after 700 cycles, whereas there was no water absorbed up to 8000 cycles with the new technology. If a cyclic load and environmental cycle were applied, it is seen that the old technology failed relatively quickly in 250 to 300 cycles, whereas the new technology endured over 8000 cycles without an ingestion of moisture or any propagation of failure.

SLIDE 23

As a result of adhesive resin technology changes and test procedures, a whole new family of test methods has been developed. Instead of using static testing, fatigue testing is used; instead of ambient conditions, a range of temperatures is tested. Instead of a dry exposure, combined moisture along with the fatigue and temperature environment is used. Instead of using a single load, we use a synergestic loading, wherein multiple loads are applied to a panel in much the same way as they are applied to the airplane itself. Instead of using small specimens, we use larger ones that can simulate the types of loading that exist in aircraft structure.

SLIDE 24

Armed with the new test techniques, we are now going to highlight some of the material and process changes that have occurred in the past 10 years. These changes have improved the corrosion resistance of bonded structure from relatively poor performance to a much improved capability.

SLIDE 25

This slide shows the elements that make up an adhesive bond. It is not just a simple interface between two pieces of metal, but actually a complex combination of oxide, primer, adhesive and, in the case of sandwich structure, honeycomb core. Each of these elements has seen a significant improvement in corrosion resistance over the past few years.

SLIDE 26

This slide shows the wedge test coupon discussed earlier and also shows how this particular speicmen was used to develop a new surface preparation; in this case, phosphoric acid anodizing. The curve at the lower right typifies the type of crack growth rate that was experienced with poor interfacial resistance of older surface preparations as compared with the phosphoric acid anodized surface preparation. This simple wedge test specimen has led to one of the most dramatic improvements in adhesive-bonding processes that has occurred in the past few years.

SLIDE 27

The chart shows the phosphoric acid anodize process in boxed format. On the left is shown the six steps necessary for FPL etch (for those of you who are not familiar with FPL etch, it is the sulfuric acid/sodium dichromate etch process). On the right is shown the eight steps that are necessary for the phosphoric acid anodize process. The main difference is in step six, where instead of rinsing and drying the parts, they are immersed in a phosphoric acid anodize bath and anodized for 20 minutes. This particular process creates a measured thickness of porous anodic coating on the adherend.

SLIDE 28

Perhaps one of the most dramatic changes that has taken place in adhesivebonded structure has been the incorporation of corrosion-resistant honeycomb core. On the left is shown the older, uncoated honeycomb; on the right, the metal, organic-coated, corrosion-resistant honeycomb_core. These particular specimens have been exposed to a salt spray environment for 25 days. On the left, the honeycomb core specimens, as well as the foil itself, are severely pitted; whereas on the right, there is no corrosion attack on the edges of the honeycomb foil or on the foil. In addition to the two changes that we have discussed here (phosphoric acid anodize and corrosion-resistant core), there have been a number of other changes to improve the corrosion resistance of bonded honeycomb structure. Specifically, the clad adherends have been changed to bare adherends to eliminate the problem of clad dissolution. Corrosion-resistant primers have been implemented. In the past, either no primers, or primers that were susceptible to moisture degradation, were used. Lastly, toughened epoxy adhesives have been used; not only do they have better toughness and resistance to peeling, but they also have higher resistance to moisture ingression. Thus, the amount of moisture that reaches the interface of the bond has been decreased.

SLIDE 29

Shown next are some of the recent test results and experimental work in the area of phosphoric acid anodizing and comparison of phosphoric acid anodzing with other surface preparations.

SLIDE 30

This slide shows cross sections or edges of three different types of oxide in electron microscope photographs. On the left is shown the traditional sulfuric acid/sodium dichromate (FPL) etch and the relatively thin oxide layer that is developed with that process. In the center is shown the phosphoric acid anodize process on 7075 bare alloy. On the surface of the anodize is seen a flake type of oxide structure. On the right photograph is shown a phosphoric acid anodize on 2024-T3 clad material; the traditional needle and very deep pore type of oxide structure can be seen. Contrasting these photographs, it can be seen that the anodize on clad material has a thickness of 5000 angstroms. The anodize on the bare material has an oxide thickness of 2500 to 3000 angstroms, and the oxide developed by the FPL etch has a thickness of 400 to 500 angstroms. Also contrasting these different types of oxide, it can be seen that the one on the far right with the needle-like structure would have a much greater surface area for bonding to a liquid adhesive primer.

SLIDE 31

This slide shows a family of micrographs with three different types of adhesive primers applied over the surface of the oxide itself. On the left photograph, there is partial primer penetration into the oxide pores; in the center photograph, there is complete penetration; and in the right photograph, there is an excessive aount of primer built up on the oxide surface. A thicker rubber coating can be seen on the surface of this particular specimen.

SLIDE 32

This photograph was taken from a cross section of an anodized surface that had been sliced into a thin wafer on a microtome device. The microtoming procedure is being developed for biological inspection and, in this case, is applied to the sectioning of an anodized surface impregnated with a primer resin. On the left photograph is shown the structure of a bare phosphoric acid anodized surface and on the right, a clad anodized surface. Both of these are shown at the same magnification and show the same type of cellular honeycomb structure for each. In both cases, the oxide wall thicknesses are on the order of 50 to 100 angstroms and the diameters or cross sections of the pores themselves are on the order of 300 to 500 angstroms. It can also be seen that the pores are all completely filled with resin such that the oxide is stabilized and there is no open structure to collapse during loading of the specimen.

SLIDE 33

This slide shows a cross section of the base metal/oxide/primer interface and the interaction between the multiphased primer and the oxide itself. Note that there are at least two phases in the adhesive primer and there is an enrichment at the interface of the second phase. Note also that there is penetration of the adhesive primer down into the cellular structure of the oxide. Ignore for the moment the artifact that exists in the center of the oxide itself. These are sectioning artifacts that occur during specimen preparation that were not present during the original bonding.

SLIDE 34

This slide is an enlargement of slide 33 showing the oxide interface with both base metal and the primer itself. Note again that in the center there is a sectioning artifact and that across the artifact there are necking pieces of material, indicating that the primer has penetrated to the bottom of the oxide pore. Note also that there is a base oxide layer at the bottom of each of the pores between the base metal and the oxide structure.

SLIDE 35

With the advancements that have been made in adhesive bonding, it is now possible to commit this technology to every greater applications in the aerospace industry.

SLIDE 36

This slide shows the YC-14 advanced medium STOL transport that was built by Boeing for the Air Force. In this particular aircraft, adhesive-bonding technology was applied to the primary structure of the aircraft. Specifically, the vertical fin and the horizontal stabilizer torque boxes were bonded aluminum honeycomb structure.

SLIDE 37

This sketch shows the details used in the fabrication of the YC-14 empennage and the type of honeycomb structure used for this application of bonded technology.

SLIDE 38

This slide shows the application of adhesive bonding to the 767 aircraft that is emerging today at The Boeing Company. On the 767, there are the traditional applications of metal bonding for tear straps and doublers, as well as for fail-safe structure and rib structure in the empennage area. However, there is an absence of some of the control surfaces that had traditionally been bonded aluminum honeycomb structure; these have been replaced with graphite structure.

SLIDE 39

Bonded aluminum structure is in competition with graphite structure as an alternative means of fabrication of aerospace components. The future of adhesive bonding is going to depend upon the advancements that can be in terms of reducing the weight of aluminum structure compared to graphite structure, such that the advantages that now exist for graphite are reduced through the use of lighter weight and stronger aluminum face sheet structure such as aluminum-lithium alloys or metal-matrix composites. In this way, bonded aluminum structure will become more attractive from a weight standpoint when compared with graphite structure.

SLIDE 40

This slide summarizes the trends occurring in adhesive-bonding technology. Specifically, the use of bonding has emerged from secondary to primary structure and, in the future, will be used for more and more hightemperature applications. At the same time, it has become necessary to establish meaningful test techniques that duplicate the loads and environments seen by the components in service. It has been necessary to simulate the types of surface failure and to identify the failure mechanisms that cause bond separation, corrosion, and delamination. What has evolved is a technology that is stable in the environments of moisture, temperature, and fatigue exposure seen on aircraft today.

HISTORICAL FLOW CHART



427

HISTORICAL FLOW CHART



MELDERCH LIDW CAR

428

EXTENT OF USAGE—ADHESIVE BONDED STRUCTURE



747 ALUMINUM HONEYCOMB USAGE



HISTORICAL FLOW CHART



EXAMPLES OF HONEYCOMB SERVICE FAILURES



WATER INGESTION



CORE DISBOND



DELAMINATION



ALD QUOTE

"THE INTEGRITY OF ALL BONDED HONEY-COMB STRUCTURE HAS BECOME AN AIR FORCE-WIDE PROBLEM. THE CURRENT TECHNOLOGY IS NOT SATISFYING AIR FORCE REQUIREMENTS BY PROVIDING A REALISTIC AND RELIABLE END PRODUCT."

> SA-ALC/MMIR LETTER TO ASD/SD5E, 25 JANUARY 1977

HISTORICAL FLOW CHART



434

GALVANIC AND CREVICE CORROSION



CHARACTERISTICS OF DELAMINATION FAILURES IN SERVICE

MECHANISM

EXAMPLE



CHARACTERISTICS

- INTERFACIAL FAILURE MODE
- **PROGRESSIVE GROWTH**
- LOW STRESS

• INITIATE AT FREE SURFACE





CREVICE CORROSION

MECHANISM



EXAMPLE



CHARACTERISTICS

- OXYGEN DEPLETION IN CRACK
- LOW pH AT CRACK TIP
- DISSOLUTION OF CLADDING AND OXIDE

WATER INGESTION



WATER INGESTION







HONEYCOMB FOIL AND ADHESION SEPARATION

HISTORICAL FLOW CHART



AFWAL-TR-81-4019 Volume II

BONDED 737 COMPONENT (CIRCA 1969) DELAMINATED IN SERVICE TESTS ON UNDELAMINATED SKIN-DOUBLER BOND AREA





VPICAL UDADING ARRANGEMENT

441

TYPICAL LOADING ARRANGEMENT





CYCLIC LOAD





CYCLIC LOAD ARRANGEMENT

CYCLIC LOAD CYCLE

GROUND—AIR—GROUND ENVIRONMENT



TYPICAL	RESULTS

BONDING TECHNOLOGY	NO STRESS	STATIC STRESS	CYCLIC STRESS
OLD	100 CELLS, WATER, 4,000 CYCLES	50 CELLS, WATER, 760 CYCLES	FAILED, 260 CYCLES
NEW	NO WATER, 8,000 CYCLES	NO WATER 8,000 CYCLES	NO FAILURE, 3,000 cycles

EVOLUTION OF TEST METHODS



HISTORICAL FLOW CHART



446

ELEMENTS OF BONDING

HONEYCOMB SANDWICH





448

Comparison of FPL Etch and Phosphoric Acid Anodize Processes





TONMYOON HO-1



HISTORICAL FLOW CHART



COMPARISON OF PRIMERS ON PHOSPHORIC ACID



50,000X



50,000X

179-08541-08-02-79

PARTIAL PENETRATION (THIN RUBBER CONTAINING PRIMER ON 2024-T3 CLAD)

COMPLETE PENETRATION PRIMER ON 2024-T3 CLAD)

EXCESSIVELY THICK PRIMER (THIN RUBBER CONTAINING (THICK RUBBER CONTAINING PRIMER ON 2024-T3 BARE)

50,000X









BARE





180,000X

TEM Photo



TEM Photo



HISTORICAL FLOW CHART



AFWAL-TR-81-4019 Volume II

BONDED STRUCTURE – YC-14 PROTOTYPE



YC-14 EMPENNAGE DESIGN



458



HISTORICAL FLOW CHART



460

FUTURE BONDING NEEDS

SECONDARY PRIMARY HIGH TEMPERATURE

REQUIRED TEST METHODS-

461

1. MEANINGFUL, DUPLICATE LOADS AND TEMPERATURE

2. SIMULATE SERVICE FAILURES

3. COMBINE EFFECTS OF MOISTURE, TEMPERATURE, SPECTRUM FATIGUE.