Effect of Time Delay Between Etching and Adhesive Bonding ("Outlife" Time) on Lap-Shear Strength of Aluminum Alloys Using Environmentally-Friendly P2 Etch

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Abstract

Raytheon Company currently uses a Forest Products Laboratory (FPL) paste etchant for preparing aluminum surfaces for adhesive bonding, and FPL is a source of hazardous hexavalent chromium. The goal of this study was to evaluate a less-toxic P2 paste etchant as a possible replacement. Coupons of 2024-T3, 6061-T6, and 7075-T6 grades of aluminum alloy were solvent-degreased, abrasively cleaned, and etched at room temperature using P2 paste following a strict protocol adopted from Raytheon. Coupons were then left exposed to air for assigned time intervals (or "outlife" times) of 0, 1, 4, 8, 16, and 63 or 72 hours. The aluminum alloy coupons were then adhesively bonded together using Loctite EA9394 adhesive with an approximate bonding area of 0.5" by 1.0" and 0.010-inch thickness into single-lap joints for testing as per ASTM D1002. Samples were placed in a tensile-test fixture on an Instron with a pull rate of .05 in/min to measure bond shear strength. Decrease in shear strength was plotted as a function of outlife for each alloy, and statistical analysis was carried out to identify outlife times for each part which bond strength decreased significantly. The information obtained will further the development of future P2 etch processes, providing maximum allowable outlife times prior to commencing structural adhesive bonding operations.

Keywords: etchant, aluminum, adhesive, lap-shear, shear strength, outlife, FPL, P2

1. Introduction

Aluminum alloys are amongst the most popular engineering alloys used worldwide in the aerospace industry (as well as countless other industries). They possess superb mechanical properties while also being relatively cheap. In structural applications, these alloys have been joined by riveting or welding, but adhesive bonding has seen increasing use in primary structural bonding of aircraft components for over 50 years and has been a direct competitor to riveting, though not as prevalent, and more recently in the automotive industry. Adhesively bonding aluminum alloys is efficient and low-cost, and confers significant weight savings in the final product. Using adhesives also has the benefit of eliminating stress concentrations and subsequent distortion of the alloy that can occur during riveting or welding operations [1]. It is also an

efficient way of eliminating manufacturing tolerance stack up, reducing the need for highly precise machining tolerances.

The goal of structural adhesive bonding is to produce a completed part that is seamless in terms of its mechanical properties. That is, the bond needs to be strong enough such that the metal itself yields before the bond does, allowing the part to be regarded as a single, continuous piece. However, the tendency of aluminum to rapidly form an oxide layer in the presence of air renders it chemically incompatible with the adhesive and will result in poor bond strength. This necessitates a process to optimize the oxide's morphology and chemically activate the surface in order to maximize bond strength [2, 3]. This can be accomplished either by etching the alloy or applying a specialized process before an adhesive is applied. It is recommended that bonding be conducted as soon after etching as possible, since the etchant produces a chemically-active surface that will quickly bind dust or impurities from the surrounding environment, all of which degrade adhesive bond strength [4]. For the remainder of this paper, the time interval during which samples are left out between etching and bonding will be referred to as "outlife".

The two most widely-used etchants in the aerospace industry are the optimized Forest Products Laboratory (FPL) and P2 etchants, the latter of which will be the focus of this investigation. The FPL etchant, developed in 1950 and refined (hence the term "optimized") in 1975, saw a great deal of use in the aerospace industry for a number of years. However, the use of toxic and potentially-carcinogenic hexavalent chromium compounds in the FPL etch process led to many countries no longer allowing its use. In the U.S. most communities impose extremely strict limits on effluent emissions in the parts per billion range. The P2 etchant was developed as a less toxic alternative, and was able to achieve similar or superior bond strengths compared to its predecessor [2].

In production, etching is generally accomplished by immersion of a pre-treated aluminum part in a tank of hot etchant solution. However, the etchants are sometimes mixed with fumed silica to form a paste etchant that is used at room temperature for preparing oversized parts or for repairing in-service adhesive joints. While the paste etch variant of the P2 etch may result in somewhat lower bond strength, Raytheon Company uses paste etchants in production, hence the

focus of this study is on paste etchants. Unfortunately, there is a lack of published literature directly comparing paste and tank etchants, and it is not precisely known how the etching mechanisms differ. Raytheon has achieved sufficient production bond strengths for its applications using an FPL paste, but lacks information on the performance of a P2 paste. This study is intended to assess this performance in order to inform the development of an alternative process to the FPL paste. Specifically, the goal of this study is to determine the effect of outlife after P2 paste etching on single-lap shear strengths of adhesively-bonded specimens of Al 2024, 6061, and 7075 alloys.

2. Literature Review

This section will provide an overview of the alloys and adhesives to be used in the study, common steps for preparing aluminum alloys for bonding, and the comparative effects of the optimized FPL and P2 etch processes on the alloys.

2.1 Aluminum Alloys Used

Aluminum alloys are commonly used in aerospace, automotive, marine, and building applications because of their high strength-to-weight ratio with a low average density of approximately 2.7g/cm^3. Specific properties can be obtained by changing their alloy compositions and temper conditions. Al 2024-T3, 6061-T6, and 7075-T6 are the alloys and tempers used in this study. Al 2024 is an Al-Mg-Cu alloy, while Al 6061 is an Al-Mg-Si alloy and Al 7075 is an Al-Mg-Zn-Cu alloy [5, 6]. The listed alloys have shear strengths of 40 ksi, 41 ksi, and 48 ksi, respectively [7].

The action of an etchant on a specific aluminum alloy depends on the pitting corrosion behavior of that alloy, since the main purpose of the etching procedure is to generate a porous surface oxide [3]. This behavior depends on the alloy composition, since pits are thought to be initiated at some heterogeneity on the surface, such as constituent particles of the alloying elements in the case of the alloys used in this study. The presence of the alloying elements is thought to cause a large difference in electrode potential with regard to the alloy matrix, which may be either anodic or cathodic depending on the specific composition in question. Cathodic particles would tend to

have a greater effect as pit initiators due to the rapid dissolution experienced by anodic particles. This dissolution, coupled with continuous galvanic action, means that cathodic particles also have a realm of influence extending to many times the size of the particle itself, creating larger pits [3, 8]. A difference in pitting behavior due to the presence of alloying elements is corroborated in the literature, as Al 2024 etched by both FPL and P2 showed a much greater degree of pitting compared to Al 1050, which has an alloy composition closely approaching that of pure aluminum [3]. Generally, the 6xxx-series alloys are considered to have better resistance to corrosion compared to the Cu and Zn-containing 2xxx and 7xxx-series alloys, and this could play a role in differences in the effects of the P2 paste etch treatment on the different alloys used in the present study [5]. Additionally, the T6 temper condition is considered to be more prone to intergranular corrosion due to short inter-particle distances that allow the advance of corrosion past the surface. Since pitting corrosion advances by way of localized sub-surface attack of the metal, the temper condition would be expected to affect the action of the etchant [6].

2.2 Overview of Pre-bonding Surface Preparation of Aluminum

Aluminum rapidly oxidizes when exposed to air, forming a thin (~10 nm) layer of aluminum oxide and/or hydroxide. This natural oxide layer is unstable and leads to adhesive bond strengths that are generally regarded as poor. This necessitates the application of a chemical or electrochemical treatment to build an oxide layer more suitable for bonding [3]. Generally speaking, these treatments improve adhesion by modifying the surface chemistry and generating a strongly adhered porous oxide layer that provides a greater degree of mechanical "keying" with the applied adhesive [10]. For several years after its development in the 1950s, use of the chromic-acid based FPL etch process and its variants was industrial practice, but a variety of replacements have since been developed as a number of countries started to phase out treatments containing chromates over toxicity concerns. When electrochemical immersion processes cannot be used, the most promising among these replacements is the sulfuric acid-based P2 etch [2].

The common steps for many surface preparation processes for adhesively bonding aluminum alloys are listed in ASTM D2651. The first step is to degrease the metal to be bonded. Vapor degreasing is recommended by using isopropanol, but this may also be combined or substituted

with an alkaline degreasing solution. It is also noted that the removal of grease may be accomplished with a large variety of common solvents. Following degreasing, oxidized surfaces should be scrubbed with a non-metallic abrasive such as aluminum oxide-impregnated nylon Scotchbrite 7449 matting as an initial deoxidizing step. The aluminum is then rinsed of abrasive and debris and subjected to a water-break test. According to ASTM D2651, successful cleaning will result in water forming a continuous sheet of water on the surface during a 30 second drainage period as opposed to individual droplets of water (water break-free condition). Parts in this condition then continue on to further process steps, where the aluminum can be treated either by immersion in an etchant solution - usually FPL or P2 - or phosphoric acid anodization [4].

Commercially, a bulk pretreatment apparatus consists of a series of tanks containing the needed solutions arranged with overhead cranes to move parts through the processing steps. These tanks may be fitted with circulation and/or temperature control mechanisms depending on specific processing needs. ASTM D2651 also lists the conditions under which surface preparation processes must be done, listing specific cleanliness standards for rinse and solution water, as well as general temperature, humidity, and cleanliness standards for room conditions. It is recommended that water for preparing solutions be treated to reach a condition of not more than 50 ppm of solids with a pH between 5.5 and 10. Conditions in the processing environment should be controlled to a temperature between 18 and 24 °C, with a relative humidity of between 40 and 65 percent, and with air pressurized to slightly above ambient condition and filtered to remove dust particles. [4].

2.3 Optimized FPL Etch Process

In its original formulation, the FPL etchant consists of 30 parts H_2O, 10 parts H_2SO_4, and 2 parts $Na_2Cr_2O_7$. The so-called “optimization” involves the addition of copper (Cu), either in the form of copper sulfate or by dissolving an amount of Al 2024 in the etchant solution. The addition of copper appears to assist in the formation of small, deep pores that enhance bonding ability [2].

Much of the existing knowledge about the FPL etchant and its function was generated by investigators at Martin Marietta Labs, who proposed that the following two reactions occur during the etch process:

$$2Al + H_2SO_4 + Na_2Cr_2O_7 \rightarrow Al_2O_3 + Na_2SO_4 + Cr_2SO_4 + 4H_2O \qquad \textbf{(Eq. 1)}$$

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O \qquad \textbf{(Eq. 2)}$$

Equation 1 shows the reaction of the etchant with the aluminum alloy, leading to the formation of an alumina (Al_2O_3) surface layer, and Equation 2 represents the dissolution of the alumina by sulfuric acid present in solution. It was found that the aluminum oxide-producing reaction proceeded at a faster rate than the reaction of the oxide with sulfuric acid, leaving a controlled amount of alumina on the alloy surface. Figure 1 shows a micrograph and isometric drawing of the surface oxide structure after FPL etching and subsequent rinsing [2].

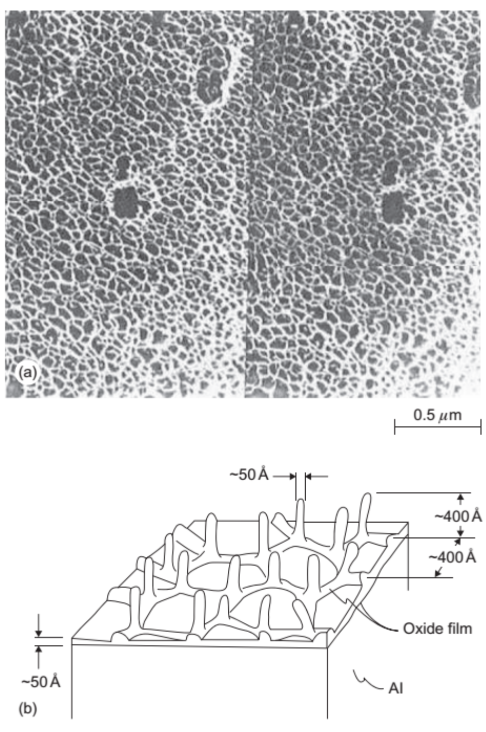

Figure 1. Stereo STEM micrograph of oxide morphology of FPL treated 2024 aluminum surface. **B)** Isometric drawing of proposed oxide structure [2]

2.4 P2 Etch Process

The P2 etchant was developed during the 1970s as a chromate-free and minimally-toxic alternative to the FPL etchant, consisting of 370 grams of concentrated sulfuric acid, 150 grams of 75% ferric sulfate, and sufficient water to make up one liter of etchant [2]. The effect of P2 etchant on Al 2024 was studied by a team of investigators at the U.S. Army's Armament Research and Development Center (ARDEC), who proposed that the etchant attacked the aluminum alloy through the following reactions:

$$2Al + 6H \rightarrow 2Al + 3H_2 \qquad \textbf{(Eq. 3)}$$

$$Cu + 4H^{+} + SO_4^{-} \rightarrow Cu^{++} + SO_2 + H_2O \qquad \textbf{(Eq. 4)}$$

$$3Fe^{+++} + Al \rightarrow Al^{++} + 3Fe^{++} \qquad \textbf{(Eq. 5)}$$

$$2Fe^{+++} + Cu \rightarrow 2Fe^{++} + Cu^{++} \qquad \textbf{(Eq. 6)}$$

Equations 3 and 4 illustrate the effects of the sulfuric acid in the P2 etchant on the 2024 alloy, showing the standard attack on Al by acids and the attack on Cu by hot sulfuric acid. These reactions with the sulfuric acid are accompanied by reactions with the ferric sulfate (Equations 5 & 6). Ferric salts are corrosive to Al, causing pitting of the alloy surface, and Cu is further attacked by ferric salts, which act as oxidizing agents and cause selective etching of Cu-containing micro-constituents, leading to non-uniform attack at specific areas [2, 3]. This contrasts with the reaction of Al with sulfuric acid alone, which results in simple dissolution of the metal [2].

2.5 Comparison of Effects of Optimized FPL and P2 Etches

The oxide layers generated by FPL and P2 have some key morphological and chemical similarities. Both etchants leave a compositionally homogeneous layer of porous alumina with thicknesses on the order of 10 nm and of similar densities. In one study of pretreatment effects

on aluminum, Energy Dispersive Spectroscopy-Scanning Electron Microscopy (EDS-SEM) analysis revealed that both etchants react with and completely eliminate traces of Fe from the alloy's surface, and reduce the concentration of Cu on Al 2024 surfaces by 50% [3]. X-ray Photoelectron Spectroscopy (XPS) analysis of etched Al 5005 from another study revealed that both etchants caused changes in the ratios of oxygen-containing species, specifically Al-O, Al-OH, and Al-OH_2 at the surface. These changes were accompanied by large variances in oxide thickness, and it was proposed that this is a result of the highly active etched surfaces reacting with atmospheric moisture. This suggests that the precise surface chemistry of the etched surfaces depends on the post-treatment environment [10].

Compared with FPL-etched aluminum alloys, P2 forms an oxide layer with enhanced porosity and roughness due to the formation of larger and more numerous pits in the alloy surface. Figure 2 shows SEM micrographs of FPL and P2-etched Al 2024 for comparison. The secondary electron (SE) micrographs (Figs. 2a & 2c) show the topography of the etched surfaces while the backscattered electron (BSE) micrographs (Figs. 2b & 2d) show differences in chemical composition. The greater roughness of the P2-etched surface contributes to the type of mechanical keying that, in principle, should lead to higher lap shear strengths. In terms of surface chemistry, the main difference between FPL and P2-etched alloys is the removal of Si by P2 when etching Al 6xxx alloys. FPL, on the other hand, minimally affects the surface concentration of Si [3].

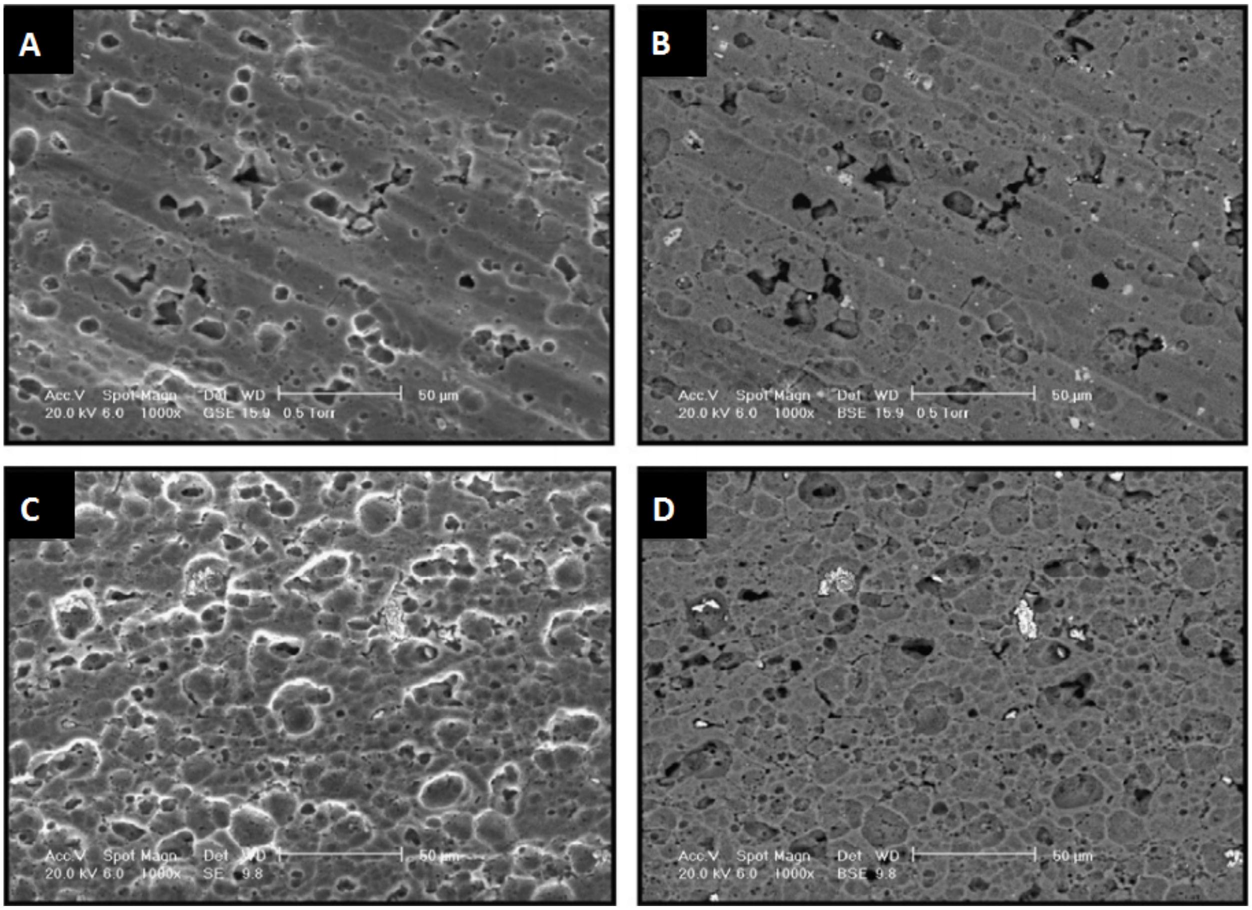

Figure 2. SEM micrographs of Al 2024 treated with FPL (top row) & P2 (bottom row). SE images show topography & BSE images show composition (x1000) **(A)** SE image of alloy after FPL etch **(B)** BSE image of alloy after FPL etch **(C)** SE image of alloy after P2 etch **(D)** BSE image of alloy after P2 etch [3].

Adhesive bonds prepared using the P2 etch have lap shear strengths similar or superior to those treated with FPL, and remain comparable even after exposure to various service conditions. This indicates that the P2 etch could potentially be used to replace FPL. After FPL etches Al 2024 and Al 7075 alloys, it produces lap shear strengths of 2.8 ksi and 3.8 ksi, respectively. After P2 etches the alloys, it produces equal or greater lap shear strength than FPL [11, 2].

2.6 Adhesive Used

For this project, the adhesive used to join the aluminum alloys together is Loctite EA9394, a two-part structural adhesive made by Henkel Aerospace for metal-to-metal bonding. Parts A and B consist of epoxy resins and amines, respectively, and are mixed in a 100:17 ratio. The adhesive cures at room temperature and possesses excellent strength to 177 °C and higher [9].

3. Experimental Procedure

3.1 Materials and Equipment

Sheets of Al 2024 T3, 6061 T6, and 7075 T6 were supplied by Raytheon and Mcmaster Carr company for aluminum coupon preparation. P2 etch paste (15% by weight $FeSO_4$, 37% H_2SO_4, and 48% H_2O, and 5% Cab-O-Sil) was supplied by Raytheon. EA9394 Adhesive (Loctite) for bonding of coupons was provided by Raytheon. 120-grit sandpaper, Ajax powder soap, and isopropanol were all purchased through external vendors by Cal Poly San Luis Obispo Materials Engineering Department.

Aluminum coupons were cut from sheet stock using a PEXTO 12-U-4-F Squaring Shear and machined on a Bridgeport Vertical Knee Mill. A ½-inch diameter, dual-flute high-speed steel end mill was used for metal at a speed of 1115 revolutions per minute.

Lap-shear testing was conducted on an Instron 3369P6252 with a 50 kN (11,250 lb) load cell in accordance with recommendations in ASTM D1002. Bluehill software was configured specifically for lap-shear testing and was used to produce line graphs showing load (lb) against tensile extension (in). Using the load at break and the area input, the Bluehill software calculated the approximate tensile stress at break (psi).

3.2 Aluminum Coupon Preparation

The aluminum sheets were sheared into approximately 1-inch wide strips and each strip was subsequently sheared into rectangular coupons measuring approximately 5 inches long. The coupons were then placed on a mill in batches of 5 coupons atop dual ⅛-inch parallel bars so any bevels from shearing could be machined off. Two cuts were made on the coupons' lengthwise edges - the first was done to a depth of approximately .020 inches to approach sample dimensions specified in ASTM D1002, and the second was a finishing cut at a depth of approximately .005 inches. Dimensions following shearing were variable, and depths of cut were

varied as needed. Machined coupons were then deburred using a manual file and placed on a flat table to be evaluated for deformation. Coupons that did not lie flat due to being deformed were rejected and not used in preparing lap-shear specimens.

3.3 Surface Preparation and Pre-Treatment

The 1 x 5-inch aluminum coupons were degreased using Kimwipes wetted with either isopropanol or acetone. The samples were then dusted with Ajax oxygen bleach cleanser and rinsed with tap water. Samples were then placed on a smooth flat surface to be scrubbed width-wise with 120-grit abrasive paper at the top 1-inch of each sample (area to be bonded) until a water break-free surface was achieved. Water break-free condition was verified by rinsing the scrubbed area with distilled water and observing sheeting as opposed to the droplet formation. Once this condition was achieved, wet samples were placed flat on paper towels with the scrubbed area facing up for etchant application.

With the water break-free surface facing upwards, the P2 etch paste was applied using a standard ¼-inch acid brush. Etchant was applied to the top 1-inch of the scrubbed surface in sufficient quantity to completely cover the surface. Coupons were then left at ambient room temperature for 25 minutes to allow the etchant to chemically activate the surface to be bonded. After etching was complete, the etchant was rinsed from the coupons over an acid waste container using tap water in a laboratory wash bottle. To comply with Environmental Health and Safety standards, standard operating procedure forms were completed and monitored in order to document our procedure and maintain safety. The volatile etchants and liquids were rinsed in a designated container by EHS and the physical tools were disposed in a secondary solid waste container provided by EHS. Etched coupons were completely rinsed and dried in a low-temperature air-circulating oven at 160℉ for 20 minutes. Following drying, the outlife test parameter was introduced by leaving the pre-treated coupons exposed to the ambient pre-treatment environment (lab room 205) for a pre-determined time interval of 0, 1, 4, 8, or 16 hours. A more detailed treatment procedure may be found in Appendix B. All aluminum alloys experienced a long exposure outlife time which ranged anywhere from 64 to 73 hours. This was done to complete the outlife data sets. Note that exposure of the bonding surfaces to an uncontrolled outside

environment was minimized by transporting samples to and from the drying oven in a closed plastic box.

3.4 Adhesive Preparation

EA9394 adhesive was prepared during the drying cycle of the no-outlife coupons or 20 minutes prior to bonding for coupons with outlife. The EA9394 adhesive used in this procedure is a two-part adhesive with a bonding agent and a curing agent mixed with a 100:17 ratio. 50 g of bonding agent was weighed into a plastic laboratory beaker using two laboratory spatulas. Spatulas were then completely cleaned using isopropanol and chemical wipes and used to add 8.5 g of curing agent to the bonding agent. *Note: Any amount of adhesive could be made as long as the 100:17 ratio is maintained.* A small scoop of .010-in diameter silica beads was added to the adhesive mixture to ensure uniform bondline thicknesses in completed lap-shear specimens. All components were then thoroughly mixed for roughly 10 minutes in the original beaker using a spatula to achieve a uniform mixture. Appendix B may be referenced for further detail regarding adhesive preparation. Over the duration of this project, 126 total lap-shear coupons were made.

3.5 Lap-Shear Sample Assembly

After the alloys were finished drying (designated outlife time) and adhesive was prepared, the coupons were ready to be assembled. Each coupon received an application of adhesive to the etched section of the alloys samples. Adhesive was applied using a clean lab spatula adequately covering the top ½-inch of each sample. It was important to ensure that there were no exposed spaces, voids, or sections of the applied surface (Fig. 3). Once applied with adhesive, the sample coupons were placed together forming a bonded interface between the surfaces of two bonded samples (Fig. 4). Ensuring a ½-inch overlap between samples, 6 lb. pinch clamps were applied at the bond interface (two per test coupon). Samples were checked to be completely straight and left out for 24 hours to allow adhesive to set. After the 24 hour cycle, the pinch clamps were removed and the samples were placed in a dry-air circulating oven for 2 hours at 200℉. The

samples were removed and taken to an Instron tensile test machine for lap shear pulling (ASTM D1002).

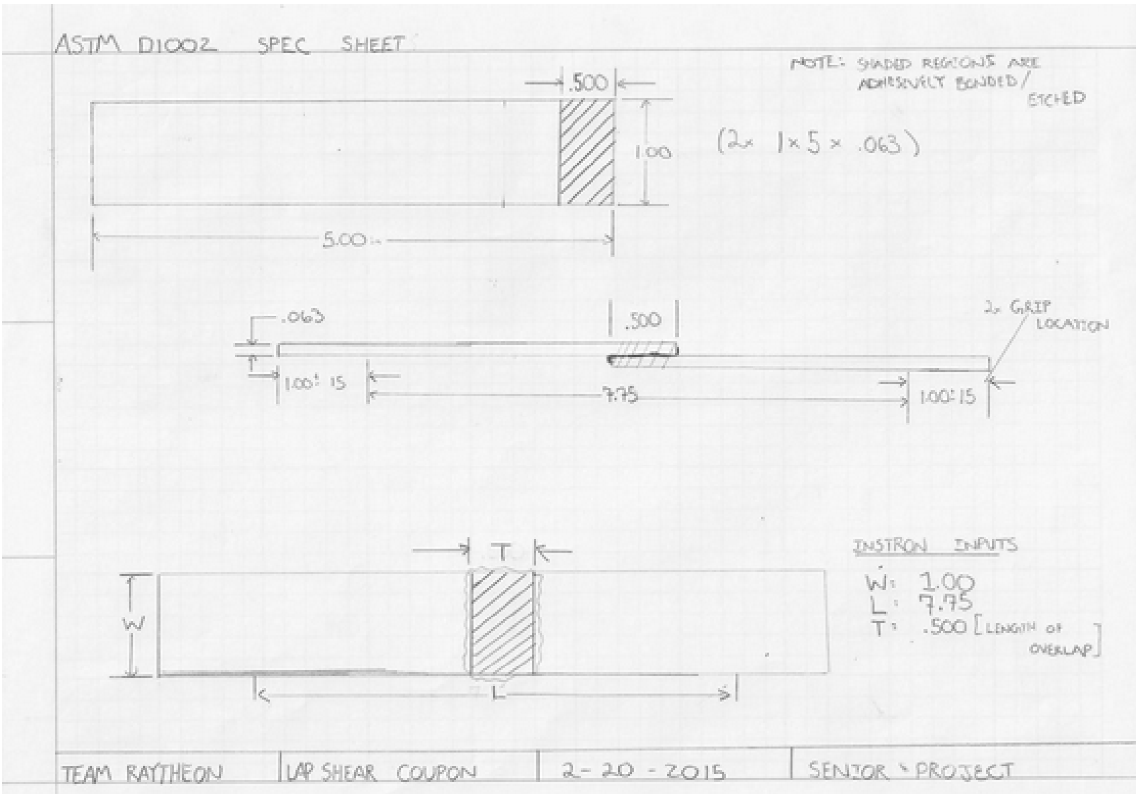

Figure 3. Example specifications for following ASTM D1002 for creating lap-shear coupons

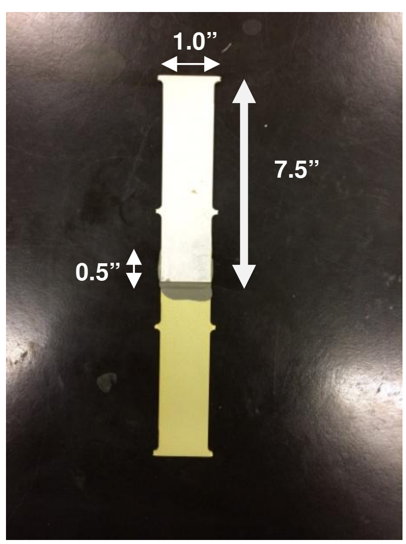

Figure 4. Finished lap-shear joint sample after being correctly joined

3.6 Lap Shear Testing

Prior to testing, each specimen was labeled by alloy type, outlife time, and trial number (i.e. sample 2/1/4 was Al 2024 with a 1 hour outlife and used in the fourth trial for that category). Once all samples were labeled, the bond widths and overlap-lengths were measured and input to the Bluehill software program. Separate files were made for each alloy and outlife. The samples were then placed 1 inch into the Instron grips on both sides for symmetrical experimentation. While samples were being pulled by the Instron machine, the Bluehill software produced a graph that showed the relation between tensile extension (in) and force exerted (lb) (Fig. 5). Bluhill also generated a table presenting the specimen label, maximum load (lbf), load at break (lbf), and tensile stress at break (ksi) along with the mean and standard variation of each value (Table II). During lap-shear testing the samples began to yield around 2.4 ksi due to the maximum shear stress of aluminum alloys. Each test lasted an average of about 40 seconds. The samples were removed from the Instron grips and measured immediately to determine bond-line thickness . At this point the two coupons were completely separated from each other and the dried adhesive was exposed. Silica beads used in the adhesive helped provide an average bond-line thickness of .010 in. Once all samples were tested and measured, coupons were taped together with their counterparts. A container with six compartments was used to organize the alloys with different outlife times.

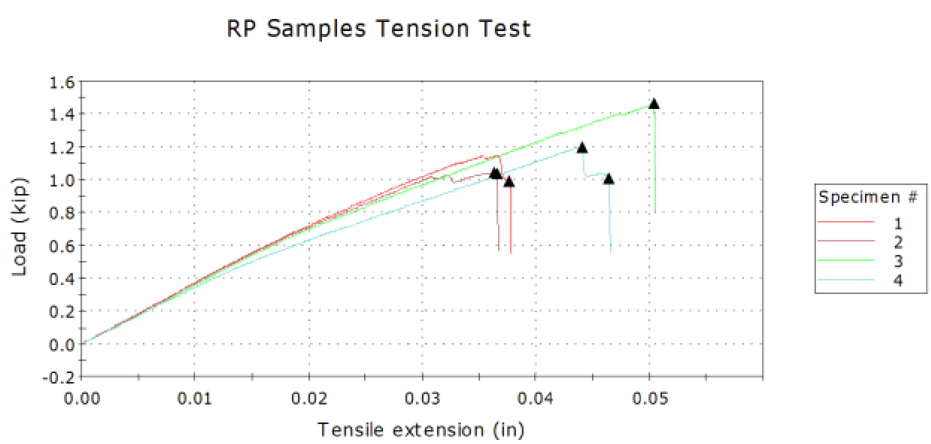

Figure 5. Graph produced by Bluehill software presenting the load vs. tensile extension of adhesively bonded 2024 aluminum alloys.

Table II. Example output from Bluehill software showing 4 hour outlife specimens

	Specimen label	Maximum Load (lbf)	Load at Break (Standard) (lbf)	Tensile stress at Break (Standard) (ksi)
1	2.4.5	1141.88	989.76	1.91
2	2.4.6	1041.18	1032.88	2.18
3	2.4.7	1461.66	1461.27	2.27
4	2.4.8	1196.20	1012.74	2.03
Mean		1210.23	1124.16	2.10
Standard Deviation		179.50279	225.42568	0.15905

3.7 Statistical Methods

Statistical analysis of the test results via one-way analysis of variance (ANOVA) was performed using the general linear model command in MINITAB, followed by Tukey's pairwise comparisons. Analysis was done separately for each alloy based on the shear strength and outlife data for all non-rejected samples (Appendix C). Shear strength was used as the "Responses" variable while outlife was used as the "Model". In addition, deleted t-residuals were stored and plotted in order to detect the presence of unequal variances. Pairwise comparisons were made with Outlife set as the "Terms" variable with a 95% confidence level.

4. Results

4.1 Specimen Failure Modes

During testing of the lap-shear specimens, two main failure modes were observed: de-bonding and peeling. De-bonding (Fig. 6) presented with an uneven distribution of adhesive where all or most of the adhesive was left on one of the coupons. This was due to preparation error as much mastery is required to get a desirable bond. Peel occurred due to yielding of the alloy, and showed curved failure surfaces and a more even distribution of the adhesive between the two coupons. The undesirable failure mode that occurred during testing was a de-bond that occurred between the adhesive and the aluminum alloy interface. Debonding is where there is a clear uneven distribution of adhesive bond on the alloy surface. This occurred due to possible errors in sample preparation, environmental contaminants, and uneven bonding of the two coupons. These samples resulted in relatively low bond strength values and did not contribute to the final

data shown in the shear strength vs. outlife data. This was indicative of poor preparation and thus not the true strength of the adhesive bond.

The desirable failure mode experienced by lap-shear samples during testing was failure by peeling, in which the alloy yielded before bond failure and peeled back the adhesive. This was indicated by a visually identifiable curvature of the aluminum coupons after testing on the Instron. The yielding behavior means that the bond failure was initiated by yielding of the metal and not by failure of the adhesive itself. Evidence for this failure mode involves the two yielded aluminum coupons with an even distribution of cured adhesive between the two coupons (Fig. 7). This indicates that failure may be attributed to the aluminum and not the adhesive bond and furthermore indicating the adhesive bond was successful in infiltrating the porous aluminum surface resulting in full bond strength.

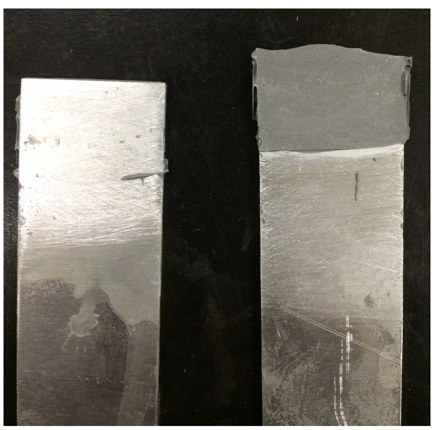

Figure 6. Representation of de-bonding

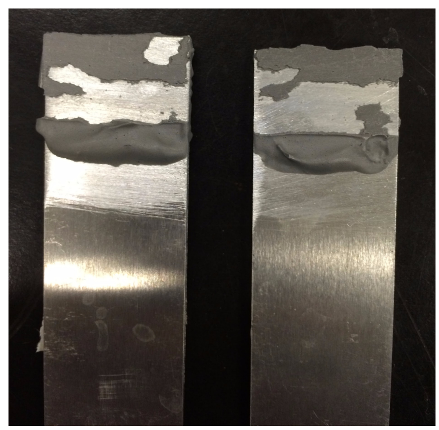

Figure 7. Representation of peeling

4.2 Effect of Etchants on Bond Strength

Average lap-shear strengths for 0-outlife Al 2024 etched with FPL and P2 pastes were obtained in order to compare the effects of the original procedure to the proposed replacement. Both etchants showed similar effects on this alloy, resulting in an increase in shear strength from 1.47 ksi to 2.77 ksi and 2.78 ksi for FPL and P2, respectively. These increases represent an approximate 92% increase in shear strength from using either treatment compared to non-etched specimens (Fig. 8).

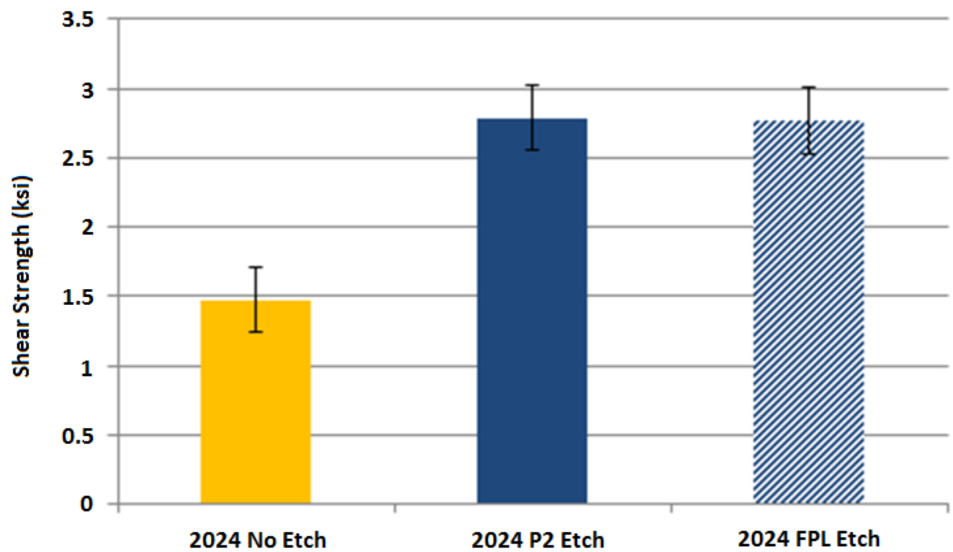

Figure 8. Bond strength nearly doubles when using either P2 or FPL etchant compared to using no etchant

4.3 Effect of Outlife on Bond Strengths

4.3.1 Outlife Effect on 2024 Etched with FPL

Data from the FPL-etched 2024 specimens was plotted in order to obtain a baseline for comparisons to be made between the outlife behavior of alloys treated with either etchant (Fig. 9). An average 15.3% decrease in bond strength was observed after the first hour of outlife time. The curve shown was hand-drawn to show the expected trend in spite of the anomalous 0-hour and 1-hour outlife averages. Due to EHS safety protocols, the FPL etched samples were prepared at Raytheon in El Segundo, CA. They were shipped to Cal Poly San Luis Obispo for testing.

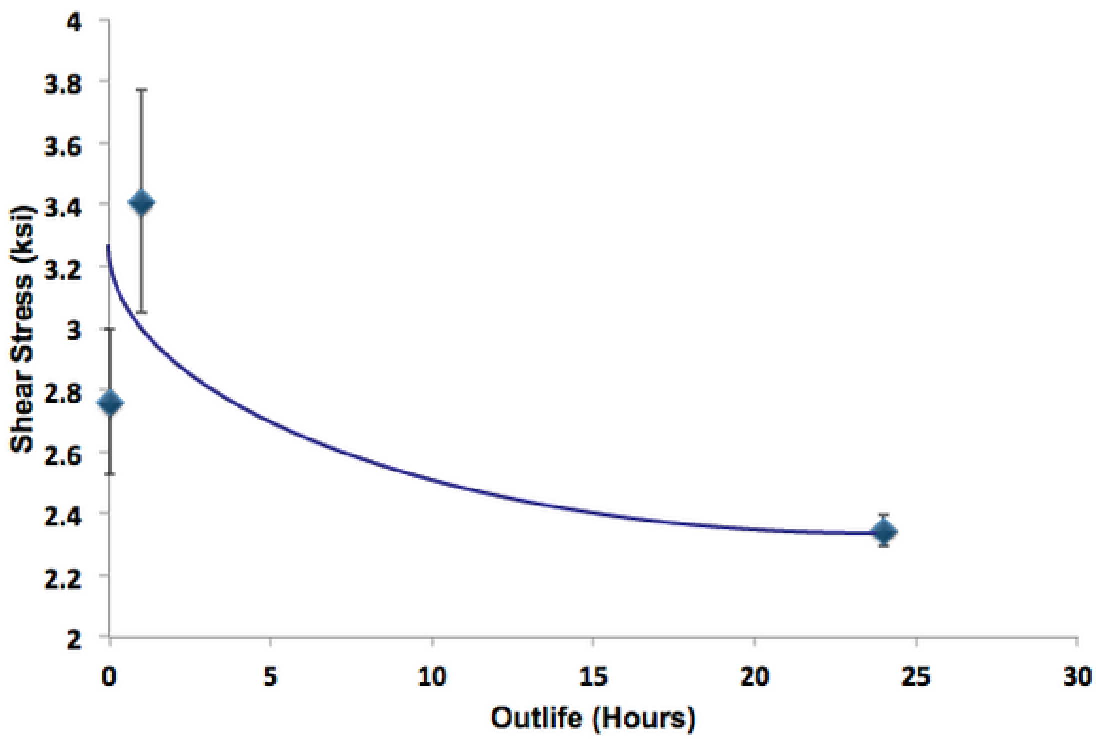

Figure 9. 2024 samples etched with FPL tested similar similar shear strengths to 2024 etched with P2

4.3.2 Outlife Effect on 2024 Etched with P2

Similar behavior was observed for the P2-etched Al 2024 samples, which displayed a 14.9% decrease in strength from 2.75 to 2.43 ksi after the first hour of outlife, with an apparent asymptote at about 2.2 ksi (Fig. 10). These alloys showed a significant amount of scatter due to improvements in the researchers' coupon assembly technique during the period of time that said samples were being tested. As the experiment progressed and more accurate samples were made, the data was more consistent with a decreasing trend. Improved sample accuracy, however, also

may have resulted in the unusually high outlier strength at the 72-hour outlife level. Even with the scatter however, there is still a decrease in the 2024 aluminum alloys samples after the first hour. A similar trend was noticed for the Al 6061 and 7075 samples as well, with decreases after the first hour of 21.0% and 20.2%, respectively (Figs. 10 - 12). Additionally, the 0-outlife bond strengths were greater for the stronger Al 6061 and Al 7075 alloys specimens. The average values are shown numerically in Tables III-V, for reference.

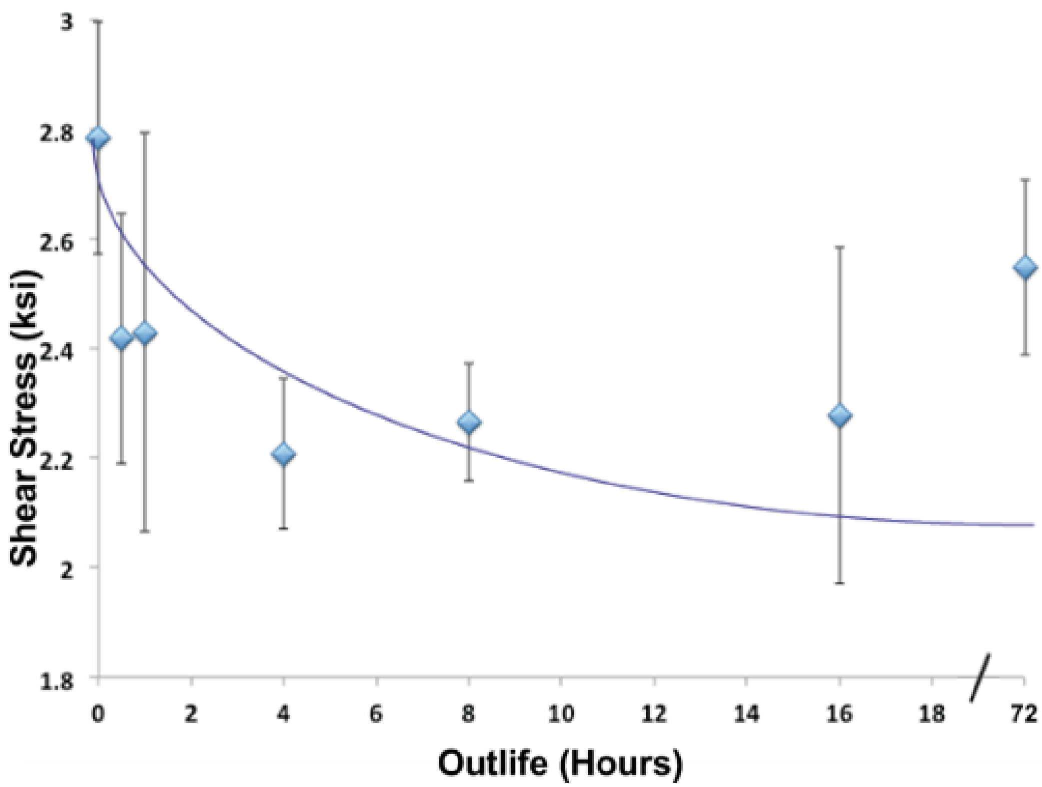

Figure 10. 2024 P2 testing showed scatter due to increasing proficiency in preparation of lap-shear joints

Table III. Average Bond Strength & Number of Samples for Each Outlife Time of P2-etched Al 2024

Outlife (hours)	Average Bond Strength (ksi)	Standard Deviation (ksi)	Number of Non-rejected Samples
0	2.78	0.363	14
0.5	2.49	0.187	3
1	2.43	0.364	8
4	3.59	0.137	8
8	2.27	0.107	4
16	2.28	0.306	4
72	2.55	0.160	4

4.3.3 Outlife Effect on 6061 Etched with P2

The 6061 aluminum alloy followed our hypothesis. The initial 0 hour outlife shear stress were the strongest test specimens for this alloy, at an average shear strength of 3.10 ksi. Following these 0 outlife specimens, there was a significant decrease in shear stress (bond strength) at a drop of 21% after the first hour of outlife and a plateau of about 2 ksi thereafter (Fig. 11). Statistical analysis using the Tukey method showed that the bond strengths observed after one hour of outlife were significantly different from those with no outlife.

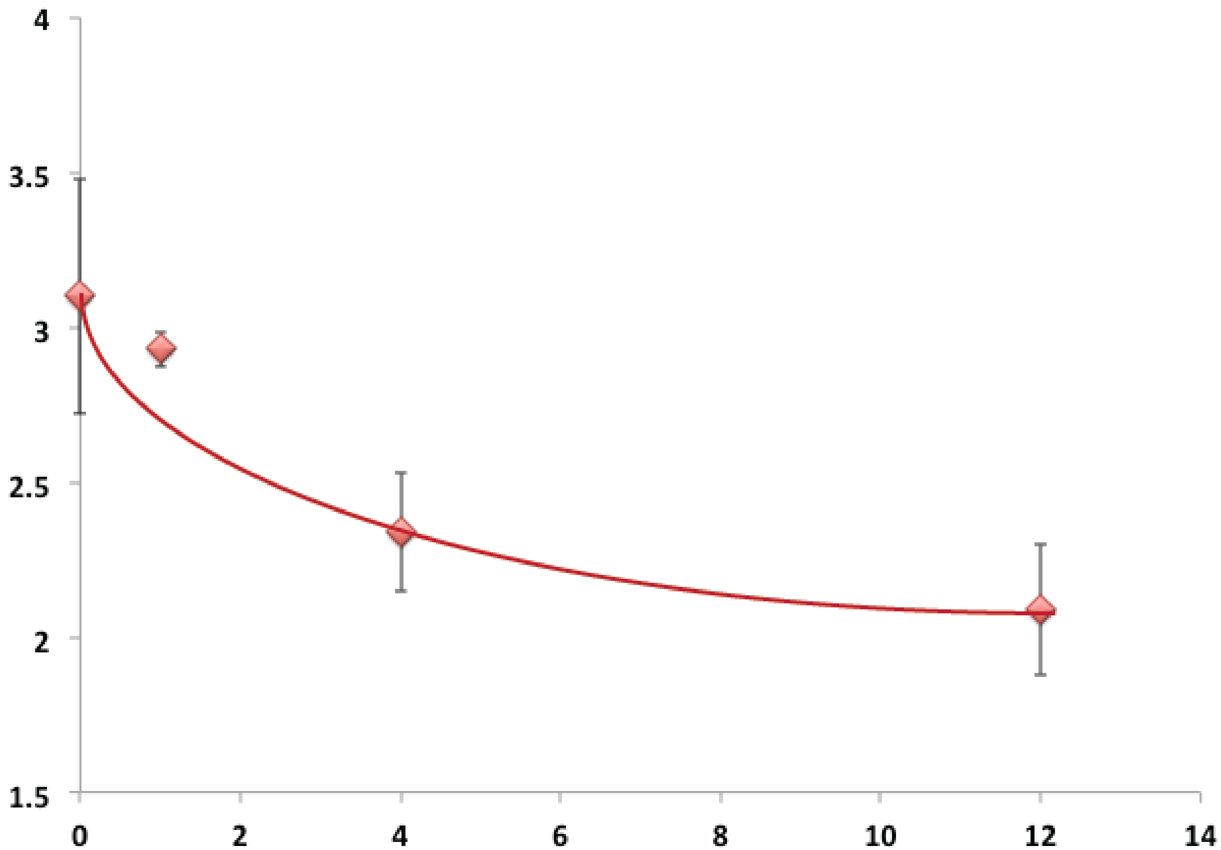

Figure 11. 6061 P2 samples best represented the trend of decreasing bond strength with increasing outlife time

Table IV. Average Bond Strength & Number of Samples for Each Outlife Time of P2-etched Al 6061

Outlife (hours)	Average Bond Strength (ksi)	Standard Deviation (ksi)	Number of Non-rejected Samples
0	3.10	0.465	7
1	2.93	0.057	2
4	2.34	0.194	4
63	2.09	0.212	4

4.3.4 Outlife Effect on 7075 Etched with P2

The 7075 aluminum alloys also accurately demonstrated that with increasing outlife time comes decreasing bond strength. The initial bond strength at 0 hour outlife was significantly stronger at 3.74 ksi. This is due to the shear strength of the alloy as it is higher than that of 6061 and 2024. Again, after the first 0 outlife test, there was a bond strength drop of 20.2% (Fig. 12). The Tukey comparison test supported this statement showing that the values were statistically different from each other.

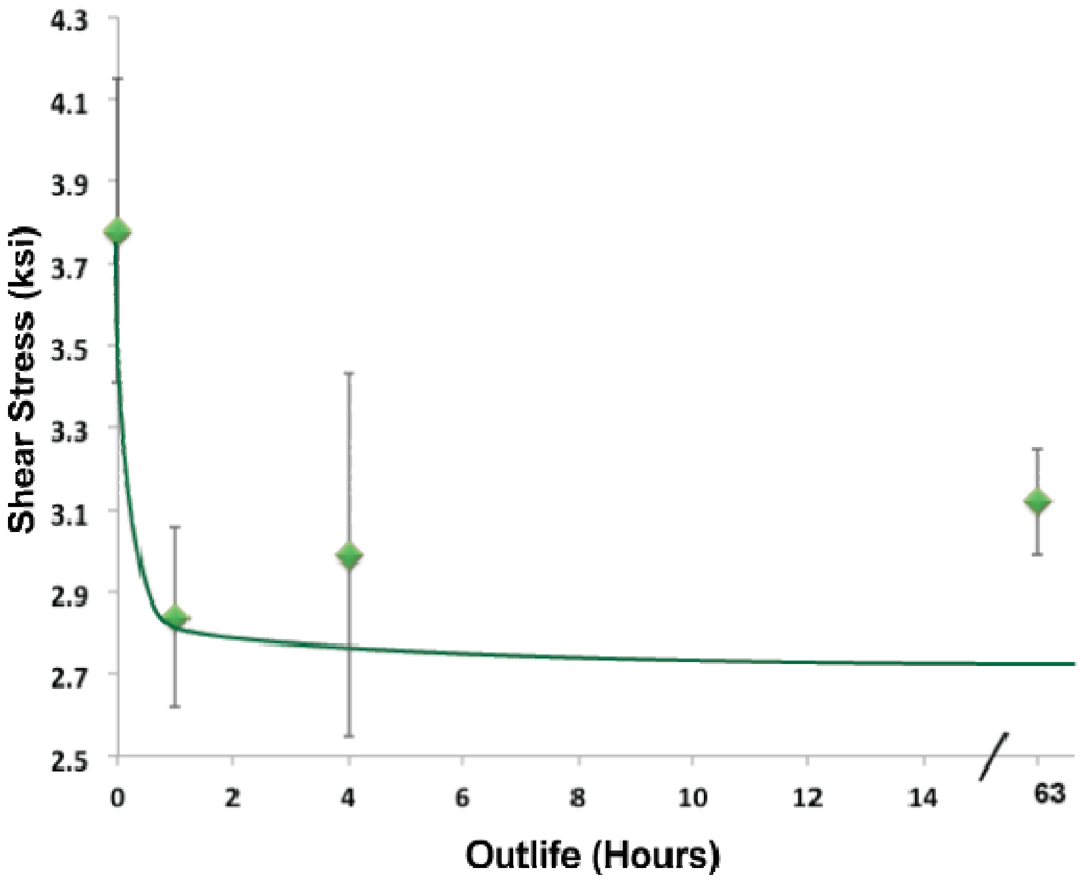

Figure 12. 7075 P2 tested with highest initial bond strength of 3.8ksi in comparison to 2024 P2 that tested at 2.8ksi

Table V. Average Bond Strength & Number of Samples for Each Outlife Time of P2-etched Al 7075

Outlife (hours)	Average Bond Strength (ksi)	Standard Deviation (ksi)	Number of Non-rejected Samples
0	3.74	0.327	6
1	2.84	0.221	3
4	2.99	0.441	3
63	3.12	0.131	3

4.3.5 Three Alloy Comparison of Bond Strength with Outlife Time

Each alloy experienced a significant bond strength drop as outlife time increased. 2024 dropped by roughly 14.9% strength drop, 6061 a 21% drop, and 7075 a 20.2% drop. The drop in strength with outlife can be seen in for each alloy in Figure 13.

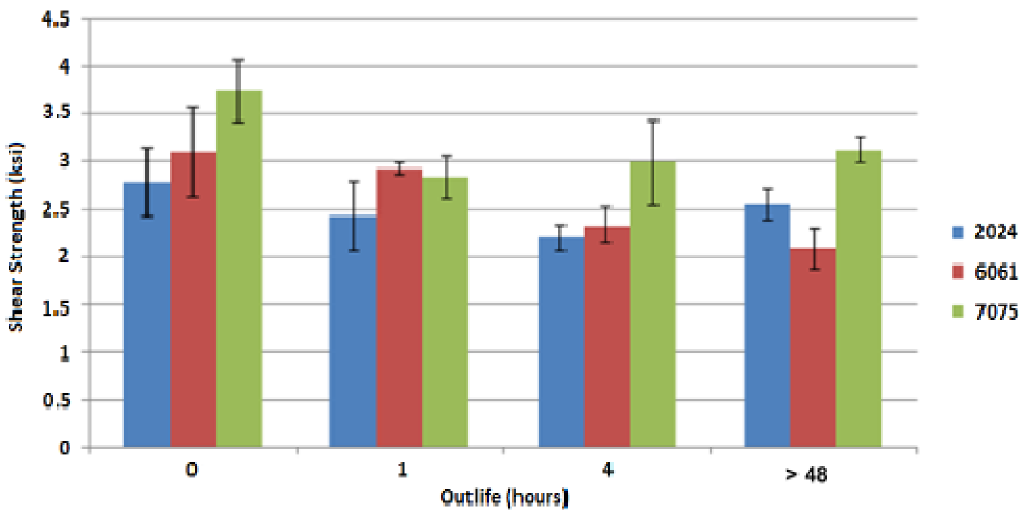

Figure 13. Initial bond strength ranges from 2.8ksi to 3.8ksi and shows a range in decrease from 15% to 21% with 2024 to 7075, respectively

4.4 Results of Statistical Analysis

One-way ANOVA with Tukey's pairwise comparisons was performed on the lap-shear test averages using MINITAB in order to determine the outlife times at which adhesive bonds for all three alloys experienced a significant decrease in shear strength. Groupings based on the Tukey analysis were generated by MINITAB and are shown in Table 5. The letters are used to indicate groupings within which the test averages were similar or significantly different. Within each alloy, outlife times that do not share a letter are significantly different, and times that share a

letter are similar. No significant differences were found between any two of the outlife times for the Al 2024 samples, and the test averages were all placed into group A. For Al 6061 samples, significant differences were found between the 0-hour samples and the 4 & 72-hour samples. The 1-hour samples, however, were similar to all the other outlife times and were placed into grouping CD. Finally, the Al 7075 samples showed significant differences between the 0-hour and 1 & 4-hour samples. Strangely, however, the 72-hour samples were placed into group EF and were statistically similar to groupings E and F. A large degree of variation was noticed in the data, likely owing to the small and inconsistent sample sizes for each combination of alloy and outlife time.

Table VI. Groupings Based on Tukey's Pairwise Comparisons

Alloy	0-hour	1-hour	4-hour	8-hour	16-hour	63-hour	72-hour
2024	A	A	A	A	A	A	-
6061	C	CD	D	-	-	-	D
7075	E	F	F	-	-	-	EF

5. Discussion

5.1 Purpose of Pretreatment

Surface pretreatment of aluminum alloys is essential for adhesive bonding applications. Strength values were increased by nearly 92% from unetched aluminum samples. The test data show that these bond strength values of etched aluminum samples nearly doubled from 1.4 ksi to 2.8 ksi (Fig. 8). The etchant changes the morphology of the aluminum surface to allow for more effective infiltration of the adhesive into the surface of the alloy.

5.2 Explanation of Outlife

The outlife time plays an important role in determining the final shear strength of an adhesive bond. During the study, the highest bond strength values were reached when the samples were bonded immediately after the etching process. Generally speaking, bond strength experienced a decrease as the outlife time was increased. The trend lines in the graphs are intended to show the expected trend, which is difficult to show from the results of the present study due to the small

number of data points. After the first hour of outlife, strength values saw a steady decreasing trend resulting in a plateau of strengths that ranged 15%-21% lower than that of the initial bond strength. The plateau effect could be due to the concentration of contaminants that interfere with adhesive infiltration and adhesion to the bonding surface reaching a point of equilibrium within or after the first hour of outlife. This would lead to a relatively constant bond strength once equilibrium is reached. Further studies using SEM-EDS and/or atomic force microscopy (AFM) would need to be conducted in order to characterize changes in the etched surfaces' morphology with increased outlife time and better explain this phenomenon.

It should be noted, however, that the values obtained from the present study are much lower than those reported in the literature. This is likely due to the lack of temperature and humidity controls in the sample preparation environment, which may have affected the rate at which moisture from the air adsorbed to the activated aluminum surface. Since this study did not include any method of monitoring the particulate and moisture content of the air in the preparation environment, it is difficult to draw any specific conclusions that may explain the observed behavior. On the other hand, however, strict monitoring of the preparation environment may prove impractical in an industrial setting and so it is possible that the results may be generally applicable or at least informative for large-scale adhesive bonding operations. It should be emphasized here that the highest bond strength was gained from bonding the treated alloy with little to no outlife, and that the outlife case should ideally be avoided altogether in practice.

5.3 Clarification of Statistical Analysis

The results of the statistical analysis indicate that there was a large degree of variability in the obtained experimental data, making it difficult to draw well-evidenced conclusions regarding the effect of outlife on bond strength. However, the analysis was inconclusive only for the Al 2024 samples. This may be explained by the fact that these were the first samples that were prepared during the study, and that large improvements in preparation technique may have occurred. Considering the relatively small sample sizes for this study and lack of randomization, this could easily have introduced the large degree of variation that was observed. Despite this, the test averages for the remaining two alloys seem to indicate that approximately the first hour of outlife time can have a significant effect upon the final shear strength of the adhesive bond.

6. Conclusion

Three aluminum alloys were tested (2024, 6061, and 7075) using two different etchants, FPL and P2, to determine the effect of outlife on bond strength. Over 200 coupons and 100 samples were prepared and tested for the investigation. FPL had an average initial bond strength of 2.72 ksi and P2 had an average initial bond strength of 2.77 ksi. Both paste etching processes led to large increases in bond strength of approximately 92% from the non-etched sample with bond strength of 1.4 ksi, demonstrating that the P2 etchant tested in this study is comparable in effect to the currently-used FPL paste. When etched with P2, 2024 had an initial bond strength of 2.8 ksi and plateaued at 2.3 ksi, 6061 had an initial bond strength of 3.1ksi and plateaued at 2.2 ksi, and 7075 had an initial bond strength of 3.8 ksi and plateaued at 2.8 ksi. These results showed that bond strength generally decreased with increasing outlife time across all tested alloys. It is recommended that the P2 paste be used with minimal outlife time to achieve the highest possible bond strengths.

7. Acknowledgments

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Appendix A: Glossary of Terms

Adhesive - Glue-like material used to bond the samples together. EA 9394 two-part adhesive by Loctite was used for this experiment.

Bond Strength - Term used to describe the shear strength value of the adhesive bond holding the two aluminum coupons together.

Coupon - Term used to describe one aluminum sample cut into a 1” by 5” rectangular shape to comply with ASTM D1002 standards.

De-bonding - The failure mechanism of lap shear where the adhesive did not completely infiltrate the samples surface, resulting in an uneven distribution of adhesive bond on the samples. This ultimately contributes to low bond strengths.

Etchant - Paste formula used to change the morphology of the aluminum surface for increased bond strength.

Lap-Shear Sample - Term used to describe two coupons adhesively bonded together for lap-shear testing.

Lap-Shear - Determines the shear strength for an adhesive when bonding two materials together.

Outlife - The amount of time delay that occurs after etching the aluminum coupons, but before bonding the two coupons together.

Overlap - Term used to describe the length of the bonded aluminum coupons that formed one lap shear sample

Peeling - The failure mechanism where the adhesive does completely infiltrate the surface and the adhesive behaves at its intended maximum strength. This results in the yielding of the aluminum alloy and failure occurs by peeling of the two samples.

Water-break free - Term used to describe the surface behavior that must be exhibited by the aluminum in order to facilitate etching. The surface is free of water beading upon the surface.

Appendix B: Detailed Sample Preparation Procedure

1. Degrease coupons using acetone/isopropanol and a chemical wipe
2. Wet area to be bonded with tap water and powder Ajax onto surface.
3. Thoroughly scrub surface to be bonded using dampened Scotch-Brite pad
4. Rinse with deionized (DI) OR distilled water and check for water-break free surface
5. Apply P2 paste onto scrubbed surfaces and let sit for 25-30 mins
6. Rinse paste etchant into acid waste bucket using tap water in a wash bottle.
7. Dry in low temperature oven at 160 F for 20 minutes, leaning samples vertically against oven walls.
8. *If introducing outlife after etching* as a variable, let samples rest in a clean area for desired time interval before proceeding
9. Mix two-part adhesive: Combine parts A and B in 100:15 ratio (or equivalent) and stir using a spatula. Add glass beads and mix thoroughly.
10. Apply thin (~0.25 inches) strip of masking tape to non-bonding side of each coupon, leaving loose ends on either side of coupon
11. Apply a thin 0.5-inch long layer of adhesive on surfaces to be bonded
12. Press bonding surfaces together and wrap loose ends of tape around opposing coupons
13. Clamp one side of bonding surface, and press opposite end against a flat surface to ensure straightness.
14. Clamp the other side and leave for ~24 hours to allow adhesive to dry. Remove clamps and cure for 2 hours at 200°F

Appendix C: Compilation of Test Sample Data (Shear Stress at Break, Maximum Load, and Bond Area)

The results show in this appendix include only sample that failed in peeling mode (Fig. 7) Samples showing debonding also showed highly anomalous bond strengths, and were excluded from the analysis presented in this document.

Test Data for Al 2024 Samples Prepared using FPL Paste

Sample ID (Alloy/Outlife Time/Test Number)	Shear Stress at Break (ksi)	Maximum Load (lbf)	Bonded Area (in^2)
2F/0/1	2.48	1239.06	0.498
2F/0/2	3.05	1440.95	0.473
2F/0/3	2.81	1319.64	0.468
2F/0/4	2.73	1407.85	0.516
2F/24/1	2.33	1101.32	0.473
2F/24/2	2.37	1159.96	0.496
2F/24/3	2.28	1164.58	0.510
2F/24/4	2.4	1157.18	0.483

Test Data for Al 2024 Samples Prepared using P2 Paste

Sample ID (Alloy/Outlife Time/Test Number)	Shear Stress at Break (ksi)	Maximum Load (lbf)	Bonded Area (in^2)
2/0/9	2.93	1524.1	0.520
2/0/10	3.14	1401.81	0.446
2/0/11	2.55	1687.68	0.662
2/0/13	2.88	1495.91	0.519
2/0/14	2.6	1257.71	0.484
2/0/21	2.55	1253.52	0.492
2/0/22	3.13	1557.62	0.498
2/0/23	2.57	1200.47	0.467
2/0/24	2.57	1156.27	0.450
2/0/25	2.86	1499.9	0.524
2/0/27	2.71	1603.85	0.592
2/0/28	2.97	1486.07	0.500
2/0/29	2.65	1323.86	0.500
2/0/30	2.87	1508.06	0.525

2/H*/5	2.7	1381.88	0.512
2/H/6	2.41	1431.95	0.594
2/H/7	2.35	1248.14	0.531
2/1/2	2.23	1391.62	0.624
2/1/5	2.9	1595.09	0.550
2/1/8	2.92	1457.6	0.499
2/1/9	1.92	1294.86	0.674
2/1/10	2.33	1254.61	0.538
2/1/11	2.27	1198.76	0.528
2/4/1	2.35	1409.7	0.600
2/4/6	2.18	1032.88	0.474
2/4/7	2.27	1461.27	0.644
2/4/8	2.03	1012.74	0.499
2/8/1	2.42	1253.65	0.518
2/8/2	2.25	1471.03	0.654
2/8/3	2.19	1521.94	0.695
2/8/4	2.2	1347.54	0.613
2/16/2	2.47	1336.76	0.541
2/16/3	2.12	1199.61	0.566
2/16/4	1.93	1045.36	0.542
2/16/5	2.59	1328.95	0.513
2/72/1	2.53	1414.71	0.559
2/72/2	2.74	1462.34	0.534
2/72/3	2.57	1323.89	0.515
2/72/4	2.35	1416.47	0.603

*** denotes a 30 minute (Half-hour) outlife time**

Test Data for Al 6061 Samples Prepared using P2 Paste

Sample ID (Alloy/Outlife Time/Test Number)	Shear Stress at Break (ksi)	Maximum Load (lbf)	Bonded Area (in^2)
6/0/1	2.64	1535.04	0.581
6/0/2	2.76	1518.92	0.550
6/0/3	2.69	1346.01	0.500
6/0/5	3.78	1885.93	0.499
6/0/6	3.46	1728.83	0.500
6/0/7	2.88	1507.24	0.523

6/0/8	3.5	1828.42	0.522
6/1/1	2.89	1469.5	0.508
6/1/2	2.97	1491.03	0.502
6/4/1	2.23	1102.27	0.511
6/4/2	2.12	1102.33	0.506
6/4/3	2.48	1262.62	0.503
6/4/4	2.52	1312.92	0.525
6/63/1	2.07	1084.96	0.524
6/63/2	2.15	1108.61	0.516
6/63/3	1.81	931.02	0.514
6/63/4	2.32	1188.22	0.512

Test Data for Al 7075 Samples Prepared using P2 Paste

Sample ID (Alloy/Outlife Time/Test Number)	Shear Stress at Break (ksi)	Maximum Load (lbf)	Bonded Area (in^2)
7/0/1	4.32	2185.75	0.506
7/0/2	3.49	1936.1	0.555
7/0/3	3.59	2038.67	0.568
7/0/4	3.75	1972.8	0.526
7/0/5	3.43	1932.87	0.564
7/0/7	3.87	1977.15	0.511
7/1/2	3.01	1545.8	0.514
7/1/3	2.92	1490.33	0.510
7/1/4	2.59	1290.23	0.498
7/4/1	2.53	1264.28	0.500
7/4/3	3.41	1605.43	0.470
7/4/4	3.03	1424.75	0.471
7/63/1	3.02	1650.16	0.546
7/63/2	3.27	1586.41	0.485
7/63/4	3.08	1518.79	0.493