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Thermabond® Surface Adhesion

Thermabond® adhesion to aluminum with various anodized coatings

The purpose of this application note is to provide a basic understanding of anodized coatings on aluminum, and to present the results of a study conducted at Arlon that evaluated the adherence of Arlon's 99990A008 Primerless Thermabond® to specified anodized coatings. Chromic and Sulfuric acid anodized coatings unsealed and with hot water and dichromate sealants as dictated by the MIL-A-8625F specification were selected for evaluation. In summary, the data indicates excellent bond strength to the six standard anodized coatings when laminated with both platen press and vacuum bag pressure. The results can be extended to Arlon's 48991A### and 48781A### Thermabond® products because the silicone adhesive to anodized aluminum surface bond interaction is very similar to that of the 99990A### product.

99990A008 Adhesive Shear Strength to Anodized Aluminum after Platen Press Lamination					
Chromic Acid Anodized			Sulfuric Acid Anodized		
Not Sealed	Hot Water Sealed	Dichromate Sealed	Not Sealed	Hot Water Sealed	Dichromate Sealed
1193	1176	1148	1230	1199	1181

Platen Press Adhesion Results in PSI

99990A008 Adhesive Shear Strength to Anodized Aluminum after Vacuum Bag Lamination					
Chromic Acid Anodized			Sulfuric Acid Anodized		
Not Sealed	Hot Water Sealed	Dichromate Sealed	Not Sealed	Hot Water Sealed	Dichromate Sealed
904	993	1035	969	966	1044

Vacuum Bag Adhesion Results in PSI

Thermal management of electronic systems is a critical component for assembly design longevity and reliable life cycle functionality. The printed circuit board and aluminum heat sink coupled assemblies used in aerospace and automotive industries operate in demanding environments. Exposure to a wide range of operating temperatures, including thermal shock situations, can easily induce printed circuit board stress. Ensuing PCB deflection and warp can subsequently result in reduced solder joint reliability and, ultimately, assembly failure. Arlon's Thermabond® adhesives offer a design solution to fundamental problems critical to many electronic assemblies. Arlon offers a unique class of elastomeric thermal interface materials that provide thermal-mechanical stress decoupling. Furthermore, these materials offer a conductive path with minimal impedance for proper PCB component thermal management. Assembly components coupled with Thermabond® are joined together, but remain capable of independent movement during thermal cycles thus eliminating PCB stress build-up. A crucial design consideration for electronic assemblies is not solely the type of adhesive chosen for thermal mechanical decoupling, but also the adhesive's compatibility

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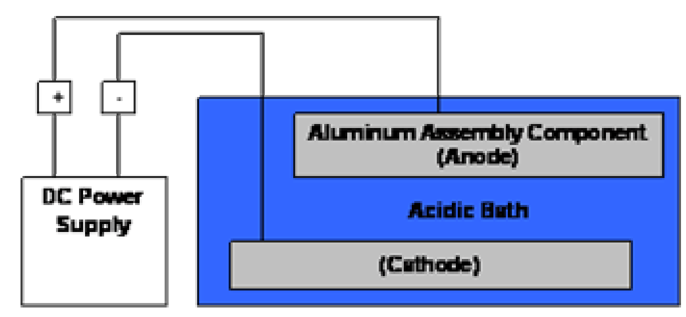
with the heat sink surface coating. Some of the most prevalent aluminum heat sink coatings are those produced through surface anodization. Thermabond® bond integrity against anodized coatings is of utmost importance for proper electronic assembly operation and service longevity.

Arlon's Primerless Thermabond® adhesives all bond to inorganic surfaces using a similar chemical process. The bonding target on an inorganic surface is the hydroxyl group. The surface of aluminum has a naturally fomed oxide layer that adheres to the metal, and the target groups within this layer form oxane bonds with the Thermabond® adhesives.[1] It is through these bonding sites that the Arlon adhesives form very strong, stable covalent linkages to surfaces such as bright aluminum. However, the aluminum alloy surface in many electronic assemblies may have an anodic coating that is added to the alloy surface to provide a hard, wear resistant, electrically insulating, corrosion inhibiting coating.[2]

Anodizing a metal surface is the process of growing an oxide film through an electrochemical process. Many types of metals can be anodized, but the focus of this application note will be the most commercially anodized alloy, aluminum. Aluminum has a naturally occurring barrier oxide layer of 2-3 nanometers in thickness. However, it is the thick, porous oxide film unique to aluminum when anodized in acid electrolytes that are of commercial interest for aluminum assemblies.[3] In particular, this application note will focus on several MIL-A-8625F anodic coatings of aluminum assemblies grown in both chromic and sulfuric acid baths.

The anodization process takes place in a cell where the assembly component is connected to the positive terminal of a DC power supply, which acts as the anode, and an unreactive, conductive, metallic component serves as the cell cathode. Cell components are submerged in an acid bath to complete a circuit. Electrons flow from the anode, and ions at the component's surface react with water to begin growth of an oxide layer. Hydrogen gas is formed as a by-product when electrons react with hydrogen ions at the cathode.[4]



Anodization Cell

The complete chemical reaction that takes place at both the anode and cathode within the acid bath during this anodization process of aluminum is as follows:

$$2Al + 3H_2O \Longrightarrow Al_2O_3 + 3H_2$$

Reactions at the anode can be separated into two fronts that include the metal/oxide interface and the oxide/electrolyte interface. At the metal/oxide interface, mobile oxygen anions in the electric field migrate and react with the aluminum metal:

$$2Al + 3O^{2-} \Longrightarrow Al_2O_3 + 6e^-$$

At the oxide/electrolyte interface, aluminum cations migrate and react with water:

$$2Al^{3+} + 3H_2O \Longrightarrow Al_2O_3 + 6H^+$$

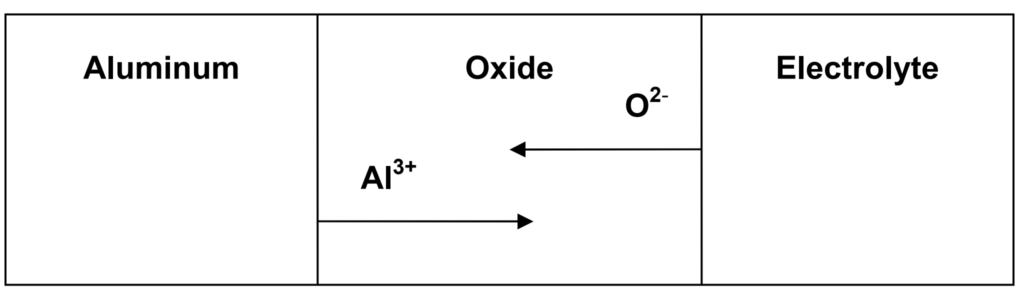
The acidic nature of the aluminum anodization bath causes some aluminum dissolution during this electrochemical process; therefore, additional reactions occur at the anode:

$$2Al \Longrightarrow 2Al^{3+} + 6e^-$$

The reaction at the conductive metallic cathode involves the development of hydrogen gas:

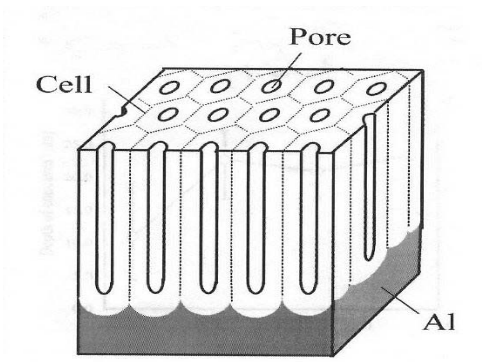
$$6H^+ + 6e^- \Longrightarrow 3H_2$$ [5]

The ion transport mechanism at the aluminum surface is represented in the following figure:



Ion transport through the oxide film[6]

A porous oxide layer actually grows inward into the aluminum metal and away from an barrier oxide at the oxide/electrolyte interface resulting in oxide growth orders of magnitude greater than either naturally occurring or annodized barrier oxide layers. The oxide layer thickness consists of column-like, geometrically shaped cells with centrally located pores. Cell diameters range from 50 to 300 nanometers with pore diameters ranging from 16 to 25 nm and 100 to 150 nm respectively. The number of cells in a square centimeter of oxide coating can range from one to ten billion. Different cell and pore sizes are generally distributed randomly throughout an oxide layer, and these properties are determined by the anodization cell processing parameters.[7]



Idealized cellular structure of an aluminum oxide coating[8]

The pores of the aluminum oxide layer can be sealed as a post processing step to provide a degree of impermeability to the porous coating. This process typically involves reacting the oxide coating with either hot water or a dichromate solution. The reaction with hot water forms a hydrous oxide over the anodized oxide coating and within the pore structure. The hot water sealing reaction is as follows:

$$Al_2O_3 + 3\ H_2O \rightarrow 2\ AlOOH{*}H_2O$$ [9]

Dichromate sealing is usually employed to improve corrosion inhibition of an anodized aluminum coating. The dichromate sealing process is two fold, first which involves chromate absorption into the oxide layer pores followed by closing of the pores with a hydrous oxide. [10]

The adhesion experiment conducted at Arlon involved six groups of 15 anodized alumimun-to-aluminum lap shear coupons bonded with 0.5 in^2 of Arlon's 99990A008 Primerless Thermabond® adhesive. All aluminum coupons were cleaned with isopropanol before application of the adhesive. One set of each group of lap shear coupons was laminated in a heated platen press for 21 minutes at 121°C. To ensure proper adhesive mating to the anodized surface, the adhesive was controllably compressed to 0.127 mm. A second set of each group of lap shear coupons was cured in a vacuum bag for 60 minutes at 121°C. A lamination press of 101 KPa generally produces less than a 0.0254 mm bondline deflection. The anodic coatings for the experiment are summarized by the MIL-A-8625F military specification as indicated below:

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Type I Chromic Acid, Sealed	Type II Conventional Sulfuric Acid, Sealed
Hot water and Dichromate	Sealed Hot water and Dichromate
Class 1 (not dyed)	Class 1 (not dyed)
Minimum Coating Weight (200 mg/ft2)	Minimum Coating Weight (600 mg/ft2) [11]

A shear strength value of 1250 psi is considered the maximum mean value for the 99990A008 adhesive when bonding mechanically abraded bright 6061 aluminum coupons in a platen press. This maximum mean value of 1250 psi is reduced by approximately 20% to 1000 psi when vacuum lamination pressure is used. The adhesive shear strength value difference is a function of adhesive surface mating. Vacuum bag lamination pressure does not force an intimate mating of the adhesive to the bonding surface quite as well as higher lamination pressures.

The 99990A008 shear strength and bond strength results to the anodized aluminum surfaces of this study are all considered very good regardless of the lamination process. Both Chromic Acid and Sulfuric Acid (Type I and Type II) anodizations produce bonding surfaces that have minimal impact on the bond strength of the 99990A008 adhesive. When compared to the idealized bonding surface of abraded bright aluminum, the anodized surfaces contribute minimally to reduction in adhesive bond strength. Furthermore, the impact of hydrous oxide sealants is relatively insignficant to the surface characteristics that are necessary for optimal adhesive performance.

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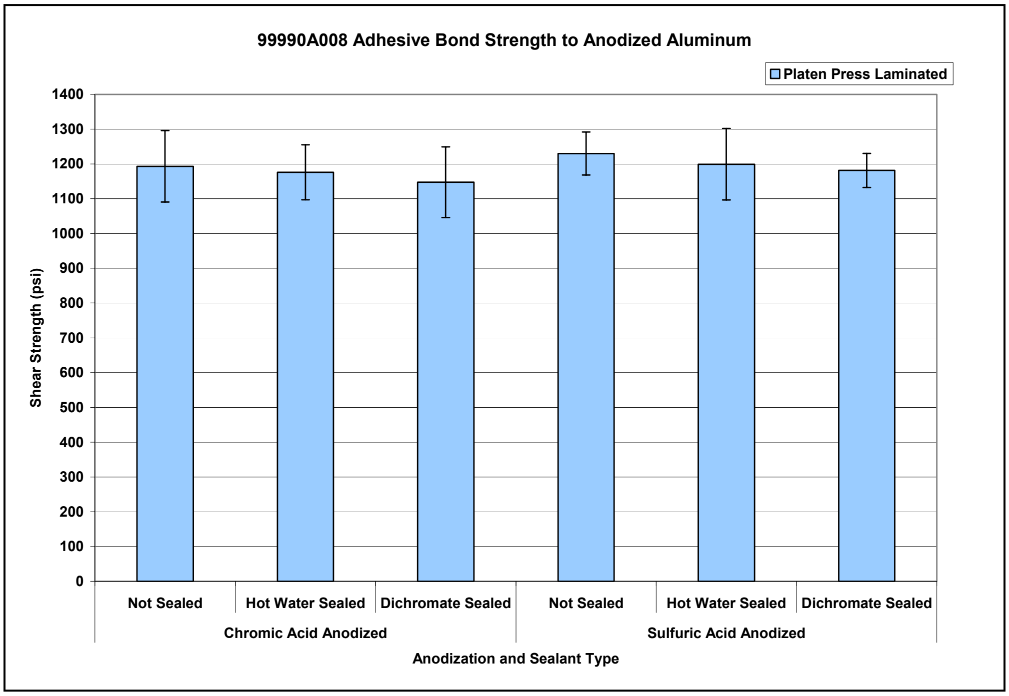
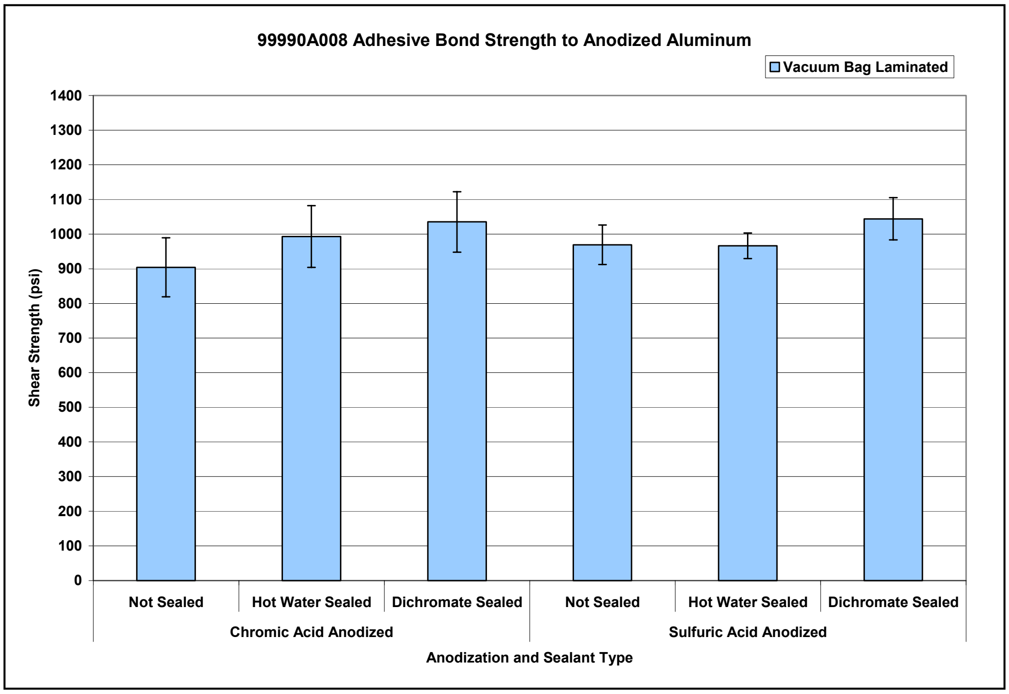


Platen Press Adhesion Results



Vacuum Bag Adhesion Results

The bond results to the selected military specification, anodized aluminum surfaces of Arlon's Improved Handling Primerless Thermabond® products, 48991A010 and 48781A008, may also be considered good because the chemical mechanism for adhesion is the same as with the 99990A008 product. While these products have a lower initial shear strength than the 99990A008 product in idealized bonding conditions, the relative bond strength values to the anodized aluminum surfaces in this study are applicable.

This Application Note is based on experimental laboratory results and should therefore be considered for reference purposes only. Specifically, we ask that this Application Note not be used in establishing process and product parameters and specifications without confirmation and validation studies conducted with actual assembly components and production processes.

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3 Robert S. Alwitt, "Anodizing," Electrochemistry Encyclopedia, (Illinois: Boundary Technologies, 2002) 1, 2.

4 Alwitt 1.

5 Alwitt 8-9.

6 Alwitt 2.

7 Alwitt 4-5.

8 Alwitt 4.

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11 Cochran 397.