Adhesive Technology: Surface Preparation Techniques on Aluminum

An Interdisciplinary Qualifying Project
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in partial fulfillment of the requirements for the
Degree of Bachelor of Science

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Henkel-Loctite

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Abstract

Chemical surface treatment of aluminum has a significant effect on the bonding characteristics and the applications in which adhesive bonding of aluminum is used. Chromic acid etching is one of the oldest and most widely conducted treatment methods in industry. Henkel Loctite often receives requests to perform the chromic acid etching process on aluminum but it can be hazardous and inefficient. An actual chromic acid etching system for aluminum was designed and compared to other surface treatment methods to determine if this system would be of benefit to the sponsor in the future.

Executive Summary

Our sponsor, Henkel Loctite, is the world's largest manufacturer and supplier of consumer and industrial adhesives. Loctite conducts in-house services to outside companies to improve any products using adhesives manufactured by Henkel Loctite. For many applications, products using adhesives need special material treatment prior to adhesion. Certain materials, such as aluminum, steel, and various plastics, undergo surface treatment preparation prior to adhesion bonding in order to improve the strength and durability of the products.

One of the most common surface treatment methods, chromic acid etching, was actually conducted on site at Henkel Loctite's laboratories. Chromic acid etching involves submersing materials into a heated chromic acid bath for approximately ten minutes then cleaning the treated parts with water prior to bonding. Chromic acid consists of 10 parts by weight sulfuric acid, 1 part by weight sodium dichromate, and 30 parts by weight water.

However, there were many flaws in the process and our sponsor decided that it was a worthwhile investment to improve the chromic acid etching process and determine if it would be of benefit to the company to implement a permanent on-site system. This process is used on a wide variety of materials before the bonding process, but it is used most extensively on aluminum, mostly because aluminum is one of the least costly materials in industry. This project focused entirely on the treating and bonding of aluminum, and more importantly focused on the chromic acid surface preparation treatment of aluminum compared to four other commonly used treatment processes.

These four were chromic acid anodizing, sulfuric acid anodizing, “hard” anodizing, and phosphoric acid anodizing. All five of these methods are used extensively in the transportation, consumer cookware, and manufacturing industries, as well as many other industries. The goal of the project was to:

- Set up and design an actual working chromic acid etching system
- Treat multiple aluminum parts using the same bath
- Identify any flaws and faulty conditions associated with the system
- Conduct various experiments to improve these flaws
- Determine when the acid bath began to degrade to the point where it was no longer effective
- Compare the chromic acid etching treatment method to various other surface treatment methods done outside of Henkel Loctite to determine if a permanent system should be implemented on site or if all parts should be shipped out for treatment prior to bonding

The chromic acid bath was constructed using a temperature-controlled water bath and placing a Pyrex baking dish, containing the chromic acid, half way into the bath. A stand was also constructed to hold the aluminum parts as they were being treated. For this project, aluminum lap shears with dimensions of 1 inch by 4 inches, provided by Henkel Loctite, were used throughout all experimentation. This apparatus was able to treat a maximum of 18 lap shears at a time, and the lap shears were submerged into the chromic acid bath at a depth of at least 0.5 inches, as this was the required bond area for testing.

In order to insure that quality results were obtained throughout the project, an appropriate adhesive had to be chosen. Given 10 adhesives recommended by the supervisor, 10 lap shears were treated with the chromic acid for each of the 10 different adhesives. Once all bonded assemblies cured, they were tested for maximum shear strength using an Instron machine. All bond strengths were recorded and the statistical software Minitab was used to analyze the data. It was proven that only three of the 10 tested adhesives had higher average bond strengths after treatment compared to bonded non-treated aluminum, and only one adhesive, H4800, had statistically significantly better bond strength after treatment. Therefore, H4800 was the chosen adhesive to be used throughout the project.

When analyzing data from the adhesive selection process, it was found to have an unusual amount of variance from substrate to substrate, even within the same adhesive. When bonding the aluminum lap shears after treatment, there appeared to be some residue left over on the lap shears possibly affecting bond strength. Therefore, a design of experiments analysis was proposed to determine if cleaning the treated surface with isopropyl alcohol would improve the bond strength and limit the variance. After analyzing the data on Minitab, it could not be proven that cleaning the lap shears with isopropyl alcohol had any impact on results.

There was still an observed water stain or some sort of residue remaining on the surface of the treated aluminum parts. A different experiment was conducted to determine if wiping the parts after treatment with a tissue instead of drying them in an oven for 10 minutes would improve the process. When testing was complete, a significant increase in bond strength occurred with the tissue-wiped specimens and it was proven that the tissue-cleaned lap shears had statistically significantly better bond strength and less variance. Therefore, this cleaning procedure was used throughout the rest of the project.

One of the main goals of the project was to determine how long it would take for the chromic acid bath to degrade to a point where it was no longer effective in treating the aluminum lap shears. According to Henkel Loctite, a project should never require more than 500 lap shears to be bonded at once. To be on the safe side, 1000 lap shears were treated. Instead of actually treating 1000 lap shears, a calculated amount of aluminum powder was dropped into the chromic acid bath to simulate the amount in order to save time and resources. Another experiment was conducted in which 10 assemblies were treated and bonded with a fresh bath and another 10 assemblies were treated and bonded with the “degraded” bath. There was no proven indication that bond strength was affected before and after the addition of the aluminum powder. Also, the chromic acid bath was analyzed before and after the aluminum powder was added to determine the difference in composition of the bath. The same was conducted for treated aluminum specimens and it was determined that very little difference occurred after 1000 lap shears were treated. This assured Henkel Loctite that the bath would not degrade during any future projects.

Once the chromic acid treatment system was fully established, this treatment method had to be compared to others to determine if the company should use this process in the future. Aluminum lap shears were sent out to various companies to perform four other treatment methods: chromic acid anodizing, sulfuric acid anodizing, sulfuric “hard” anodizing, and phosphoric acid anodizing. A control group of untreated aluminum was also used in the analysis for comparative purposes. All treatment methods were bonded with adhesives H4800, 435, and 332, and some were sent for environmental conditioning for two weeks. Environmental conditioning consisted of a salt fog chamber, a regular fog chamber, and lower temperature oven, and a higher temperature oven. The lap shears that were not conditioned were compared to those that were and various treatment methods were compared to each other of the same adhesive used for bonding. Again, using Minitab, it was proven that phosphoric acid anodizing had overall stronger bond strengths than other treatment methods, but also was the only treatment method that didn’t show a statistical significant drop in bond strength after being exposed to environmental conditioning. We also examined other factors such as cost, ease of use (safety), and use in industry to determine the best overall surface treatment. It was determined that the best performing surface treatment, phosphoric acid anodizing, was also the safest and most widely used in industry. It was concluded that phosphoric acid anodizing was the best aluminum surface treatment for Henkel to pursue for future testing.

Introduction

The first adhesives can be traced back to 4000 B.C., when archaeologists uncovered clay pots that had been repaired using tree sap. Adhesives have a history of about 6000 years, longer than most current industries. The Greeks and Romans used many natural adhesives, including tar and beeswax, used for several military purposes such as naval vessels and bows used by troops. Beginning around 1700, the first glue factory opened up in Holland to manufacture animal glue from hides. It was not until the Industrial Revolution that technical advances in adhesives began to improve. At this time, the first glue made from a polymer was introduced, and as plastics were discovered during the early 1900s, new and specific advances developed in adhesive technology, such as flexibility, toughness, and chemical resistance.[1] Currently, the adhesive industry is a multi-billion dollar industry and is located throughout 125 countries in the world. Today, adhesives hold together almost every piece of manufactured equipment used throughout the world. Whether it is the automotive industry, electronics, aerospace, metal, assembly, or construction industries, products could not be made without the application of adhesives.

Our sponsor, Henkel Loctite, has been in the adhesive industry for over 50 years. With products currently being marketed in more than 80 countries around the world, Henkel Loctite is the leading developer and manufacturer of adhesives, sealants and other specialty chemicals.[2] Henkel Loctite offers a service to its clients where engineers find the best solution to their needs based on desired specifications and cost. In some instances, in order to increase bond strength, the surface of the substrate prior to bonding is altered in some way. The focus for this specific application was the analysis of various chemical surface preparation techniques. The first and most important technique is known as chromic acid etching or FPL (Forest Product Laboratory) etch, named after the company where it was invented in 1950, where a chemical alteration of the surface of a given substrate undergoes an oxidation process which “eats away” at the surface, creating a rough texture, thus increasing the surface area. Chromic acid is simply a mixture of 10 parts by weight sulfuric acid, 1 part by weight sodium dichromate, and 30 parts by weight water. By increasing the surface area of substrate, the adhesive has more available area to bond. However, there was a limit as to how many preparations could be completed using a single batch of the chromic acid. Henkel Loctite’s primary interest was to know how long the bath could be used before having to replace it and the issues associated with having to replace the acid bath.

The chromic acid etching process had been used before at Henkel Loctite but was not permanently implemented. Testing on aluminum samples had previously been conducted using set temperatures, bath exposure times, and certain adhesives, but the testing apparatus was taken down since it was only used for one at a time custom procedures. Because chromic acid etching of aluminum used as a preparation for adhesion is not a widely used process, Henkel believed that it would not be economical to run the testing process on a continuous basis.

However, with the adhesives industry becoming more technologically advanced and the need for more improved product performance, the implementation of this testing apparatus appeared to provide excellent future opportunities and benefits for Henkel Loctite. It could have allowed them to interact with a larger number of customers and other companies who could find the need for Henkel Loctite to perform these tests on their products. The main purpose of this project, determining the life of the chromic acid bath, gave the company a good idea as to how efficient this process was. Other chemical surface preparation techniques were evaluated as well, such as various anodizing processes. These other techniques were not analyzed to the extent of the chromic acid etching process; however, they were used for comparative data.

Using standard aluminum test specimens provided by Henkel Loctite, a bench top etching system was designed. By submersing and exposing the desired bond area to this chromic acid bath for a set time and temperature, the area was prepared for adhesion. The design was able to handle 40 standard Lap Shears and the concentration profile of acid throughout the system was equal at all points. Also in order to determine when the chromic acid bath began to degrade, various tests were performed on the solution throughout the entire process to evaluate pH, aluminum content, and chromate levels. The system allowed for an easy and safe removal of the acid solution. Structural adhesives with different curing mechanisms were evaluated in order to identify possible trends. These standard bonded test specimens were then evaluated using different mechanical property tests. These tests determined the bond area's maximum shear strength. Environmental chambers were used in order to simulate advance aging in a short period of time. A design of experiments was established in order to avoid variations in data and to provide accurate statistical analysis of the results. This statistical analysis ranked each run according to bond strength. By using the previous tests based on the content of the solution at various times and bond strengths of the corresponding test specimen, it was determined when the bath needed to be altered or changed. This provided information with regards to how many test specimens could be treated before the bath was no longer effective. Using this information, other surface preparation techniques were investigated in order to analyze if this process was indeed reasonable for future implementation.

1.0 Literature Review

Before proposing the designs for certain bench-top surface preparation systems, we had to be well versed in the technology that was being used. To truly understand the scope of this project, we must look at what had been done previously and in the current industry today.

1.1 History of Adhesives

The adhesives industry is one of the largest in the world, spanning over 750 companies comprising of the multi-billion dollar industry. 50 of those 750 companies are responsible for 50% of sales in the adhesive world. Henkel-Loctite, one of those 50 companies, is one of the largest adhesive companies in the world, and because adhesives are literally found in almost every piece of manufactured equipment in today's high and ever-changing technological world, Henkel-Loctite has a huge impact not only on the adhesives industry, but also in everyday life.[3]

In order to understand the importance of the role adhesives play in the world, it was necessary to understand the history behind adhesives. The first observed adhesive can be dated back to 4000 B.C. in which pre-historic tribes plugged broken pottery vessels with tree sap in which they stored foodstuffs in the coffins of dead people. Between 2000 and 1000 B.C., animal glue began to be used throughout civilization, as paintings, murals, and caskets contained glue in their construction. Artifacts from ancient Egypt, such as the tombs of pharaohs, were observed to be bonded or laminated with some form of animal glue.[4]

The Greeks and Romans, approximately 2000 years later, began to improve on this glue by incorporating various natural substances into adhesives to provide better bonding strength. Ingredients such as egg whites, blood, bones, hide, milk, cheese vegetables, grains, beeswax, and tar were all used in various forms of manufacturing and artwork, such as ship construction and veneering and marquetry, in which thin sections of layers of wood were bonded together.[5]

For the next several hundred years, adhesives became more widespread as furniture and cabinet makers incorporated adhesives into their work. Some of these makers can be recognized today, such as Chippendale and Duncan Phyfe. Adhesives also have played an important role in military history, as most weapons parts in the early part of the millennium were bonded solely with adhesives. Violins were laminated with a specialty adhesive, and violin makers today have yet to recreate the lamination process of the 1500 and 1600s.[6]

In the 1700s, the adhesive industry really began to take off, as the first glue factory was constructed in Holland in which animal glues were manufactured from hides. In the late 1700s, patents began to be issued for glues and adhesives, as fish glue and adhesives using natural rubber, animal bones, fish, starch, and milk protein were all patented. By the start of the industrial revolution, the United States had several large glue-producing factories. As the 1900s progressed, the discovery of oil helped the adhesive industry take off in great proportion, as this led to the discovery of plastics. The introduction of Bakelite phenolic allowed adhesives using resin to be put on the market, and within the next 40 years, as new plastics and rubbers were being synthetically produced, the present day technology of adhesives were discovered. This development of plastics and elastomers has allowed the properties of adhesives to be changed and improved, such as flexibility, toughness, curing or setting time, temperature and chemical resistance. [7]

1.1.1 Importance of Adhesives in Industry Today

Adhesives are everywhere in the highly technological manufacturing world today, and it is no surprise that adhesives are one of the most important substances used in industry. Many adhesives have taken the place of other joining processes, such as bolts and welding, which reduced the cost of manufacturing and labor. Adhesive companies on-sell their products to companies in the construction sector, aircraft manufacturers, automotive manufacturers, and packaging industries.[8] The following is a list of several commonly used adhesives and their role in industry and every-day products.

Fish Glue: Used for photo emulsion for photo films and photo resist coatings.

Casein Glue: A waterproof adhesive used in the sealing of cigarette paper.

Starch: Used to bond paper products such as bookbinding, corrugated boxes, paper bags, wallpaper paste.

Cellulose Adhesive: The adhesive used on decals on windows and on strippable wallpaper.

Rubber-based Solvent Cements: Used on counter tops, cabinets, desks and tables. Also used on self sealing envelopes and shipping containers, and widely used in the shoe and leather industries.

Epoxies: Often used to bond metals and have replaced some traditional metal-joining processes, such as rivets, bolts, welding, brazing, and soldering. These metals are used to build rotor blades on helicopters and to build skis and snowboards.

RTV Silicone Adhesives: Used as sealant and caulking compounds in the construction industry as well as sealants for windows and doors on space shuttles.

Anaerobic Adhesives: Used in any industry that needs fasteners, gaskets, bearings or any mechanical device to be sealed or secured.

Cyanoacrylates: Also known a Super Glue. Used in electronics for printed circuit board wires and components and on disposable plastic medical devices.[9]

1.2 Surface Preparation Techniques

The purpose of surface treatment in preparation of adhesion is to modify the material to provide the best conditions for bonding. In this project, the material to be tested for adhesion was aluminum. Metal surfaces usually have an oxide layer on their surface, making it highly polar and ideal for adhesion. The major focus of surface treatment for metals, in particular chemical treatment, is to enhance the bonding strength and most importantly, to increase the endurance of metal bonds, especially in humid environments.[10]

In preparation of metals, the organic adhesive is intended to only make contact with the adherend material, as there should be no layers of oxide film, paint, chromate coating, chromate-free coating, phosphate coating, or silicon release agents. These are called weak boundary layers and drastically reduce the effectiveness of adhesion. When the materials are bonded to the adhesive, the bond should always be broken within the organic adhesive material, and not between the adhesive and the adherend. A *cohesive failure* is the desired failure in which the adhesive remains of both pieces of adherend, whereas an *adhesive failure* is one that occurs at the interface between the layers. 100 % cohesive failure is always the desired failure mechanism when describing materials bonded to organic adhesives.[11]

In preparing the test aluminum samples for adhesion, the three most important steps involve cleaning, abrading the surface mechanically to increase contact surface, and chemical treatment to improve corrosion resistance. In this project, chemical treatment was the variable studied and several different chemical surface treatments were compared based upon their effectiveness of bonding with a particular adhesive.

1.2.1 Chromic Acid Etch

The chemical treatment that was under the most investigation for this project was chromic acid etching, or the Forest Products Laboratory (FPL) etch, named after the aluminum surface preparation for Clad 24S-T3 in 1950, and later revised in 1975. The etching bath consists of 10 parts by weight sulfuric acid, 1 part by weight sodium dichromate, and 30 parts by weight distilled water. This solution is commonly referred to as chromic acid. When the aluminum is etched with the chromic acid, a layer of aluminum oxide is formed. There are two reactions present in this etching process[12]:

(1) $2AI + H_2SO_4 + Na_2\,Cr_2O_7$ ---------> $Al_2O_3 + Na_2SO_4 + Cr_2SO_4 + 4H_2O$

(2) $Al_2O_3 + 3H_2SO_4$ -----------> $Al_2(SO_4)_3 + 3H_2O$

The first reaction produces the aluminum oxide, which then reacts with the sulfuric acid to produce aluminum sulfate. However, the first reaction proceeds much faster than the second one, allowing a controlled amount of aluminum oxide on the surface. It was part of the project to determine not only how long it took for the chromic acid bath to lose the effective amount of sulfuric acid,

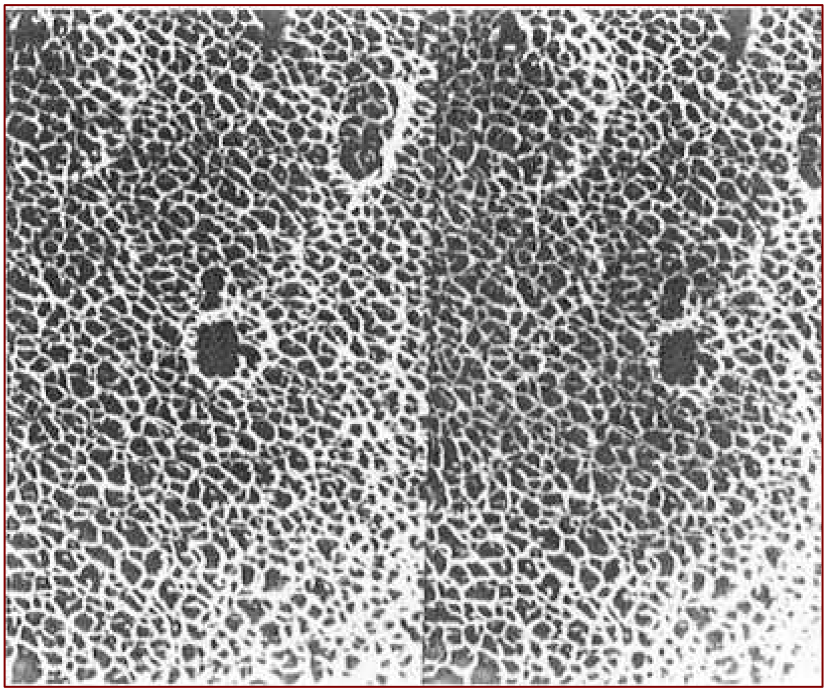


Figure 1: Stereo STEM Micrograph of Chromic Acid Etched Surface of Aluminum

but also if there was an appropriate amount of aluminum oxide on the surface of the test sample ready for adhesion.

Figure 1[13] shows the surface of the aluminum after chromic acid etching, and **Figure 2**[14] shows a proposed sketch of the aluminum oxide structures.

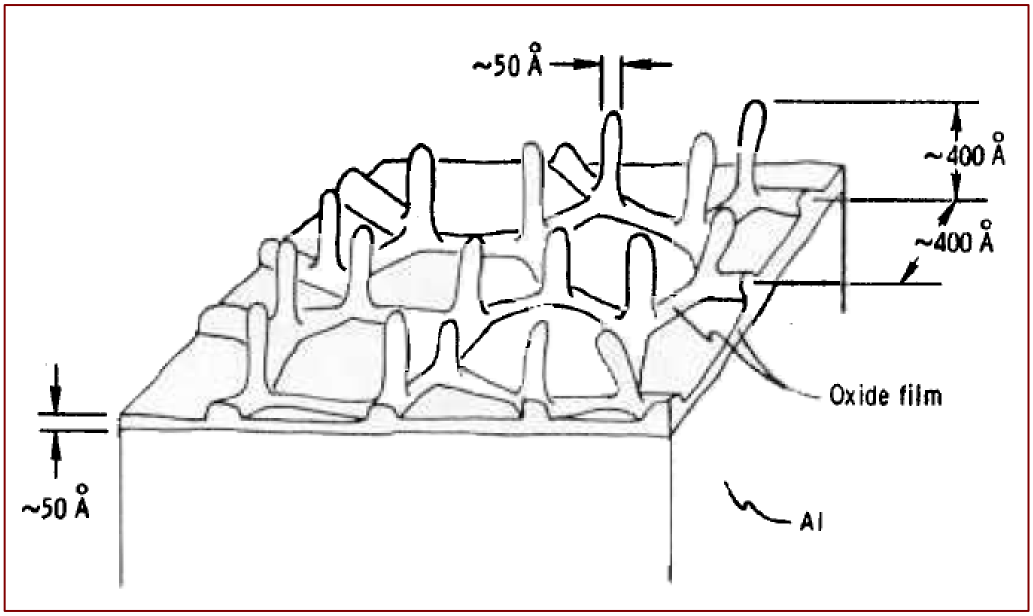


Figure 2: Drawing of Oxide Structure for Chromic Acid Etching

After the etching process is complete, the sample must be rinsed with water, but it is a better idea to spray the aluminum surface instead of submerging it because residue from the surface will eventually contaminate the water bath, thus lowering the pH level and possibly leading to bond failures.

1.2.2 Sulfuric Acid Anodizing and “Hard” Anodizing

In addition to submerging the aluminum in an acid bath and removing it after a given period of time, another surface preparation process involves running an electric current through a sulfuric acid/water bath while the aluminum sample is submerged. The solution is similar to chromic acid minus the sodium dichromate. Like the chromic acid etch, a very thin layer of aluminum oxide is formed on the surface of aluminum. This is called sulfuric acid anodizing and is used considerably by the automotive and consumer cookware industries.

A variation of sulfuric acid anodizing is hard anodizing, which uses the same process as regular sulfuric acid anodizing except the acid is cooled to the freezing point of water and the current through the bath is substantially increased. Compared to the regular anodizing process, a much thicker layer of aluminum oxide is produced, as holes and fissures in the surface give the treated aluminum a more uniform appearance. The oxide layer has a much stronger bond to the original aluminum surface, making it more durable in harsh weather and salty environments, as well as increasing bond strength when an adhesive is applied to the treated surface.[15]

1.2.3 Phosphoric Acid Anodizing

Aside from etching, anodizing is one of the most widely used surface treatments of metals, especially in the aerospace industry. During the process, stable coatings or films are formed on the aluminum surface in a wide variety of electrolytes. The test samples are submerged in a bath of 9-12 weight % phosphoric acid at 19-25 degrees Celsius between a voltage from 9 to 16 V under a direct current. Compared to the chromic acid etch, this process is less dependent on certain variables, such as time between treatment and rinsing. This is the preferred treatment in the aerospace industry because the oxide layer formed is thicker than the chromic acid, and the "whiskers," as shown in **Figure 2** (above), are generally longer in the anodizing process. However, the immersion time is almost twice as long compared to the chromic acid etching process, which only lasts for about 10 minutes, compared to the 20 to 25 minutes required for anodizing.[16]

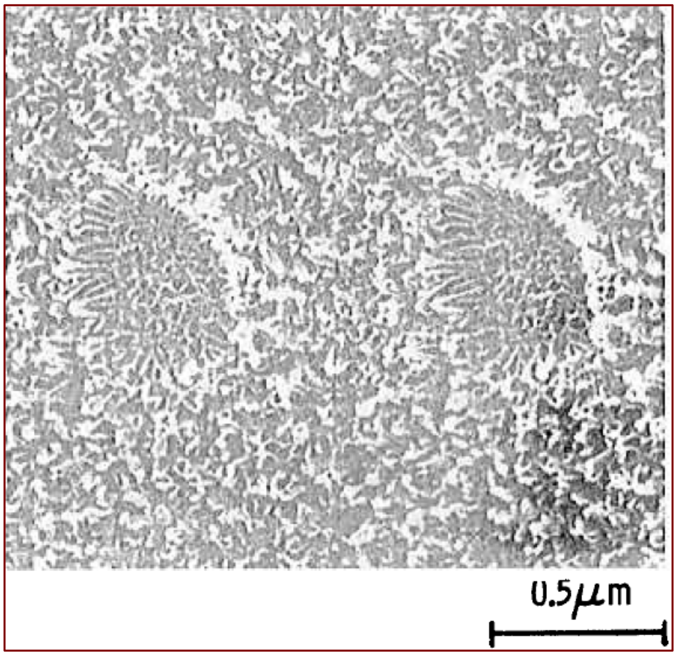


Figure 3: Stereo STEM Micrograph of Aluminum Surface after Phosphoric Acid Anodizing

Figure 3[17] shows the surface of the same aluminum test sample as shown in **Figure 1**Error! Reference source not found., but after phosphoric acid anodizing treatment.

Figure 4[18] shows the oxide layer drawing of the aluminum surface.

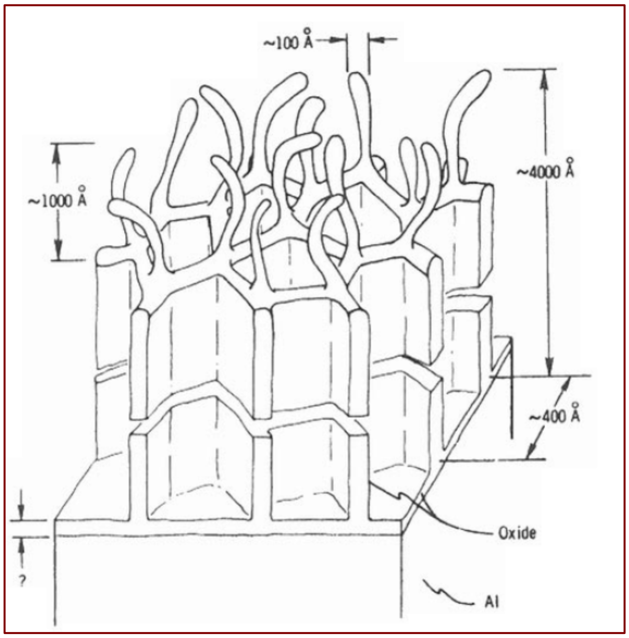


Figure 4: Drawing of the Oxide Structures after Phosphoric Acid Anodizing

1.2.4 Chromic Acid Anodizing

Finally, the chromic acid anodizing process is similar to phosphoric acid anodizing, in which the aluminum test specimen is subjected to a voltage and applied current, thus forming an electrolyte layer. The chromic acid in the solution leaves a strong layer of aluminum oxide on the surface, allowing for a strong bonding environment.[19]

An actual chromic acid etching process was devised in this project and the main variable to be tested was how long an individual bath could be used until it was no longer effective. The bonding strengths of the adhesives used on the chromic acid etched samples were compared to those of the three other surface treatment methods discussed.

1.3 Adhesive Chemistry

In order to adhere properly and efficiently to a substrate, an adhesive must first do two things. First it must “wet” the surface, by spreading material throughout the entire bond area and making a contact angle approaching zero. The contact angle is the angle at which the vapor/liquid interface meets the solid surface **[See Figure 5].**[20] Secondly the adhesive must harden to a cohesively strong solid.[21]

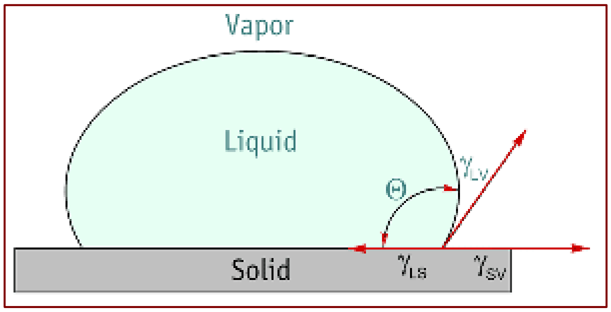


Figure 5: Contact Angle

Wetting is important since it involves making intimate contact between the molecules of the adhesive and the molecules in the surface of the substrate. This application technique is extremely important with every adhesive. By applying adhesive in this fashion, it permits maximum interactions on the surface of the substrate, in turn, increasing bond strength. After the substrates are mated, hardening can occur by chemical reaction, loss of solvent or water, or by cooling/heating. When this intimate contact is made, van der Waals forces are built, but other intermolecular forces may occur such as chemical bonds. This is where things can vary depending on the chemistry of the particular adhesive and substrate being used. If the adhesive can penetrate into the substrate before hardening, then mechanical interlocking will contribute to the overall strength of the bonded area. Intertwining of polymer molecules in the adhesive with those in the substrate would result in molecular interdiffusion across the interface. These four phenomena underlie the *physical adsorption, chemical bonding, mechanical* *interlocking* and *diffusion* theories of adhesion. The remaining two theories that provide a backing as to how adhesives work are *electrostatic* theory and *weak boundary layer* theory. Electrostatic theory states that if two metal substrates are placed in contact, electrons will be transferred from one to the other. This forms an electrical double layer, which in turn gives a force of attraction. Lastly, weak boundary layer theory proposes that clean surfaces give stronger bonds to adhesives. Some contaminants such as rust and oils produce a layer which is cohesively weak, which in turn, weakens the overall bond strength.[22]

The remainder of this section covers the particular chemistries involved with the type of adhesives that were evaluated.

1.3.1 Epoxy Resin Adhesives

Epoxy resins are reactive with a number of different curing agents and yield a wide variety of products with different cure requirements and end use performance. Epoxy resins cure with no byproducts, have low shrinkage and adhere to many different substrates. Although epoxy adhesives represent only a small part of the total adhesives market, they are unequalled in performance where high strength and endurance properties are significant.[23]

Epoxy adhesives are made up of the resins themselves, plus the hardeners that produce the curing reactions. The first commercial epoxy resins, and still the most important, are those from the diglycidyl ether of bisphenol A (DGEBA resins). Bisphenol A epoxy resins are difunctional, with epoxide groups on the ends of the chain. As the molecular weight is increased, the resin retains its epoxide difunctionality while adding *n* repeating groups as shown above.[24] **[See Figure 6]**[25]

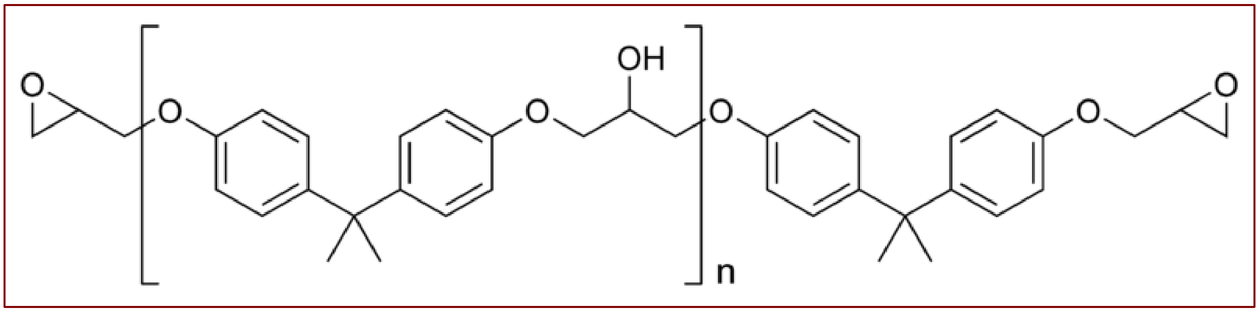


Figure 6: Diglycidyl Ether of Bisphenol A (DGEBA Resins)

Hardeners, or curing agents, determine the type of chemical bonds formed and the degree of crosslinking which occur with the epoxy resin. The type of curing agent will also determine the rate of reactivity, degree of exotherm, gel time, formulation viscosity, and the heat requirement during the cure cycle. These factors, in turn, affect the electrical and physical properties, chemical resistance, and the heat resistance of the cured adhesive. The types and number of curing agents available continues to grow rapidly.[26] The two types of curing agents that will be focused on are amine based hardeners and polyamide based hardeners.

1.3.1.1 Amine Hardeners

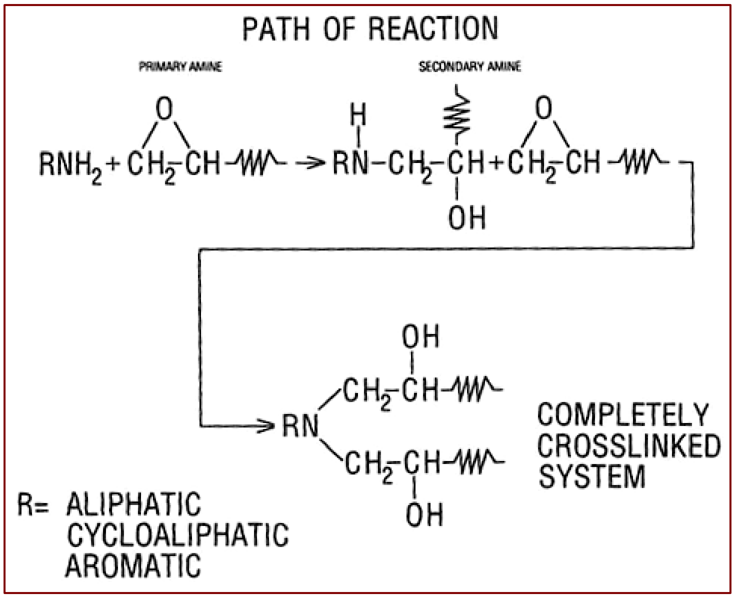


Figure 7: Amine Reaction Sequence

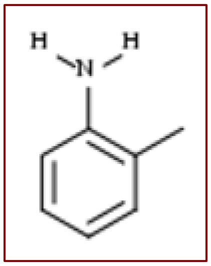


Figure 8: Aromatic Amine

The functionality of an amine is determined by the number of amine hydrogens present on the molecule. A primary amine group (nitrogen with two hydrogens bound to it) will react with two epoxide groups. A secondary amine group (nitrogen with only one hydrogen bound to it) will react with on epoxide group. A tertiary amine group (nitrogen with no hydrogens bound to it) will not react readily with any epoxide groups; however it will serve as a catalyst to accelerate epoxy reactions **[See Figure 7].**[27] There are three types of amines that when used will affect the various adhesive properties as discussed in section 2.4.1. These three types are aliphatic amines, cycloaliphatic amines, and aromatic amines.[28] In all cases, regardless of the type, an amine group must be present in order for it to be considered an amine. In aliphatic compounds, atoms can be joined together in straight chains, branched chains, or non aromatic rings. Cycloaliphatic amines are when atoms are joined in a ring structure that is not aromatic. Lastly, aromatic amines are atoms joined in a ring structure that is in fact aromatic. Aromaticity is a chemical property in which a conjugated ring of unsaturated bonds, lone pairs, or empty orbitals exhibit a stabilization stronger than would be expected by the stabilization of conjugation alone **[See Figure 8].**[29]

1.3.1.2 Polyamide Hardeners

The most commonly used polyamides are the condensation products of dimerized fatty acids and aliphatic amines such as diethylene triamine. The amide link is produced from the condensation reaction of an amino group and a carboxylic acid or acid chloride group, at which point a small molecule, usually water, is eliminated[30] **[See Figure 9].**[31]

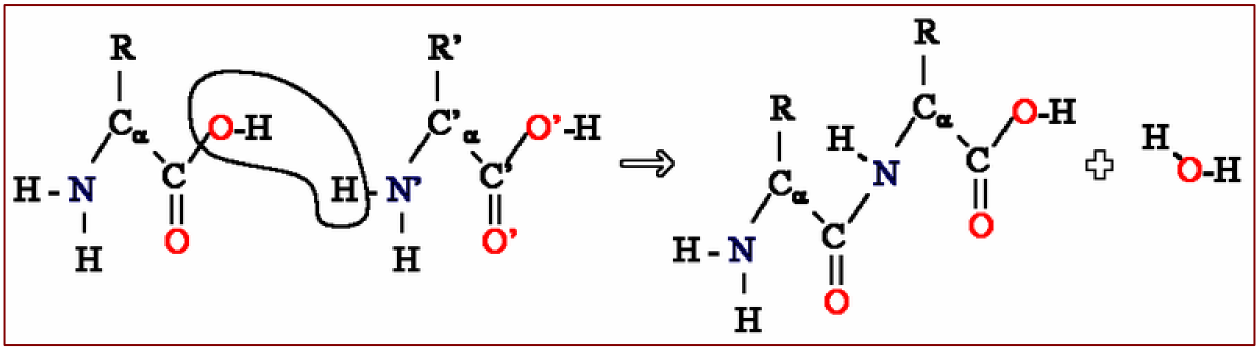


Figure 9: Condensation Reaction

The polyamides react with epoxide groups through the unreacted amine functional groups in the polyamide backbone, similar to that of basic amine hardeners. However, as a result of their relatively large molecular weight, the ratio of polyamide to epoxy resin is more forgiving (less critical) than with low molecular weight polyamines.[32]

1.3.2 Acrylic Adhesives

Acrylic adhesives today are a large class of specifically designed products made to meet the needs of industry in the assembly of a wide variety of components.[33] These adhesives are solvent-free ‘reactive’ engineering adhesives that include but are not limited to cyanoacrylate, anaerobic and modified acrylic adhesives.[34]

Acrylic adhesive polymers are widely used for applications such as pressure sensitive tapes, labels, and other decorative and functional pressure sensitive products. These applications thrive on the adhesive's versatile adhesion ability and excellent aging characteristics. Acrylic adhesives are also widely used as elastomers and thickener components in a variety of waterborne construction adhesives, laminating adhesives, and packaging adhesives.[35]

Acrylic chemistry is the basis for a number of 100% solids reactive engineering adhesives used in structural bonding applications, generally involving a metal or plastic nonporous surface.[36]

1.3.2.1 Cyanoacrylate Adhesives

Cyanoacrylate adhesives are unique among the many classes of adhesives, in that they are the only single component, instant bonding adhesives that cure at ambient conditions without requiring an external energy source. This characteristic, and its ability to bond to a wide variety of substrates, has made cyanoacrylate adhesives ideal for numerous bonding applications.

In this case we focused particularly on ethyl cyanoacrylate[37] **[See Figure 10].[38]**

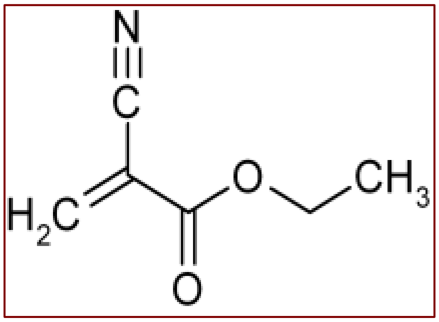


Figure 10: Ethyl Cyanoacrylate

The reactivity of cyanoacrylates is directly traceable to the presence of two strong electron withdrawing groups (designated X and Y) **[See Figure 11]**.[39]

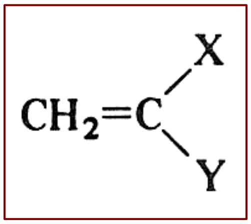


Figure 11: Electron Withdrawing Groups

Where: X = CN
Y = COO-CH_2-CH_3

These groups make the double bond highly susceptible to attack by weak bases. More specifically, cyanoacrylate rapidly polymerizes in the presence of water (specifically hydroxide ions) in air, forming long, strong chains which join the bonded surfaces together **[See Figure 12].** The nucleophile represents the hydroxide ions found in air.

This reaction will continue until all available monomer is consumed or until growth is interrupted by the presence of an acidic species.

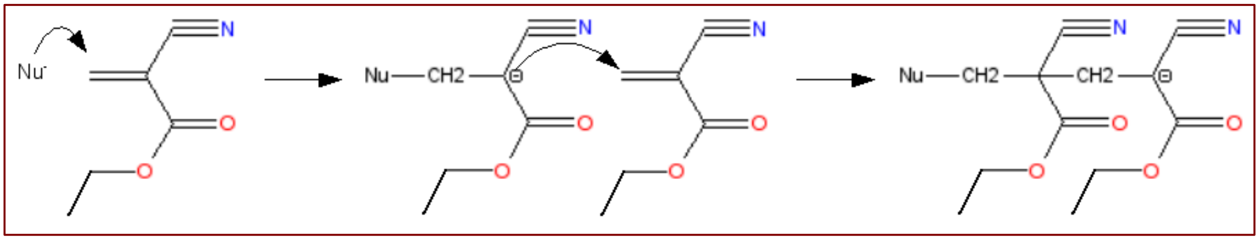
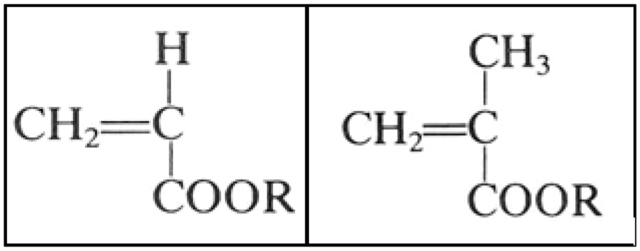


Figure 12: Ethyl Cyanoacrylate Mechanism of Polymerization

1.3.2.2 Methacrylates and Acrylates

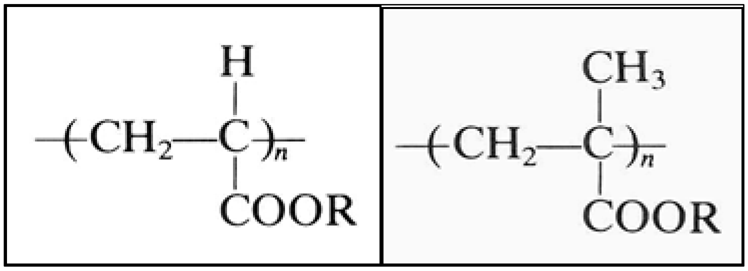
Polymers made from esters of methacrylic and acrylic acids have been widely used for many years. As a result of this, many methacrylate and acrylate monomers are available commercially for use in making liquid monomeric adhesives. Also, the technology for making other monomers as required is well established, therefore, it is now possible to have monomers specifically designed to meet particular adhesive requirements.[40] These monomers, which during cure form long polymeric chains, can have many different traits based on the chemical structure of said monomers. The characteristic properties of a polymer are greatly influenced by the conditions of polymerization. Variations in catalyst level, reaction time, temperature, and monomer concentration make it possible to adjust the polymer's molecular weight and ultimately its physical properties.[41] The basic monomeric structures for acrylates and methacrylates can be seen below in **Figure 13.**[42]



$CH_2{=}C(H)COOR$ $\quad$ $CH_2{=}C(CH_3)COOR$

Figure 13: Basic Monomeric Structures

Polymerization is started by a free-radical initiator, often times a peroxide. The monomers then polymerize rapidly, adding onto the growing chain to form the final polymer **[See Figure 14].**[43]



$$-\!\left(CH_2-\overset{\overset{\large H}{|}}{\underset{\underset{\large COOR}{|}}{C}}\right)_n\!- \qquad -\!\left(CH_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large COOR}{|}}{C}}\right)_n\!-$$

Figure 14: Final Polymers

The acrylate polymers have an alpha hydrogen adjacent to the carbonyl group and, therefore, have more rotational freedom than the methacrylates. The substitution of a methyl group for the hydrogen atom (producing a methacrylate polymer) restricts the freedom of rotation of the polymer and thus produces harder, higher tensile strength and lower elongation polymers than their acrylate counterparts **(See Table 1).**

Table 1: Mechanical Properties

Polymethacrylate	**Tensile Strength (psi)**	**Elongation (%)**
Methyl	**9,000**	**4**
Ethyl	**5,000**	**7**
Butyl	**1,000**	**230**
Polyacrylates	**Tensile Strength (psi)**	**Elongation (%)**
Methyl	**1,000**	**750**
Ethyl	**33**	**1,800**
Butyl	**3**	**2,000**

1.4 Loctite® Standard Test Method

Loctite standard test methods were used to evaluate various properties with certain bonded substrates. The main concern for our specific application is bond strength. There were various ways of observing bond strength, and different types of bond strength. For our particular application, we observed the shear strength of our bonded assemblies. In order to do so we used STM (Standard Test Method) 700: *Shear Strength of Adhesives Using Lap-Shear Specimens.*

This involved the lap shears being pulled on the Instron 4505 machine using a 50 kN load cell at 0.05 inches per minute. Peak load and failure mode were then recorded after bond failure.

Shear strength is the strength of a material or part of an assembly in which the material fails in shear. Shearing is the deformation of a material in which parallel surfaces slide past each other. The aluminum lap shears used in this project were 1 inch by 4 inches and bonded together at an area of 0.5 inches. Force was applied in opposite directions at each end of the bonded assemblies until failure occured. Even though substrate failure was the desired goal when testing bonded assemblies, many times the substrates underwent adhesive and cohesive failures, resulting in various bond strengths. For an image of adhesive failure, see **Figure 15** and for an image of cohesive failure see **Figure 16**.

Please See Appendix A for STM 700.

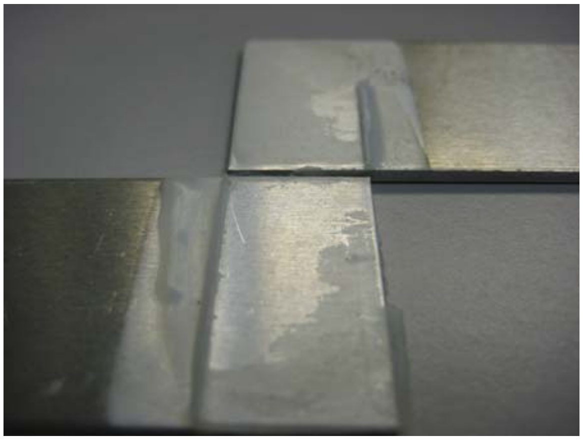


Figure 15: Adhesive Failure

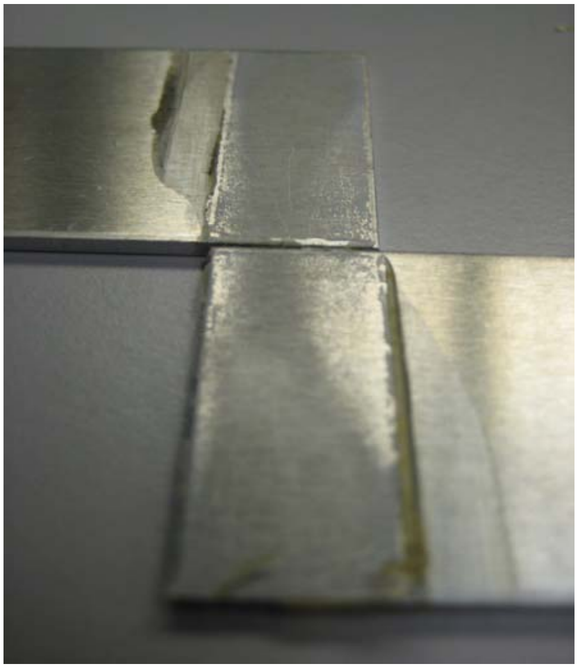


Figure 16: Cohesive Failure

2.0 Experimental Techniques

The overall goal was to design and evaluate a bench-top chromic acid etching system for aluminum prior to adhesion. Once that was completed, the results of this system were compared to other chemical surface preparation techniques. These techniques could use the system previously created for the chromic acid etch, or a completely new system. The previous chromic acid etching system at Henkel-Loctite consisted of a large beaker filled with the acid on a hot plate in which the lap shears were hand placed into the beaker and then hand removed after 10 minutes. The other surface preparation techniques could also be provided by an outside vendor in the interest of time and lack of resources. In order to complete this task, mission objectives were laid out.

1) Design and build a Bench-top chromic acid etching System.
2) Determine when the batch of chromic acid degraded to a point where it was no longer useable.
3) Evaluate other possible surface preparation techniques.
4) Determine which system suited the needs of our sponsor the best.

1) Using our knowledge of safe lab practices obtained over a four year period at WPI, and researching previous systems used by our sponsor and other companies alike, a system was designed. The designed system also took into account sizing specifications, as well as repeatability.

2) Appropriate adhesives were selected for use during testing in order to ensure the best results. The most optimal cleaning method prior to bonding was also determined.

3) By evaluating the strength of our bonded assemblies, we were able to determine when the batch began to degrade. By using the same batch for multiple assemblies, it became apparent when the strength of the bonds began to decrease or become erratic. Evaluating the aluminum content and chromate levels of the batch throughout the entire preparation process gave us a closer look at the changes in the bath as the bond strengths of the samples decreased.

4) Evaluating the bond strengths of the chromic acid etching samples, compared to those of different surface preparation techniques, allowed us to determine which technique was best for adhesion. By having multiple surface preparation techniques for aluminum, it allowed the company to rely on multiple options. It also opened up opportunities to explore avenues that Henkel had yet to observe.

5) Using statistical analysis, it was determined which surface preparation techniques yielded the best bond strengths. Using that data, and other information such as the cost, safety of the techniques, and efficiency it was determined which system best suited our sponsor.

2.1 Assembly Method for Chromic Acid Bath

Figure 17: Complete Assembly of Chromic Acid Bath

Since the acid bath being constructed needed to hold a constant temperature of 70°C, it was necessary to evaluate various possibilities of achieving this. After consulting with several lab managers both on the WPI campus and here at Henkel-Loctite, a water bath was decided on because it provided the most accurate acid temperature in the safest manner. Assembly of the acid bath first began by selecting an appropriate vessel to place the acid into. Since glass was one of the only materials that could be used with chromic acid, because of its highly reactive potential with other materials, we settled on a Pyrex baking dish. By partially submerging the dish into the water bath, above the line of the chromic acid, good heat transfer throughout the dish and the bath was assured. Aluminum handles were then glued to the sides of the dish to act as stops to keep the dish remaining at the proper level, and to also aid in removing the dish from the water bath for waste disposal.

The chromic acid bath was created using 10 parts by weight sulfuric acid, 1 part by weight sodium dichromate dehydrate, and 30 parts by weight water, which after conducting several conversion calculations, resulted in 82 mL of sulfuric acid, 15.25 grams of sodium dichromate, and 452 mL of water **[See Appendix B for Calculations]**. The bath was stirred regularly with a glass rod and placed into the water bath. In order to keep the chromic acid bath at 70 degrees Celsius, the water bath temperature had to be kept at 80 degrees Celsius. The apparatus, as shown in **Figure 17**, which was fabricated at the machine shop here at Henkel-Loctite, was used as a fixture to hold the aluminum test specimens in place during the etching process. It also was used to hold the specimen in place during the rinsing process, shown in **Figure 18**, once etching was completed.

Figure 18: Spraying of De-Ionized Water on Treated Specimens

2.2 Adhesive Selection Testing

An appropriate adhesive candidate for an eventual chromic acid bath degradation study was chosen based on a study evaluating 10 adhesives, as shown in the test matrix in **Table 2**. 10 replicates per run were chosen based on a Minitab analysis, assuming that a minimum difference of 383 psi could be detected using the same adhesive from treated to non-treated specimen with a 90% chance that this difference would be found. The candidate was selected based on the greatest mean difference in bond strengths achieved from treated to non-treated specimen, given the difference in the mean was statistically significant.

Table 2: Adhesive Selection Test Matrix

Run	Adhesive	Treatment	Test Method	Primer	Reps
1	E-60HP	None	STM 700	None	6*
2	E-30UT	None	STM 700	None	10
3	H8010	None	STM 700	None	10
4	E-40FL	None	STM 700	None	10
5	H4800	None	STM 700	None	10
6	H8000	None	STM 700	None	10
7	480	None	STM 700	None	10
8	435	None	STM 700	None	10
9	331/7387**	None	STM 700	7387	10
10	332/7387**	None	STM 700	7387	10
11	E-60HP	Chromic Acid	STM 700	None	10
12	E-30UT	Chromic Acid	STM 700	None	10
13	H8010	Chromic Acid	STM 700	None	10
14	E-40FL	Chromic Acid	STM 700	None	10
15	H4800	Chromic Acid	STM 700	None	10
16	H8000	Chromic Acid	STM 700	None	10
17	480	Chromic Acid	STM 700	None	10
18	435	Chromic Acid	STM 700	None	10
19	331/7387**	Chromic Acid	STM 700	7387	10
20	332/7387**	Chromic Acid	STM 700	7387	10
21	E-60HP	Chromic Acid	STM 700	None	10

* Data acquisition was only obtained for 6 specimens on the 1st run due to software issues.

** 7387 Primer was used for Runs 9, 10, 19 & 20 NOTE: Run 21 was completed in order to see if the bath began to degrade after a set order of runs, based on the performance of this specific adhesive (E-60HP).

2.2.1 Methodology

The first tests consisted of applying adhesive to untreated aluminum lap shear specimens and letting them cure for at least 3 days. Prior to the application of the adhesive, all bonding surfaces were cleaned with isopropyl alcohol. Adhesive was then manually applied to one lap shear specimen and was mated with a second lap shear with a 0.5” overlap. The mated assembly was clamped with two (2) Brink and Cotton No. 1 clamps and allowed to cure for at least 72 hours at ambient conditions prior to testing **[See Figure 19]**.

The same testing procedure was then conducted on the chromic acid treated lap shear specimens using the same adhesives.


Figure 19: Clamped Assembly

The aluminum lap shears, with a clamp holding 2 specimens separated by a polypropylene block, were lowered into the bath 20 at a time for 10 minutes as 1 inch of the specimens were submerged into the bath. After 10 minutes, each batch of 20 aluminum lap shears were sprayed with de-ionized water and dried in an oven held constant at 80 degrees Celsius for another 10 minutes. Both the temperature of the water bath and acid bath were monitored in between each run to ensure the correct temperature was maintained. Once the test specimens were taken out of the oven, they were immediately bonded with the selected adhesive and let out to cure for 72 hours.

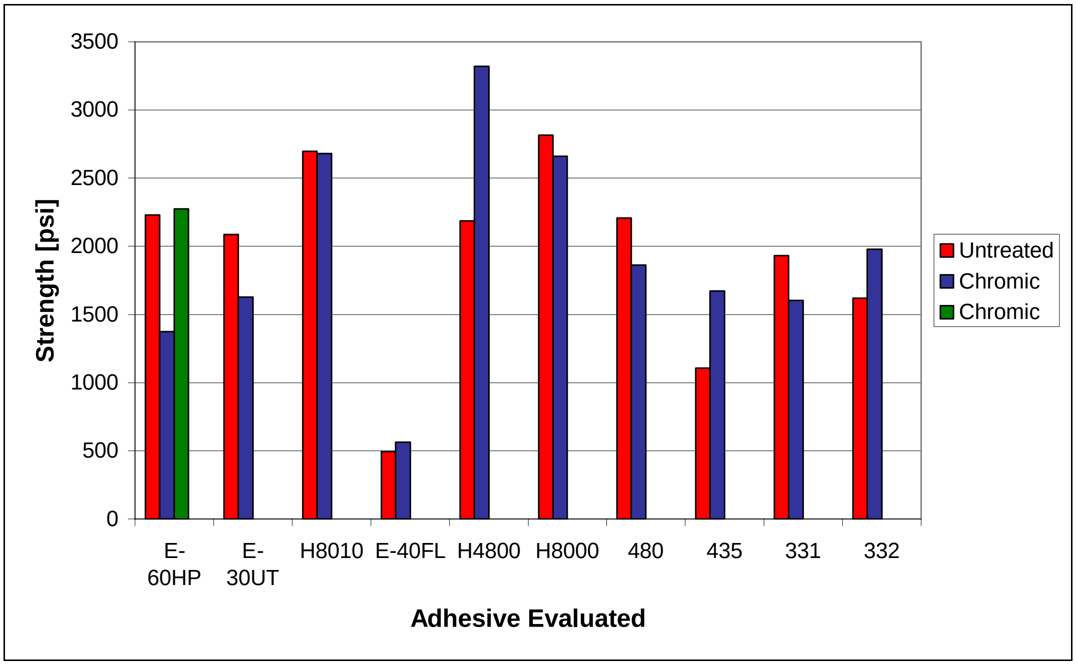
The bond strengths of the lap shears from the adhesive selection process were determined using the Instron 4505 machine using a 50 kN load cell. All assemblies were tested according to STM-700 where samples were pulled at 0.05 inches per minute and peak load and failure mode were recorded **[See Figure 20]**. The bond strengths were then analyzed by maximum strength and adhesive type using an F-test to determine if there was a significant difference in the variance between the treated and untreated specimen and a t-test to determine if there was a significant difference between the means.

Figure 20: Testing of Specimen on Instron

2.2.2 Results & Discussion

The mean maximum bond strengths of all 10 adhesives are shown in **Figure 21**, and the full tabulation of results is shown in **Appendix C**.

Figure 21: Results of Average Bond Strengths for Adhesive Selection Testing



NOTE: Run 21 (represented here by the green bar) was completed in order to see if the bath began to degrade after a set order of runs, based on the performance of this specific adhesive (E-60HP).

As shown in the above chart, the four adhesives that produced improved bond strength from untreated to treated were E-40FL, H4800, 435, and 332. Data analysis was performed on these adhesives to determine if the improvement in bond strength was statistically significant. Therefore, we used both Excel and Minitab to perform a t-test and F-test for the bond strength data from the following adhesives: E-40FL, H4800, 435, and 332.

2.2.2.1 Loctite® E-40FL™

F-Test Two-Sample for Variances

Table 3: F-Test for E-40FL

	Untreated	**Treated**
Mean	493.5	562.7
Variance	10673	35410
Observations	10	10
df	9	9
F	0.301	
P(F<=f) one-tail	0.044	
F Critical one-tail	0.315	

From this result, since the p-value <0.05, at a 95% confidence level, we could conclude that the variances were statistically significantly different.

t-Test: Two-Sample Assuming Unequal Variances

Table 4: t-test for E-40FL

	Untreated	**Treated**
Mean	493.5	562.7
Variance	10673	35410
Observations	10	10
Hypothesized Mean Difference	0	
df	14	
t Stat	-1.02	
P(T<=t) one-tail	0.165	
t Critical one-tail	1.76	
P(T<=t) two-tail	0.325	
t Critical two-tail	2.14	

From this result, since the p-value >0.05, at a 95% confidence level we could not prove that the differences in the means between the treated and untreated samples were statistically significant.

2.2.2.2 Loctite® H4800™

F-Test Two-Sample for Variances

Table 5: F-test for H4800		
	Untreated	**Treated**
Mean	2185.9	3319.8
Variance	70694	73684
Observations	10	10
df	9	9
F	0.959	
P(F<=f) one-tail	0.476	
F Critical one-tail	0.315	

From this result, since the p-value >0.05, at a 95% confidence level, we could not conclude that the variances were statistically significantly different.

t-Test: Two-Sample Assuming Equal Variances

Table 6: t-test for H4800		
	Untreated	**Treated**
Mean	2185.9	3319.8
Variance	70694	73684
Observations	10	10
Pooled Variance	72189	
Hypothesized Mean Difference	0	
df	18	
t Stat	-9.44	
P(T<=t) one-tail	1.08E-08	
t Critical one-tail	1.73	
P(T<=t) two-tail	2.16E-08	
t Critical two-tail	2.10	

From this result, since the p-value is <0.05, at a 95% confidence level we could assume that the differences in the means between the treated and untreated samples were statistically significant.

A graphical representation for the strength values obtained for H4800 is shown in the individual value plot shown below **[Figure 22]**.

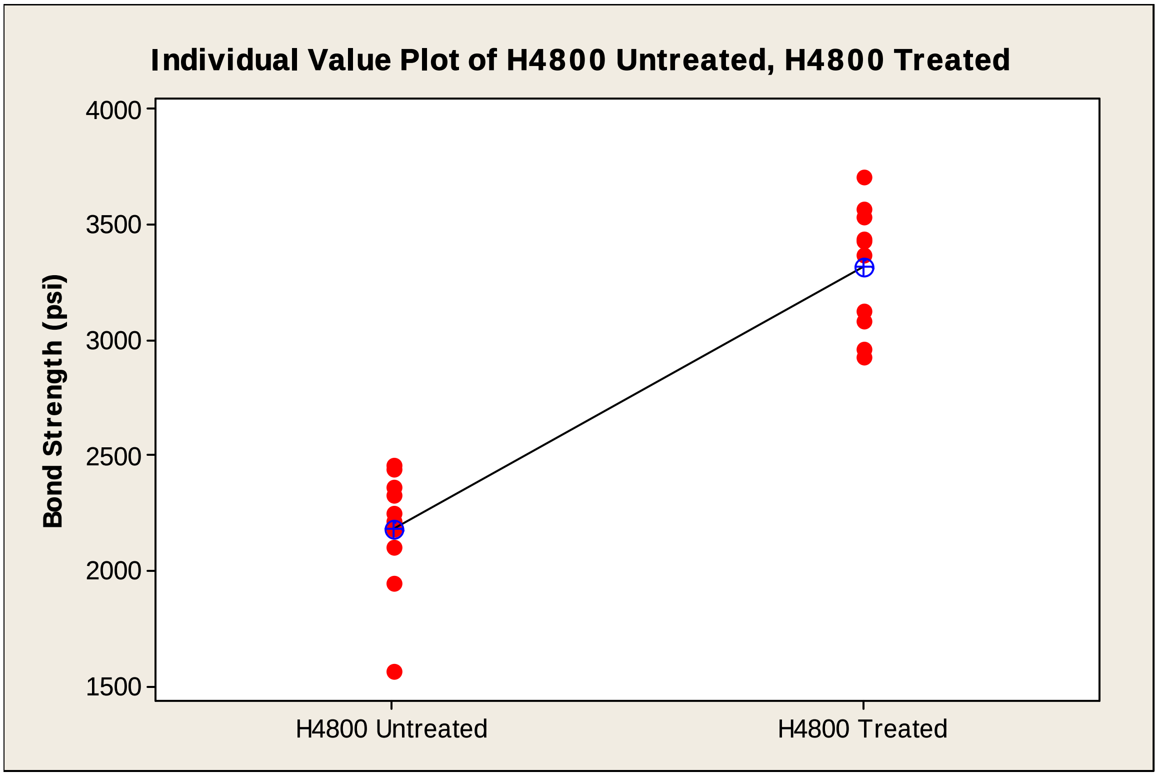


Figure 22: Individual Value Plot for H4800

The previous individual value plot presents the difference in the data from treated to untreated specimen while also identifying the scatter.

2.2.2.3 Loctite® 435™

F-Test Two-Sample for Variances

Table 7: F-test for 435

	Untreated	**Treated**
Mean	1106.5	1671.8
Variance	172581	410221
Observations	10	10
df	9	9
F	0.421	
P(F<=f) one-tail	0.107	
F Critical one-tail	0.315	

From this result, since the p-value >0.05, at a 95% confidence level, we could not conclude that the variances were statistically significantly different.

t-Test: Two-Sample Assuming Equal Variances

Table 8: t-test for 435

	Untreated	**Treated**
Mean	1106.5	1671.8
Variance	172581	410221
Observations	10	10
Pooled Variance	291401	
Hypothesized Mean Difference	0	
df	18	
t Stat	-2.34	
P(T<=t) one-tail	0.015	
t Critical one-tail	1.73	
P(T<=t) two-tail	0.031	
t Critical two-tail	2.10	

From this result, since the p-value is <0.05, at a 95% confidence level we could assume that the differences in the means between the treated and untreated samples were statistically significant.

A graphical representation for the strength values obtained for 435 is shown in the individual value plot shown below **[Figure 23]**.

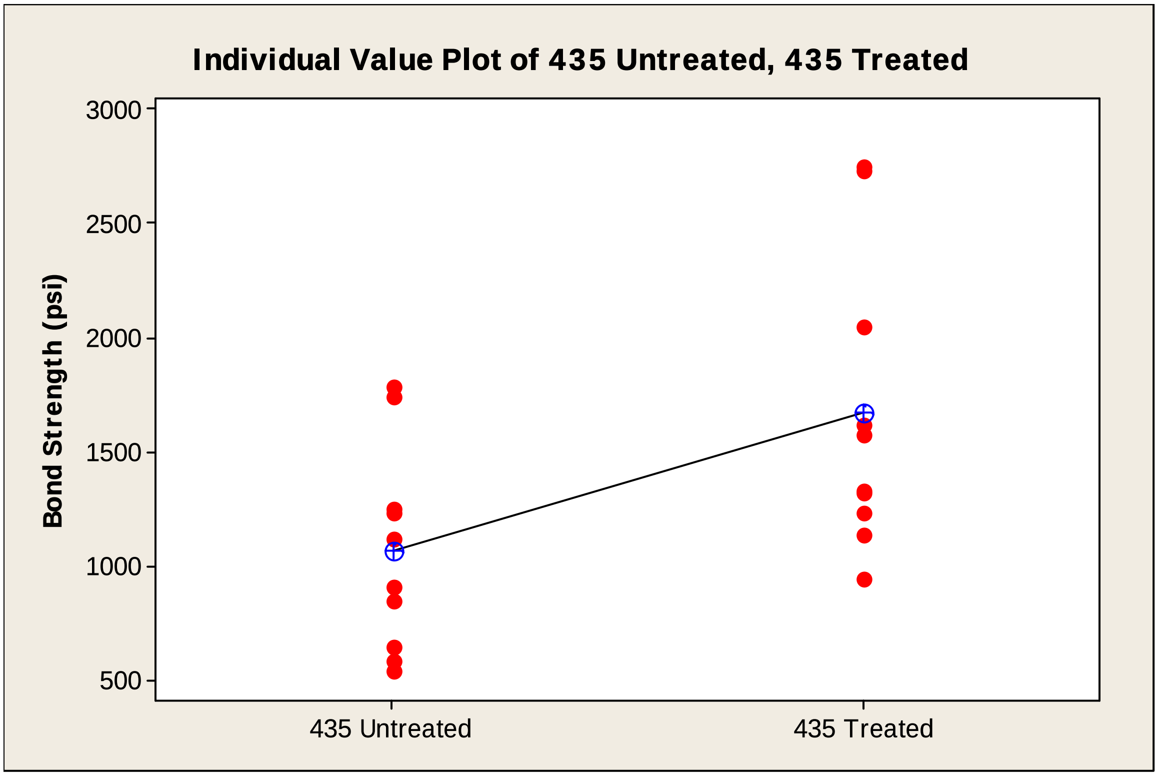


Figure 23: Individual Value Plot for 435

The previous individual value plot presents the difference in the data from treated to untreated specimen while also identifying the scatter.

2.2.2.4 Loctite® 332™

F-Test Two-Sample for Variances

Table 9: F-test for 332		
	Untreated	**Treated**
Mean	1619.2	1978.2
Variance	12339.73333	323025.2889
Observations	10	10
df	9	9
F	0.038200518	
P(F<=f) one-tail	2.0925E-05	
F Critical one-tail	0.314574906	

From this result, since the p-value <0.05, at a 95% confidence level, we could conclude that the variances were statistically significantly different.

t-Test: Two-Sample Assuming Unequal Variances

Table 10: t-test for 332		
	Untreated	**Treated**
Mean	1619.2	1978.2
Variance	12339.73333	323025.2889
Observations	10	10
Hypothesized Mean Difference	0	
df	10	
t Stat	-1.960358798	
P(T<=t) one-tail	0.03919477	
t Critical one-tail	1.812461102	
P(T<=t) two-tail	0.078389541	
t Critical two-tail	2.228138842	

From this result, since the p-value is <0.05, at a 95% confidence level we could assume that the differences in the means between the treated and untreated samples were statistically significant.

A graphical representation for the strength values obtained for 332 is shown in the individual value plot shown below **[Figure 24]**.

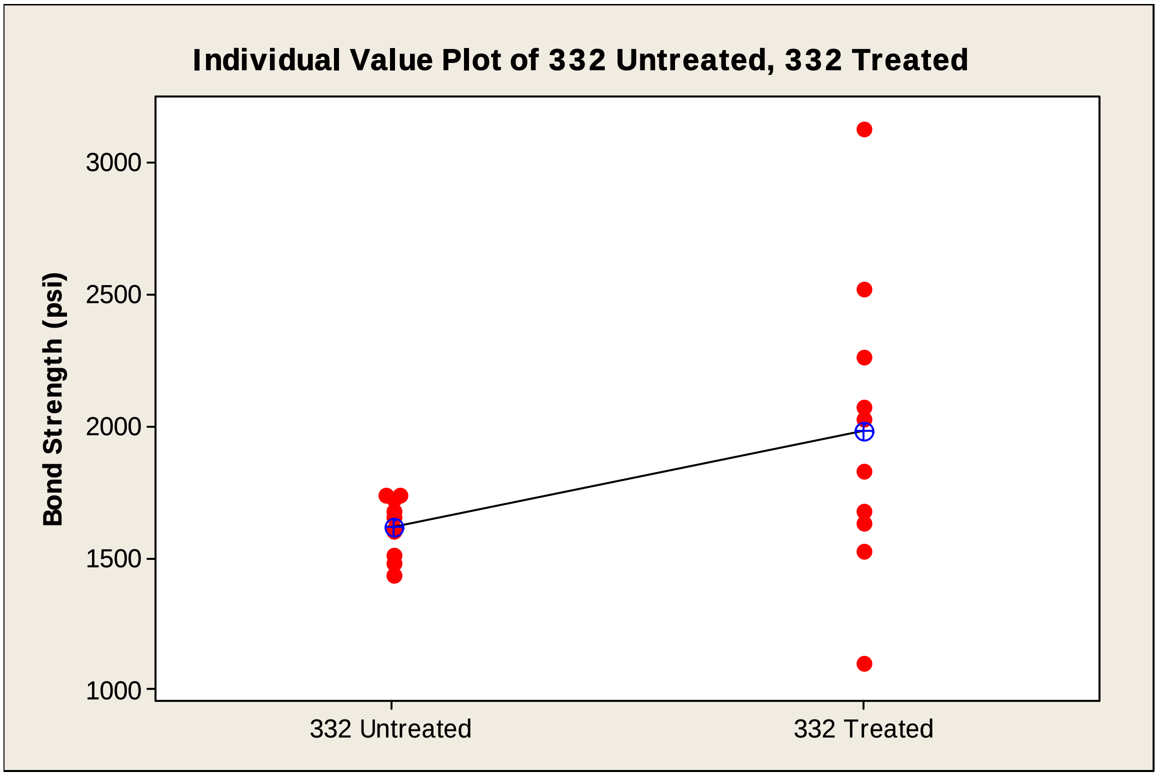


Figure 24: Individual Value Plot for 332

The previous individual value plot presents the difference in the data from treated to untreated specimen while also identifying the scatter.

It was observed that H4800 had the greatest mean difference in strength from untreated to treated specimens, a value of 1184 psi. According to the t-test for H4800, the difference in the means was also determined to be statistically significant, thus qualifying this to be the adhesive used to perform the upcoming bath degradation testing. Also, because 435 and 332 proved to have statistically significantly different means, these adhesives were also chosen to be used in the upcoming comparative analysis of different aluminum surface treatments. Since many of the treated specimens had coefficients of variance above 15%, it was decided that a further test to discover whether or not an IPA wipe prior to bonding had any affect on the variance was appropriate.

2.3 Design of Experiments Using IPA Cleaning and Chromic Acid Etching Treatment

The variance in the results of the adhesive selection experiment was undesirable, therefore it was decided that further experimentation was warranted. It was important to investigate the reason for the variance, as one possible reason was some residue from the bath remained on the specimens **[See Figure 25]**. An additional cleaning method was proposed in which isopropyl alcohol (IPA) was applied to the treated area and wiped off prior to bonding. A Design of Experiments (DOE) analysis was created using Minitab to determine if the IPA cleaning process did have an effect on the variance as well as bond strength.


Figure 25: Residue that Remained on Specimen

2.3.1 Methodology

Minitab was used to perform a Design of Experiments investigation in which lap shears were etched with chromic acid and bonded with adhesive H4800, while others were bonded without treatment. Half of these were cleaned with isopropyl alcohol prior to bonding, while others were not. The test matrix, as shown in **Table 11**, indicates that only 5 replicates were performed at once and were let to cure for 72 hours.

Table 11: Design of Experiments Test Matrix					
Standard Order	**Run Order**	**Treatment**	**Cleaning**	**Cure**	**Replicates**
1	1	None	None	72 hr	5
4	2	Chromic Acid	IPA wipe	72 hr	5
5	3	None	None	72 hr	5
7	4	None	IPA wipe	72 hr	5
2	5	Chromic Acid	None	72 hr	5
6	6	Chromic Acid	None	72 hr	5
3	7	None	IPA wipe	72 hr	5
8	8	Chromic Acid	IPA wipe	72 hr	5

The lap shears were treated and cleaned in the exact order listed in the test matrix, and the same procedure for treating and bonding mentioned in section 2.2.1 was used in this experiment, except that half were sprayed with IPA then wiped off before the adhesive was applied.

2.3.2 Results & Discussion

The average bond strengths and the standard deviations of each of the 8 runs are shown in **Table 12**. It was apparent that cleaning the surface with isopropyl alcohol prior to bonding had little to no effect on the bond strength, while treating the aluminum with chromic acid had a significant effect on strengthening the bond of the adhesive.

Table 12: DOE Results for IPA Wipe Testing							
Standard Order	**Run Order**	**Treatment**	**Cleaning**	**Average**	**Std. Dev.**	**Res. 1**	**Res. 2**
1	1	none	none	1815	165	-3	0.5
4	2	treated	IPA wipe	2975	164	206	-206.5
5	3	none	none	1821	164	3	-0.5
7	4	none	IPA wipe	1956	42	80	-81
2	5	treated	none	2885	476	297.5	-200.5
6	6	treated	none	2290	877	-297.5	200.5
3	7	none	IPA wipe	1796	204	-80	81
8	8	treated	IPA wipe	2563	577	-206	206.5

Figure 26 is a graphical representation averaging the bond strengths of the 4 different types preparations used during this experiment.

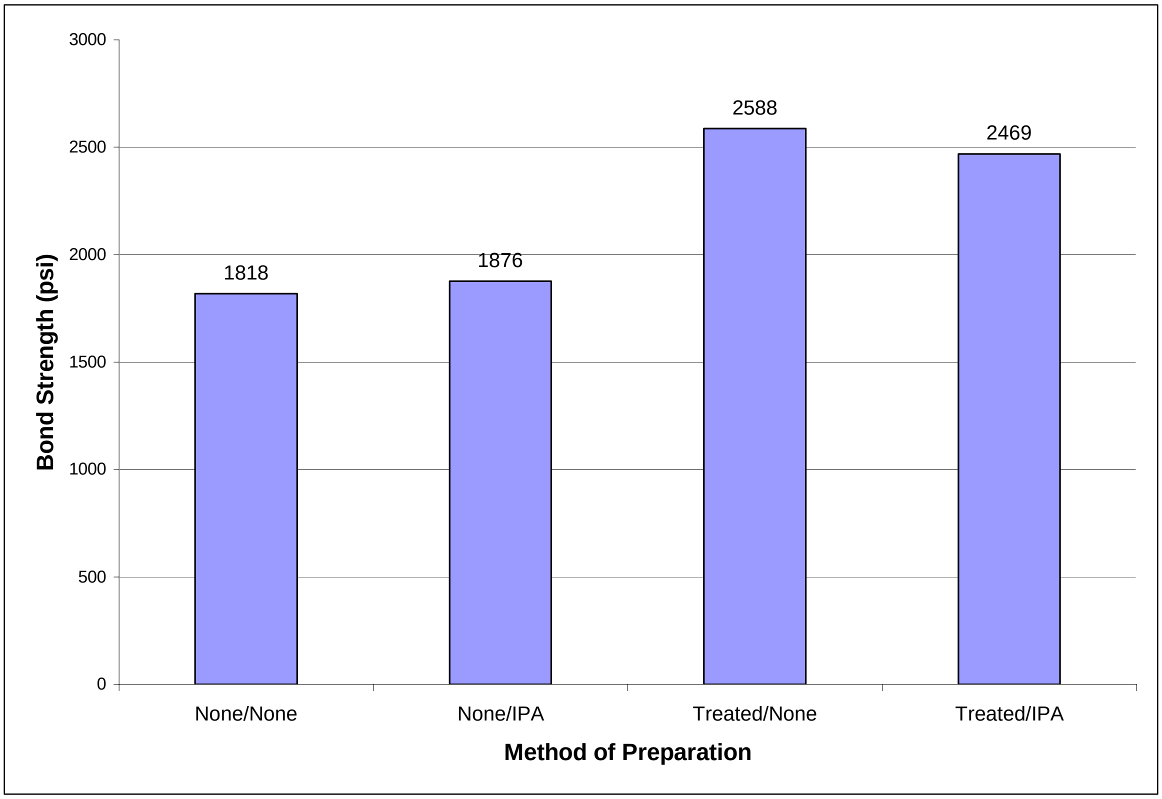


Figure 26: Averaged Bond Strength Results

The residuals indicate the difference between the averages of two similar runs. For example, the average of the means of runs 1 and 3 is 1818 and the residual 1 of each run is just the difference between the average of this particular run and the average of both runs. Residual 2 works the same way for the standard deviations of two similar runs.

Minitab performed a factorial fit for the average versus treatment and cleaning and for the standard deviation versus treatment and cleaning. The calculated P-value for average versus treatment was 0.011 and the P-value for standard deviation versus treatment was 0.064 **[see full Minitab results in Appendix D].** Because the P-value for average versus treatment was less than 0.05, it was proven that the means were statistically significantly different, indicating that treatment had an effect on average bond strength. The P-value for standard deviation versus treatment was slightly greater than 0.05, thus at a confidence interval of 95%, it could not be proven that the difference was statistically significant. However, at a confidence interval of 93.6%, it can be proven that the standard deviations are statistically significantly different from treated to untreated assemblies.

2.4 Post Treatment Cleaning Method Analysis

It was observed during previous analysis that the method used to clean the aluminum lap shears after they were taken out of the chromic acid bath often left behind a water stain that may have had an effect on bond strength, possibly contributing to large variances in bond strengths. The new proposed method involved wiping the lap shears clean with DI water and a Kimwipe (sterile tissues used in the Loctite® lab), as opposed to drying them in a convection oven at 80° C for 10 minutes. The surfaces of the etched aluminum appeared to be much cleaner after wiping them with Kimwipes, as shown in **Figure 27,** therefore an experiment was performed to determine if the new proposed cleaning method had a significant effect on the bond strength.

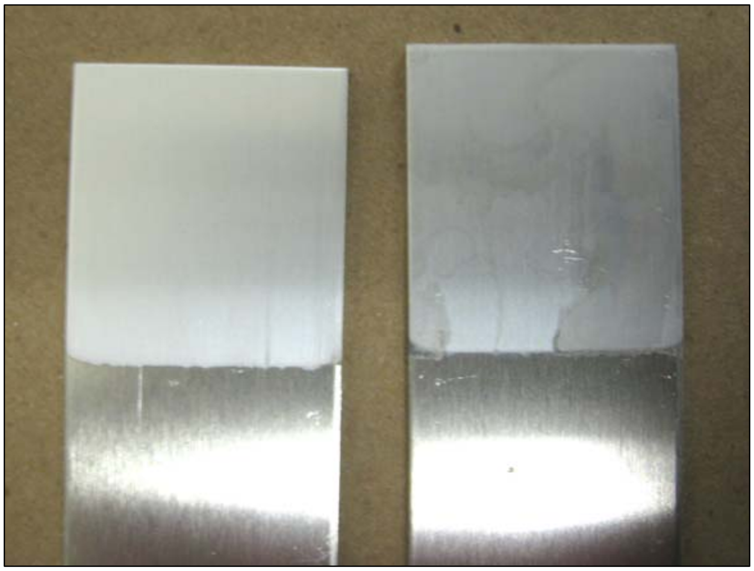


Figure 27: "New" Cleaning Method (right) vs. "Old" Cleaning Method (right)

2.4.1 Methodology

10 replicates were treated in the chromic acid bath in the same manner as discussed in section 2.2.1. After being sprayed with de-ionized water, they were placed in the oven at 80 degrees Celsius for 10 minutes. Once removed from the oven, the etched surfaces were cleaned with isopropyl alcohol prior to bonding. Again, the lap shears were bonded with adhesive H4800 in the same procedure as outlined in section 2.2.1 and let to cure for 48 hours.

An additional 10 replicates were treated in the chromic acid bath, but instead of being placed in the oven for 10 minutes, they were hand wiped with Kimwipes, ensuring no water or residue remained on the surface when complete. Like the “oven dried” specimens, they were then cleaned with isopropyl alcohol prior to bonding and let to cure for 48 hours.

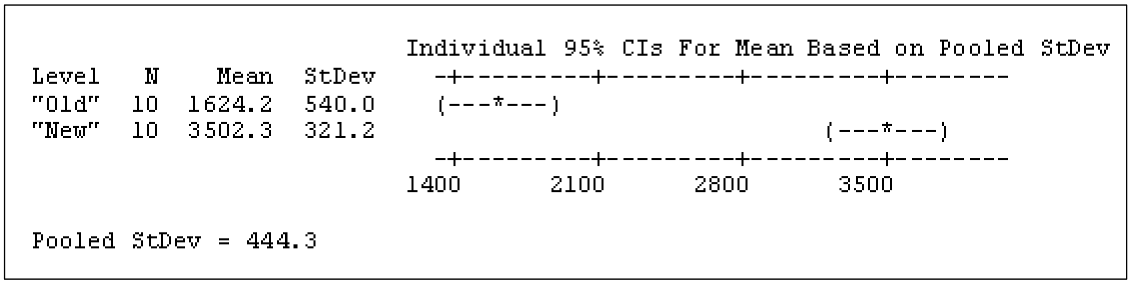
2.4.2 Results & Discussion

Once the bonded lap shears were allowed to cure for 48 hours, the bond strengths were determined using STM 700 on the Instron machine, as discussed in section 2.2.1. The bond strengths of the two different cleaning methods are shown in **Table 13**.

Table 13: Bond Strength Results

Replicate	Cleaning Method			
	"Old"		"New"	
	Strength [psi]	Failure Mode	Strength [psi]	Failure Mode
1.	1008	Adh/Coh	3137	Cohesive
2.	1519	Adh/Coh	3406	Cohesive
3.	1367	Adh/Coh	3219	Cohesive
4.	2282	Adh/Coh	3400	Cohesive
5.	1059	Adh/Coh	3498	Cohesive
6.	1267	Adh/Coh	3886	Cohesive
7.	1972	Adh/Coh	3445	Cohesive
8.	2518	Adh/Coh	3663	Cohesive
9.	2054	Adh/Coh	3209	Cohesive
10.	1196	Adh/Coh	4160	Cohesive
Average	**1624**		**3502**	
Stand. Dev.	540		321	
COV	0.332		0.092	
Minimum	1008		3137	

A one-way ANOVA analysis was performed using Minitab and is shown in **Figure 28** below:



```
                              Individual 95% CIs For Mean Based on Pooled StDev
Level    N    Mean   StDev    -+---------+---------+---------+--------
"Old"   10  1624.2   540.0    (---*---)
"New"   10  3502.3   321.2                               (---*---)
                              -+---------+---------+---------+--------
                            1400      2100      2800      3500

Pooled StDev = 444.3
```

Figure 28: ANOVA Analysis for Cleaning Methods

As shown in the data, the average bond strength of the assemblies cleaned using the “Old” method were considerably less than those cleaned using the “New” method. On average, the new cleaning method produced bond strengths more than double those achieved from the old cleaning method using the oven (1624 psi vs. 3502 psi).

According to the Minitab analysis, since the p-value was less than 0.05, at a 95% confidence interval, it was proven that the bond strengths were statistically significantly different. This can be interpreted visually on the above Minitab output in which the distributions of the two sets of data do not overlap. Therefore, it was concluded that the new cleaning method using Kimwipes instead of an oven after acid treatment should be used in the overall chromic acid etching process at Henkel Corporation.

2.5 Bath Degradation Testing

After a certain number of lap shears are treated in the chromic acid, the bath will eventually begin to degrade, as indicated by the chemical equation shown in section 2.2.1, when aluminum reacts with chromic acid (sulfuric acid and sodium dichromate). The bond strengths of the treated assemblies will be a direct reflection of this bath degradation, as the oxide layer on the surface of aluminum will become thinner. Henkel should never receive a single order requiring more than 500 aluminum lap shears to be treated at once, so it was essential to determine if treating 500 specimens would degrade the bath. To be safe, it was decided that 1000 lap shears were to be treated before analyzing the chromic acid bath. However, treating 1000 lap shears would be rather tedious, and instead a calculated amount of aluminum powder was added to the acid bath to simulate 1000 lap shears. Specimens were treated before and after the addition of the aluminum powder, bonded, and tested for their bond strengths. The shear strengths of assemblies before and after the 1000 lap shear simulation were then compared and determined if the differences were statistically significant. Two specimens (1 before addition of Al powder, 1 after addition of Al powder) were submitted for energy dispersive X-ray spectroscopy (EDS) analysis to determine the chromium content on the etched surface of the aluminum. Two liquid samples (1 before addition of Al powder, 1 of after addition of Al powder) of the acid bath were submitted for ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) to determine the chromium content in solution. If the bond strengths between the two runs were proven to be statistically significantly different, it would be confirmed that the bath did degrade before 1000 lap shears were treated and a critical ratio of chromium to aluminum content could later be determined.

2.5.1 Methodology

A fresh bath of chromic acid was prepared and 10 lap shear replicates were treated using the same procedure used throughout the project and cleaned using Kimwipes as discussed in the previous experiment. They were then bonded with adhesive H4800 and let to cure for 48 hours.

0.16 grams of aluminum powder was added to the acid bath to simulate 1000 aluminum lap shears **[calculations shown in Appendix E],** and 10 more replicates were treated, cleaned, and bonded in the same procedure as those before the powder was added. For both runs, a designated test specimen was submitted for energy dispersive X-ray spectroscopy (EDS) analysis to determine the chromium content on the etched surface of the aluminum, according to ASTM E1508-93a **[see Appendix F for ASTM E1508-93a].** The EDS analysis was conducted using a Kevex detector attached to Hitachi S-570 SEM. An accelerating voltage of 20 KeV and a sampling scan duration of 200 seconds was used for data collection.

Also an approximate 3 mL sample of the chromic acid bath was taken before and after the addition of aluminum powder and submitted for ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) to determine the chromium content in solution. These liquid samples were tested and analyzed according to STM-40 **[See Appendix G for STM-40]** using a Varian Vista. 0.2 grams of the sample was diluted to 25 mL with de-ionized water and a 10 fold dilution was then prepared and analyzed.

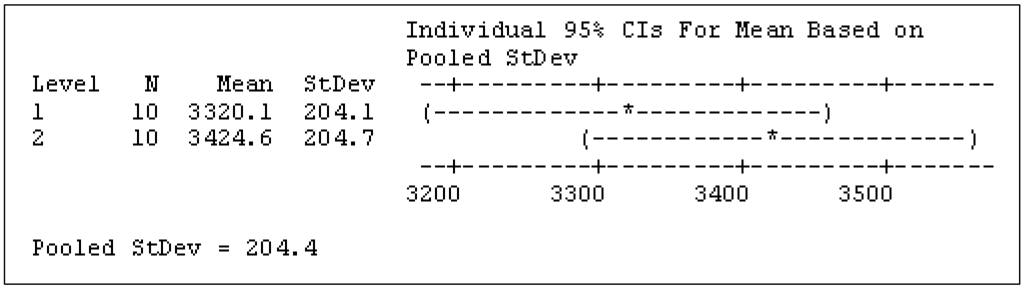
2.5.2 Results & Discussion

The bonded assemblies were pulled using the Instron machine according to STM-700 and the maximum bond strengths of the two runs are shown in **Table 14**.

Table 14: Bath Degradation Results

Replicate	Bath Condition			
	Before Addition of Al Powder		After Addition of Al Powder	
	Strength [psi]	Failure Mode	Strength [psi]	Failure Mode
1.	3538	Cohesive	3173	Cohesive
2.	3383	Cohesive	3405	Cohesive
3.	3425	Cohesive	3586	Cohesive
4.	3586	Cohesive	3709	Cohesive
5.	3345	Cohesive	3676	Cohesive
6.	3285	Cohesive	3262	Cohesive
7.	3132	Cohesive	3089	Cohesive
8.	2944	Cohesive	3493	Cohesive
9.	3108	Cohesive	3392	Cohesive
10.	3455	Cohesive	3467	Cohesive
Average	3320		3425	
Stand. Dev.	204		206	
COV	0.061		0.060	
Minimum	2944		3089	

A one-way ANOVA analysis was performed using Minitab and is shown in **Figure 29** below:



```
                              Individual 95% CIs For Mean Based on
                              Pooled StDev
Level   N    Mean  StDev   --+---------+---------+---------+-------
1      10  3320.1  204.1   (-------------*-------------)
2      10  3424.6  204.7             (------------*-------------)
                           --+---------+---------+---------+-------
                            3200      3300      3400      3500

Pooled StDev = 204.4
```

Figure 29: ANOVA Analysis for Bath Degradation Testing

According to the Minitab analysis, no statistical significant difference in bond strength from the fresh to degraded chromic acid bath can be determined. Since the P-value was greater than 0.05, with a 95% confidence interval, it could not be proven that the difference in the means between the fresh and degraded samples was statistically significant.

The EDS spectrum of the etched area of the aluminum lap shear sample before the addition of aluminum powder is shown in **Figure 30**, and the spectrum after the addition of aluminum powder is shown in **Figure 31.**

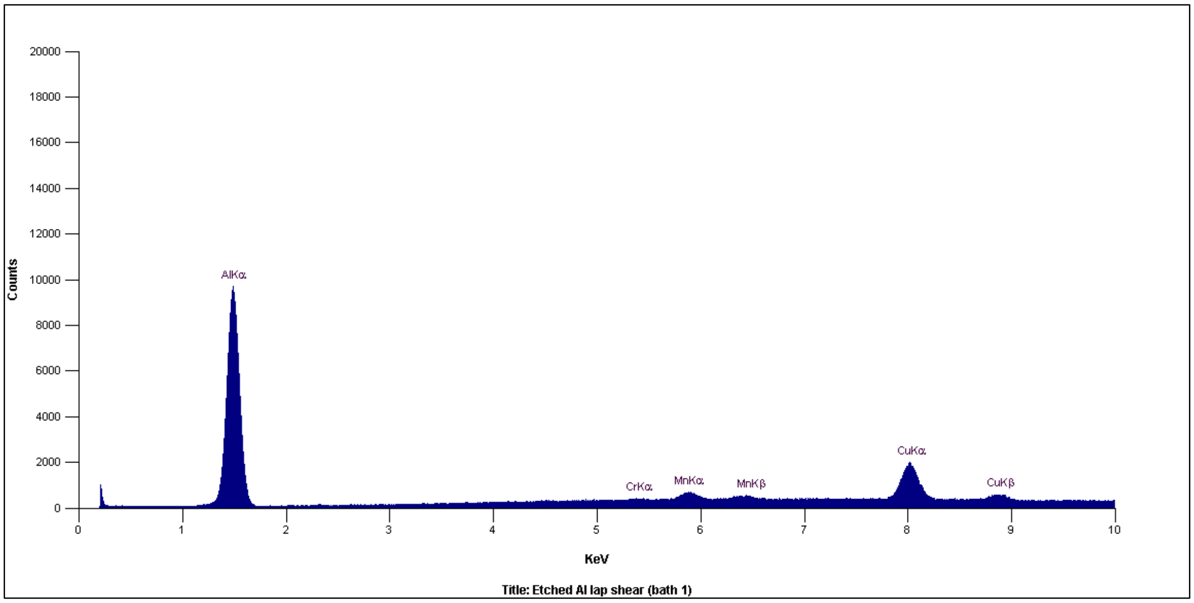


Figure 30: EDS Spectrum of Aluminum on Etched Surface, Fresh Bath

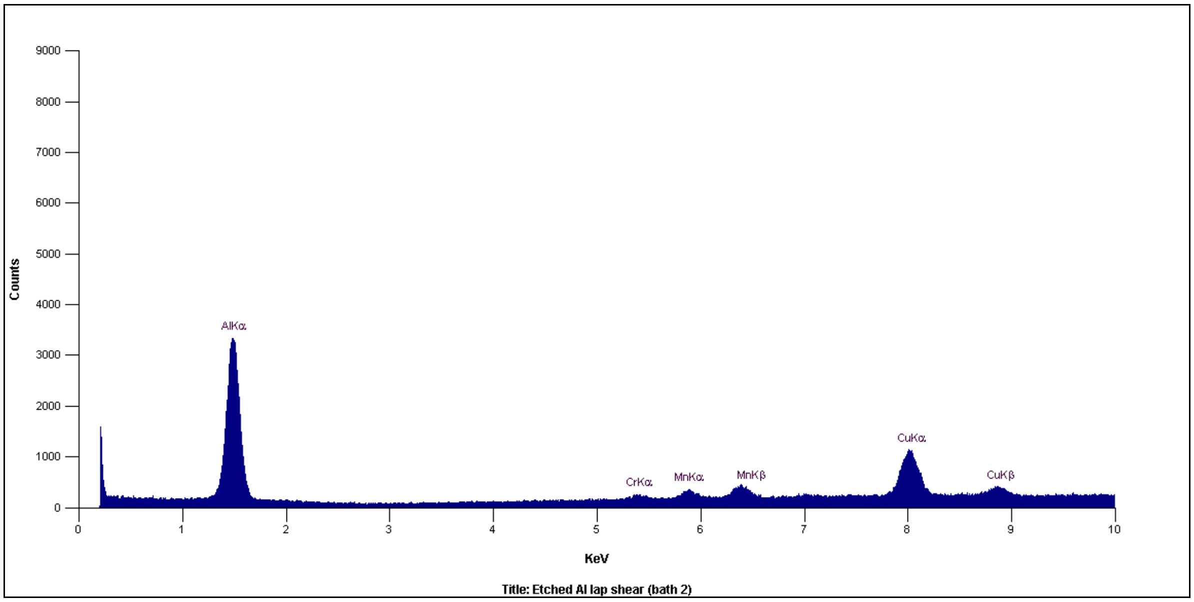


Figure 31: EDS Spectrum of Aluminum on Etched Surface, Degraded Bath

According to these EDS spectrums, the etched area of the aluminum lap shear treated before aluminum powder was added contained 63.9 weight % aluminum, 0.52 weight % chromium, 3.49 weight % manganese, and 32.05 weight % copper. The lap shear treated after the addition of aluminum powder contained 56.10 weight % aluminum, 1.59 weight % chromium, 3.89 weight % manganese, and 38.43 weight % copper.

The ICP-AES revealed that the chromium content of the acid bath before the addition of aluminum powder was 1.45 % and the chromium content after the addition of aluminum powder was 1.24 %.

It was concluded that after the addition of 0.16 grams of aluminum powder to the chromic acid bath (simulating 1000 lap shears), no significant difference in bond strength was apparent, warranting no further investigative analysis of the physical data obtained on the etched surfaces and acid bath samples.

2.6 Comparative Analysis Study on Chemical Surface Treatments for Aluminum

A comparative analysis study was performed on multiple chemical surface preparation techniques for aluminum prior to adhesion bonding. Five of the most commonly used surface treatment techniques in industry were chosen to be used on aluminum lap shears: sulfuric acid anodizing, sulfuric "hard" anodizing, chromic acid etching, chromic acid anodizing and phosphoric acid anodizing **[See Figure 1]**. The experiment used three different adhesives (H4800, 435, and 332), which were chosen from the adhesive selection process because they produced higher mean bond strengths after surface treatment. Treated assemblies along with the control (untreated aluminum) underwent heat aging and humidity testing for a period of two weeks. After environmental conditioning was complete, the data was analyzed to determine the best chemical surface treatment for maximizing bond strength and minimizing variance. Once the ideal treatment was identified, other variables such as cost, safety, and time efficiency were taken into consideration for the final determination of the best chemical surface treatment to be used at Henkel in the future.

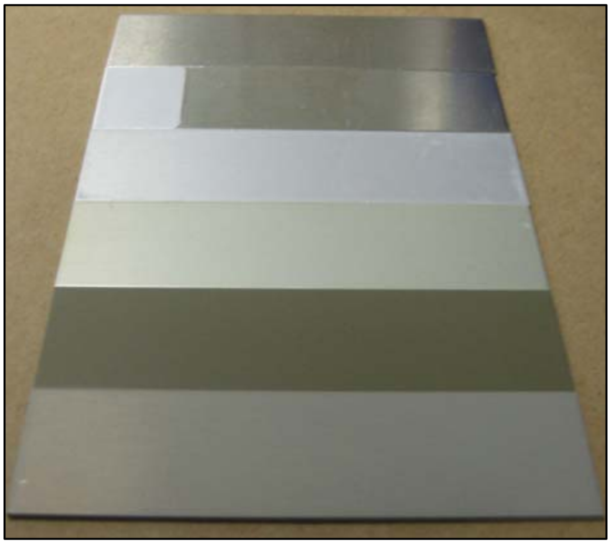


Figure 32: (Near to Far) Chromic Acid Anodized, Sulfuric "Hard" Anodized, Phosphoric Acid Anodized, Sulfuric Acid Anodized, Chromic Acid Etched, No Treatment

2.6.1 Methodology

Aluminum lap shears were treated and bonded as shown in the test matrix in **Table 15**.

Table 15: Comparative Analysis Experimental Test Matrix

Run	Adhesive	Treatment	Conditioning	Replicates
1	H4800	Chromic Acid Etch	None	10
2	H4800	Chromic Acid Etch	Salt Fog	10
3	H4800	Chromic Acid Etch	Condensing Humidity	10
4	H4800	Chromic Acid Etch	125° C	10
5	H4800	Chromic Acid Etch	175° C	10
6	435	Chromic Acid Etch	None	10
7	435	Chromic Acid Etch	Salt Fog	10
8	435	Chromic Acid Etch	Condensing Humidity	10
9	435	Chromic Acid Etch	100° C	10
10	435	Chromic Acid Etch	125° C	10
11	332/7387	Chromic Acid Etch	None	10
12	332/7387	Chromic Acid Etch	Salt Fog	10
13	332/7387	Chromic Acid Etch	Condensing Humidity	10
14	332/7387	Chromic Acid Etch	125° C	10
15	332/7387	Chromic Acid Etch	175° C	10
16	H4800	Chromic Acid Anodized	None	10
17	H4800	Chromic Acid Anodized	Salt Fog	10
18	H4800	Chromic Acid Anodized	Condensing Humidity	10
19	H4800	Chromic Acid Anodized	125° C	10
20	H4800	Chromic Acid Anodized	175° C	10
21	435	Chromic Acid Anodized	None	10
22	435	Chromic Acid Anodized	Salt Fog	10
23	435	Chromic Acid Anodized	Condensing Humidity	10
24	435	Chromic Acid Anodized	100° C	10
25	435	Chromic Acid Anodized	125° C	10
26	332/7387	Chromic Acid Anodized	None	10
27	332/7387	Chromic Acid Anodized	Salt Fog	10
28	332/7387	Chromic Acid Anodized	Condensing Humidity	10
29	332/7387	Chromic Acid Anodized	125° C	10
30	332/7387	Chromic Acid Anodized	175° C	10
31	H4800	Sulfuric Acid Anodized	None	10
32	H4800	Sulfuric Acid Anodized	Salt Fog	10

Table 16: Comparative Analysis Experimental Test Matrix				
Run	**Adhesive**	**Treatment**	**Conditioning**	**Replicates**
33	H4800	Sulfuric Acid Anodized	Condensing Humidity	10
34	H4800	Sulfuric Acid Anodized	125° C	10
35	H4800	Sulfuric Acid Anodized	175° C	10
36	435	Sulfuric Acid Anodized	None	10
37	435	Sulfuric Acid Anodized	Salt Fog	10
38	435	Sulfuric Acid Anodized	Condensing Humidity	10
39	435	Sulfuric Acid Anodized	100° C	10
40	435	Sulfuric Acid Anodized	125° C	10
41	332	Sulfuric Acid Anodized	None	10
42	332	Sulfuric Acid Anodized	Salt Fog	10
43	332	Sulfuric Acid Anodized	Condensing Humidity	10
44	332	Sulfuric Acid Anodized	125° C	10
45	332/7387	Sulfuric Acid Anodized	175° C	10
46	H4800	Sulfuric ‘Hard’ Anodized	None	10
47	H4800	Sulfuric ‘Hard’ Anodized	Salt Fog	10
48	H4800	Sulfuric ‘Hard’ Anodized	Condensing Humidity	10
49	H4800	Sulfuric ‘Hard’ Anodized	125° C	10
50	H4800	Sulfuric ‘Hard’ Anodized	175° C	10
51	435	Sulfuric ‘Hard’ Anodized	None	10
52	435	Sulfuric ‘Hard’ Anodized	Salt Fog	10
53	435	Sulfuric ‘Hard’ Anodized	Condensing Humidity	10
54	435	Sulfuric ‘Hard’ Anodized	100° C	10
55	435	Sulfuric ‘Hard’ Anodized	125° C	10
56	332/7387	Sulfuric ‘Hard’ Anodized	None	10
57	332/7387	Sulfuric ‘Hard’ Anodized	Salt Fog	10
58	332/7387	Sulfuric ‘Hard’ Anodized	Condensing Humidity	10
59	332/7387	Sulfuric ‘Hard’ Anodized	125° C	10
60	332/7387	Sulfuric ‘Hard’ Anodized	175° C	10
61	H4800	Phosphoric Acid Anodized	None	10
62	H4800	Phosphoric Acid Anodized	Salt Fog	10
63	H4800	Phosphoric Acid Anodized	Condensing Humidity	10
64	H4800	Phosphoric Acid Anodized	125° C	10
65	H4800	Phosphoric Acid Anodized	175° C	10
66	435	Phosphoric Acid Anodized	None	10
67	435	Phosphoric Acid Anodized	Salt Fog	10
68	435	Phosphoric Acid Anodized	Condensing Humidity	10

Table 17: Comparative Analysis Experimental Test Matrix				
Run	**Adhesive**	**Treatment**	**Conditioning**	**Replicates**
69	435	Phosphoric Acid Anodized	100° C	10
70	435	Phosphoric Acid Anodized	125° C	10
71	332/7387	Phosphoric Acid Anodized	None	10
72	332/7387	Phosphoric Acid Anodized	Salt Fog	10
73	332/7387	Phosphoric Acid Anodized	Condensing Humidity	10
74	332/7387	Phosphoric Acid Anodized	125° C	10
75	332/7387	Phosphoric Acid Anodized	175° C	10
76	H4800	None	None	10
77	H4800	None	Salt Fog	10
78	H4800	None	Condensing Humidity	10
79	H4800	None	125° C	10
80	H4800	None	175° C	10
81	435	None	None	10
82	435	None	Salt Fog	10
83	435	None	Condensing Humidity	10
84	435	None	100° C	10
85	435	None	125° C	10
86	332/7387	None	None	10
87	332/7387	None	Salt Fog	10
88	332/7387	None	Condensing Humidity	10
89	332/7387	None	125° C	10
90	332/7387	None	175° C	10

Note:

- The condensing humidity chamber operated at 50°C.
- See **Appendix H** for operating conditions of the salt fog chamber.

All 5 types of surface treated aluminum lap shears and the non-treated laps were bonded in the same manner as described in section 2.2.1. The chromic acid etched specimens were treated on site in the same procedure outlined in section 2.2.1 and the sulfuric acid anodized samples were taken from inventory at Henkel-Loctite. Aluminum lap shears were sent out to various companies to be phosphoric acid anodized, sulfuric "hard" anodized, and chromic acid anodized. The addresses for these companies are as follows:

Chromic Acid Anodized:

Plainville Plating Company
21 Forestville Ave
Plainville, CT 06062

See Appendix I for specifications on treatment methods used.

Sulfuric "Hard" Anodized:

Plainville Plating Company
21 Forestville Ave
Plainville, CT 06062

See Appendix J for specifications on treatment methods used.

Phosphoric Acid Anodized:

Aerospace Defense Coatings of Georgia
7700 N. Industrial Blvd
Macon, GA 31206

See Appendix K for specifications on treatment methods used.

2.6.2 Results & Discussion

In this section the results are presented in a specific structure. First, they are presented with respect to conditioning, more specifically, how all the bonded assemblies compared when they were exposed to specific environmental conditioning. Next, they are presented with respect to surface treatment, where it shows how a specific surface treatment reacted after being exposed to various environmental conditions.

See Appendix L for full tabulation of results

2.6.2.1 Results by Conditioning

2.6.2.1.1 Unconditioned Assemblies

Table 18 presents a summary of the results obtained for the unconditioned assemblies.

Table 18: No Conditioning – Pulled After at Least 72 Hours

Adhesive		Aluminum Surface Treatment					
		None	**Chromic Acid Etch**	**Chromic Acid Anodize**	**Sulfuric Anodize**	**Sulfuric “Hard” Anodize**	**Phosphoric Acid Anodize**
H4800	**Average Strength (psi)**	**2217**	**2845**	**2563**	**2709**	**2614**	**2910**
	Stand. Dev.	921	570	116	349	362	202
	COV	0.415	0.201	0.045	0.129	0.139	0.069
	Minimum	682	2164	2412	2223	1767	2546
435	**Average Strength (psi)**	**2104**	**2522**	**2264**	**1687**	**2394**	**3609**
	Stand. Dev.	243	241	142	203	137	178
	COV	0.116	0.096	0.063	0.120	0.057	0.049
	Minimum	1870	2196	1969	1195	2215	3256
332	**Average Strength (psi)**	**1871**	**2998**	**2129**	**2511**	**834**	**2174**
	Stand. Dev.	100	184	96	223	406	142
	COV	0.053	0.061	0.045	0.089	0.487	0.065
	Minimum	1695	2580	1982	1971	285	1959

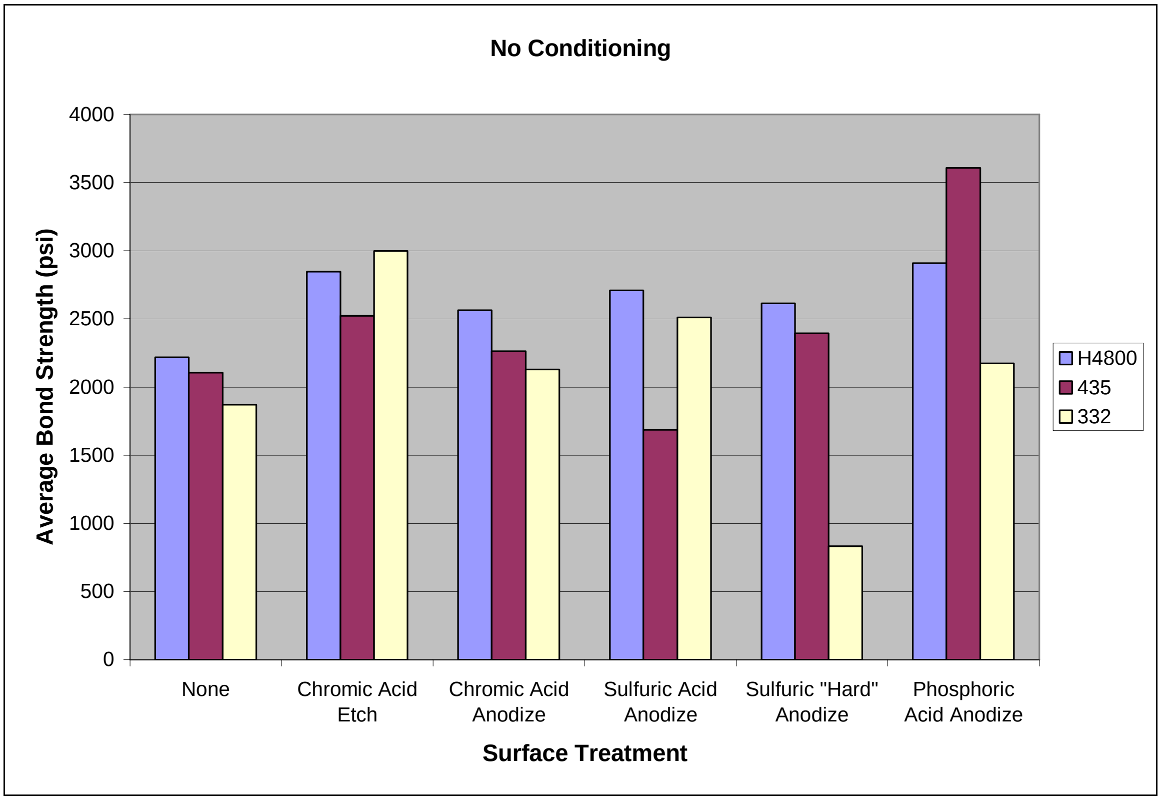


Figure 33: Bond Strength vs. Surface Treatment (No Conditioning)

As shown in **Figure 33**, bond strength varied greatly by not only treatment method, but also by adhesive type. To organize this data, each adhesive type was analyzed separately using Minitab.

2.6.2.1.1.1 Loctite® H4800™

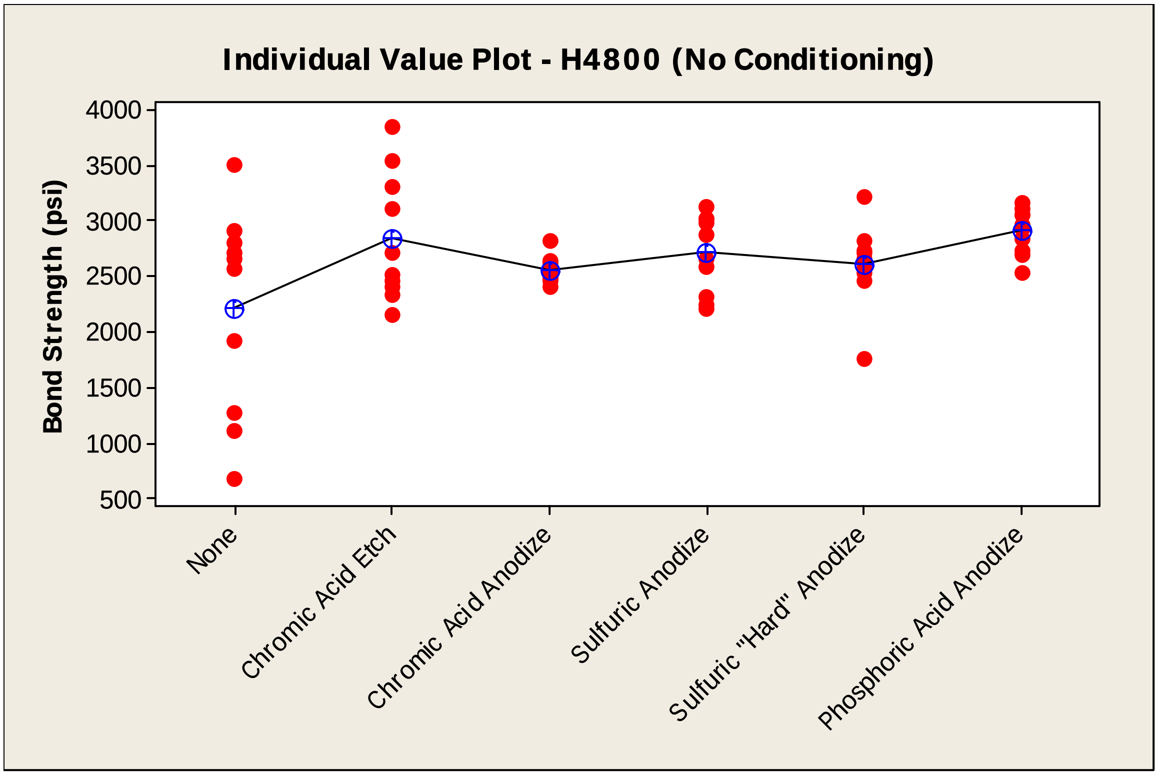
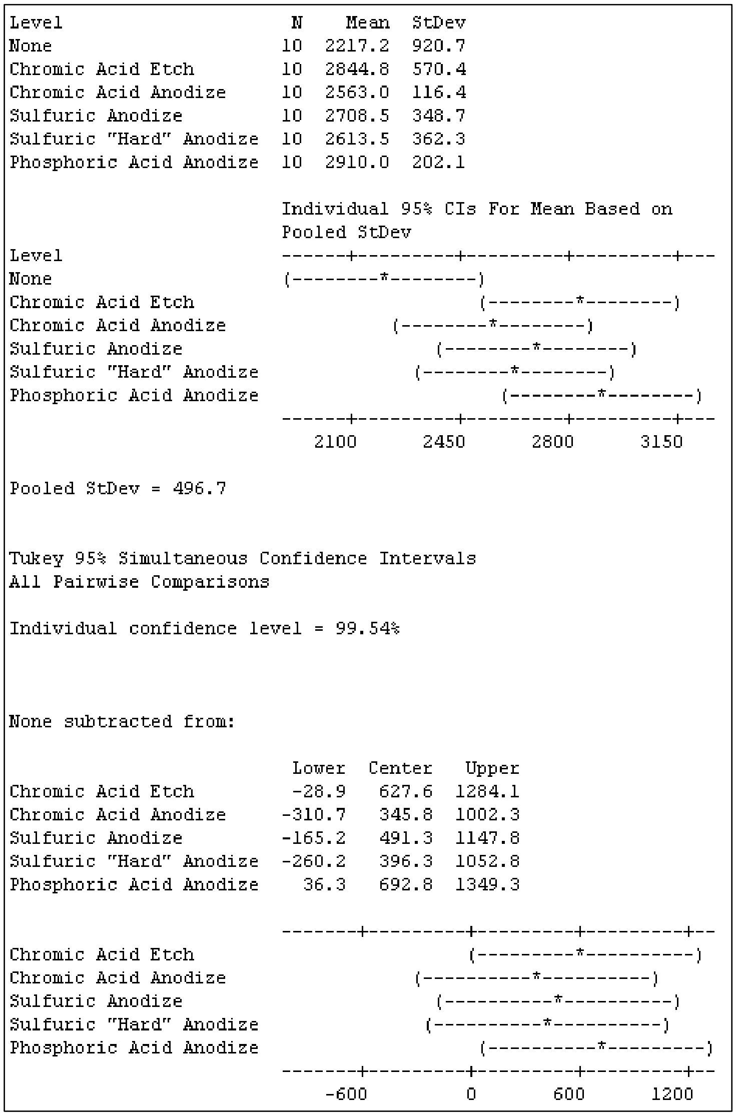


Figure 34: Individual Value Plot - H4800 (No Conditioning)

The above individual value **[See Figure 34]** plot may also be referred to as a scatter plot. Essentially, it plots every single bond strength result obtained for each particular surface treatment. It gives the viewer an idea to the amount of scatter associated with each run.

Shown in **Figure 35** is a method of statistical analysis known as Tukey’s. The lower and upper values of the Tukey analysis represent the difference in the range of bond strengths of the treated assemblies from the bond strengths of the control assemblies. If a given treatment had all positive values from lower to upper, it proved that the bond strengths were statistically significantly stronger than the non-treated samples at a 95 % confidence interval. On the other hand, if a given treatment had all negative values from lower to upper, it would prove that the bond strengths were statistically significantly weaker than then non-treated samples at a 95% confidence interval. Lastly, if a given treatment contained the value zero from lower to upper, it could not be proven that the bond strengths were statistically significantly different at a 95% confidence interval.



```
Level                     N    Mean  StDev
None                     10  2217.2  920.7
Chromic Acid Etch        10  2844.8  570.4
Chromic Acid Anodize     10  2563.0  116.4
Sulfuric Anodize         10  2708.5  348.7
Sulfuric "Hard" Anodize  10  2613.5  362.3
Phosphoric Acid Anodize  10  2910.0  202.1

                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level                    ------+---------+---------+---------+---
None                     (--------*--------)
Chromic Acid Etch                          (--------*--------)
Chromic Acid Anodize               (--------*--------)
Sulfuric Anodize                       (--------*--------)
Sulfuric "Hard" Anodize              (--------*--------)
Phosphoric Acid Anodize                      (--------*--------)
                         ------+---------+---------+---------+---
                            2100      2450      2800      3150

Pooled StDev = 496.7


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%



None subtracted from:

                          Lower  Center   Upper
Chromic Acid Etch         -28.9   627.6  1284.1
Chromic Acid Anodize     -310.7   345.8  1002.3
Sulfuric Anodize         -165.2   491.3  1147.8
Sulfuric "Hard" Anodize  -260.2   396.3  1052.8
Phosphoric Acid Anodize    36.3   692.8  1349.3

                         -------+---------+---------+---------+--
Chromic Acid Etch                         (---------*----------)
Chromic Acid Anodize                 (----------*----------)
Sulfuric Anodize                       (----------*----------)
Sulfuric "Hard" Anodize               (----------*----------)
Phosphoric Acid Anodize                    (----------*---------)
                         -------+---------+---------+---------+--
                             -600         0       600      1200
```

Figure 35: Tukey's Analysis - H4800 (No Conditioning)

Ranked Average Bond Strengths (psi) – H4800 (No Conditioning):

1. Phosphoric Acid Anodize (2910)*
2. Chromic Acid Etch (2845)
3. Sulfuric Anodize (2709)
4. Sulfuric “Hard” Anodize (2614)
5. Chromic Acid Anodize (2563)
6. None (2217)

According to the Tukey analysis **[See Figure 35]**, only one of the previous surface treatments had a greater average bond strength that proved to be statistically significantly different from the control (None) at a 95% confidence interval. The lower and upper values of the Tukey analysis represent the difference in the range of bond strengths of the treated assemblies from the bond strengths of the control assemblies. Since phosphoric acid anodizing had all positive values from lower to upper, it proved that the bond strengths were statistically significantly better than the non-treated samples at a 95 % confidence interval.

2.6.2.1.1.2 Loctite® 435™

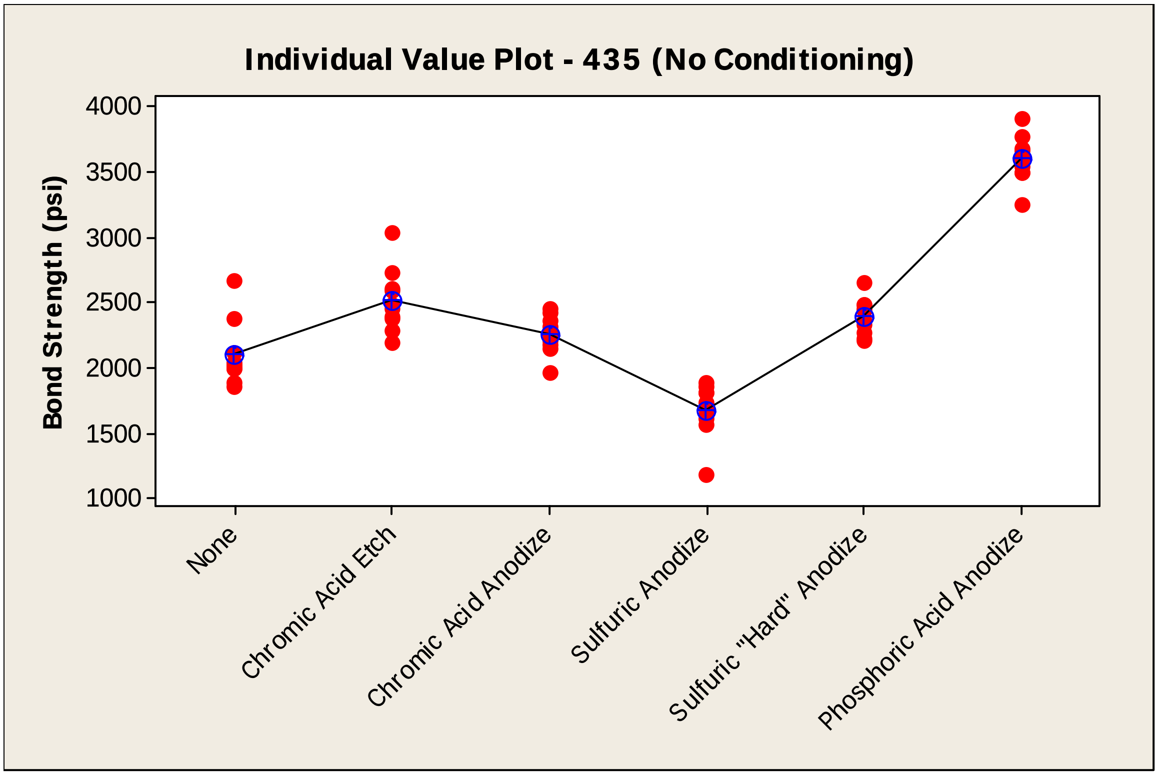


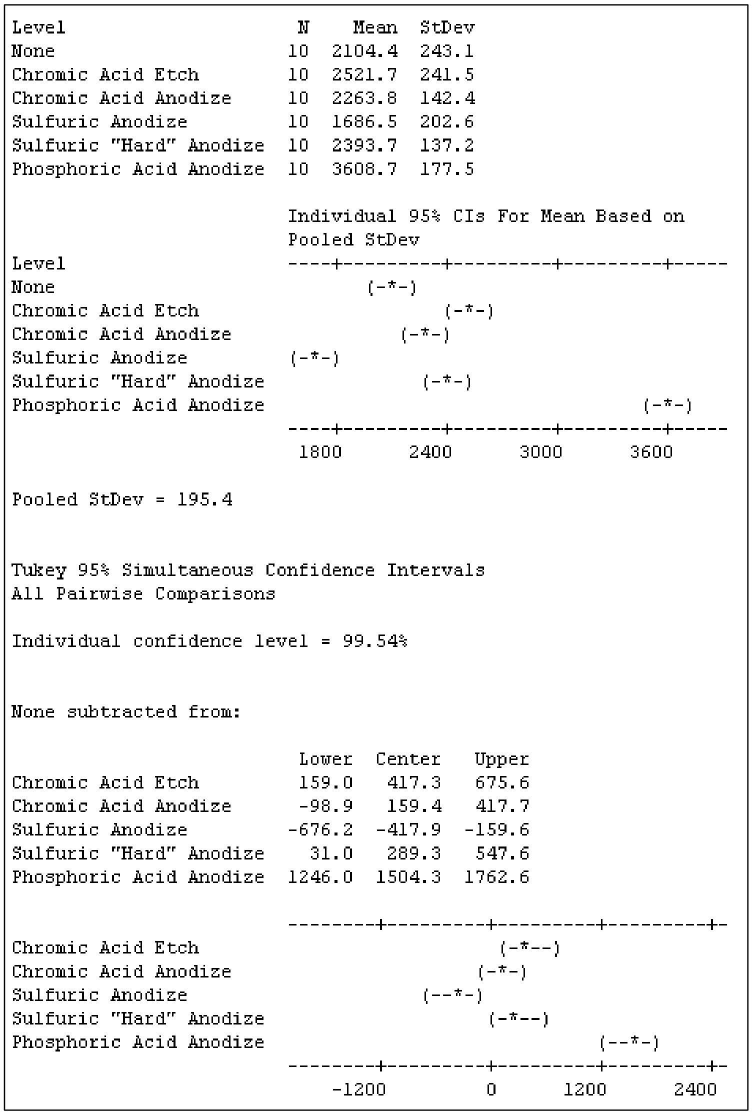
Figure 36: Individual Value Plot - 435 (No Conditioning)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – 435 (No Conditioning):

1. Phosphoric Acid Anodize (3609)*
2. Chromic Acid Etch (2522)*
3. Sulfuric “Hard” Anodize (2394)*
4. Chromic Acid Anodize (2264)
5. None (2104)
6. Sulfuric Anodize (1687)

According to the Tukey analysis **[See Figure 37]**, phosphoric acid anodize, chromic acid etch & sulfuric “hard” anodize all had greater average bond strengths that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                     N    Mean  StDev
None                     10  2104.4  243.1
Chromic Acid Etch        10  2521.7  241.5
Chromic Acid Anodize     10  2263.8  142.4
Sulfuric Anodize         10  1686.5  202.6
Sulfuric "Hard" Anodize  10  2393.7  137.2
Phosphoric Acid Anodize  10  3608.7  177.5

                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level                    ----+---------+---------+---------+-----
None                            (-*-)
Chromic Acid Etch                      (-*-)
Chromic Acid Anodize                (-*-)
Sulfuric Anodize         (-*-)
Sulfuric "Hard" Anodize              (-*-)
Phosphoric Acid Anodize                                (-*-)
                         ----+---------+---------+---------+-----
                          1800      2400      3000      3600

Pooled StDev = 195.4


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                          Lower  Center   Upper
Chromic Acid Etch         159.0   417.3   675.6
Chromic Acid Anodize      -98.9   159.4   417.7
Sulfuric Anodize         -676.2  -417.9  -159.6
Sulfuric "Hard" Anodize    31.0   289.3   547.6
Phosphoric Acid Anodize  1246.0  1504.3  1762.6

                         --------+---------+---------+---------+-
Chromic Acid Etch                          (-*--)
Chromic Acid Anodize                     (-*-)
Sulfuric Anodize                     (--*-)
Sulfuric "Hard" Anodize                   (-*--)
Phosphoric Acid Anodize                             (--*-)
                         --------+---------+---------+---------+-
                             -1200         0      1200      2400
```

Figure 37: Tukey's Analysis - 435 (No Conditioning)

2.6.2.1.1.3 Loctite® 332™

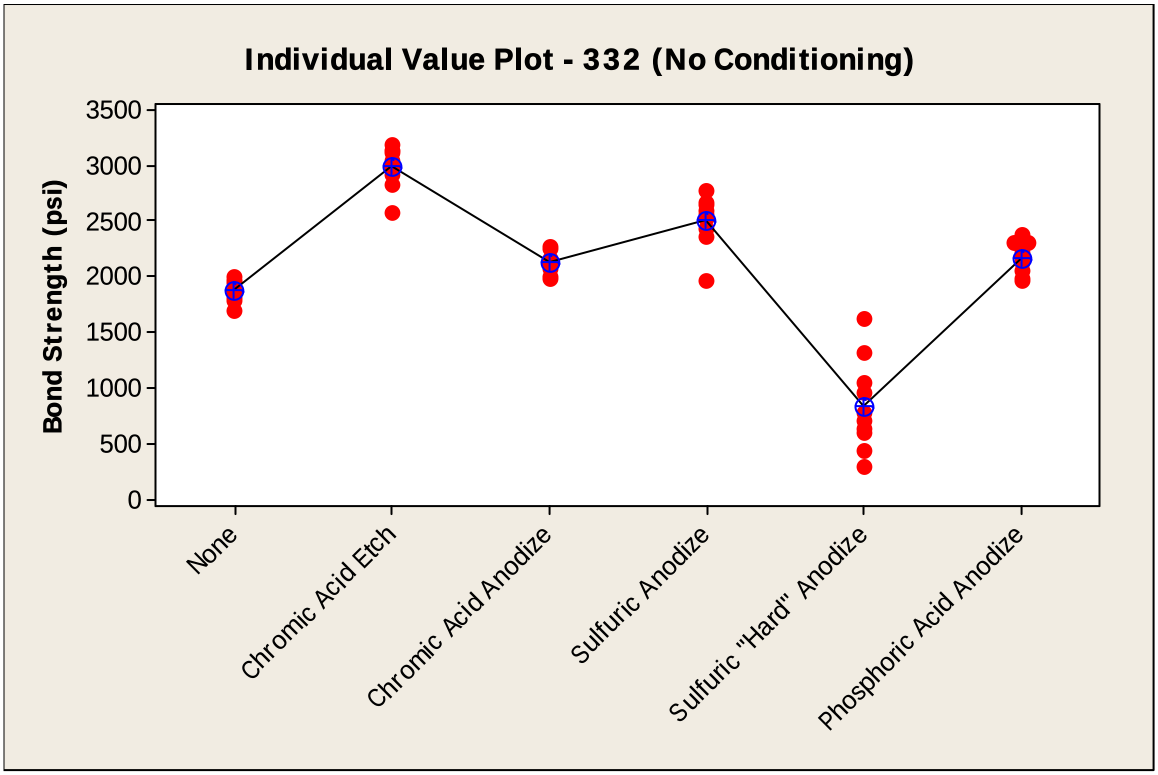


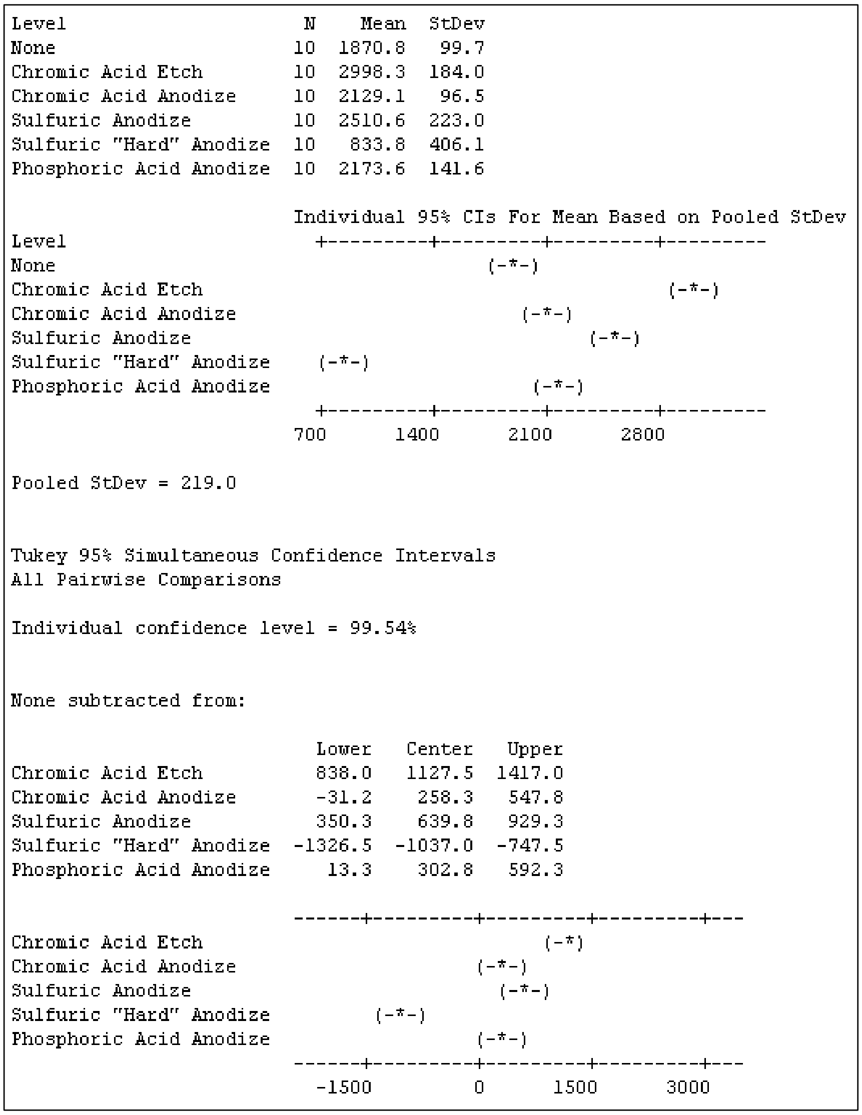
Figure 38: Individual Value Plot - 332 (No Conditioning)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – 332 (No Conditioning):

1. Chromic Acid Etch (2998)*
2. Sulfuric Anodize (2511)*
3. Phosphoric Acid Anodize (2174)*
4. Chromic Acid Anodize (2129)
5. None (1871)
6. Sulfuric Hard Anodize (834)

According to the Tukey analysis **[See Figure 39]**, chromic acid etch, sulfuric anodize & phosphoric acid anodize all had greater average bond strengths that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                      N    Mean  StDev
None                      10  1870.8   99.7
Chromic Acid Etch         10  2998.3  184.0
Chromic Acid Anodize      10  2129.1   96.5
Sulfuric Anodize          10  2510.6  223.0
Sulfuric "Hard" Anodize   10   833.8  406.1
Phosphoric Acid Anodize   10  2173.6  141.6

                         Individual 95% CIs For Mean Based on Pooled StDev
Level                      +---------+---------+---------+---------
None                                      (-*-)
Chromic Acid Etch                                         (-*-)
Chromic Acid Anodize                         (-*-)
Sulfuric Anodize                                   (-*-)
Sulfuric "Hard" Anodize    (-*-)
Phosphoric Acid Anodize                       (-*-)
                           +---------+---------+---------+---------
                         700      1400      2100      2800

Pooled StDev = 219.0


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                           Lower   Center   Upper
Chromic Acid Etch          838.0   1127.5  1417.0
Chromic Acid Anodize       -31.2    258.3   547.8
Sulfuric Anodize           350.3    639.8   929.3
Sulfuric "Hard" Anodize  -1326.5  -1037.0  -747.5
Phosphoric Acid Anodize     13.3    302.8   592.3


                         ------+---------+---------+---------+---
Chromic Acid Etch                              (-*)
Chromic Acid Anodize                     (-*-)
Sulfuric Anodize                           (-*-)
Sulfuric "Hard" Anodize         (-*-)
Phosphoric Acid Anodize                  (-*-)
                         ------+---------+---------+---------+---
                           -1500         0      1500      3000
```

Figure 39: Tukey's Analysis - 332 (No Conditioning)

2.6.2.1.2 Salt Fog Conditioned Assemblies

Table 19 presents a summary of the results obtained for the salt fog assemblies.

Table 19: Salt Fog Conditioning Results							
Adhesive		**Aluminum Surface Treatment**					
		None	**Chromic Acid Etch**	**Chromic Acid Anodize**	**Sulfuric Anodize**	**Sulfuric “Hard” Anodize**	**Phosphoric Acid Anodize**
H4800	**Average Strength (psi)**	**2058**	**1334**	**2351**	**2562**	**1900**	**3005**
	Stand. Dev.	406	790	306	244	176	494
	COV	0.197	0.592	0.130	0.095	0.093	0.164
	Minimum	2058	1334	2351	2562	1900	3005
435	**Average Strength (psi)**	**0**	**64**	**2296**	**1278**	**2203**	**3468**
	Stand. Dev.	0	202	356	130	147	441
	COV	--	3.162	0.155	0.102	0.067	0.127
	Minimum	0	64	2296	1278	2203	3468
332	**Average Strength (psi)**	**1247**	**1540**	**1921**	**2436**	**549**	**2094**
	Stand. Dev.	222	671	166	167	279	76
	COV	0.178	0.436	0.086	0.068	0.508	0.036
	Minimum	936	0	1561	2079	130	1974

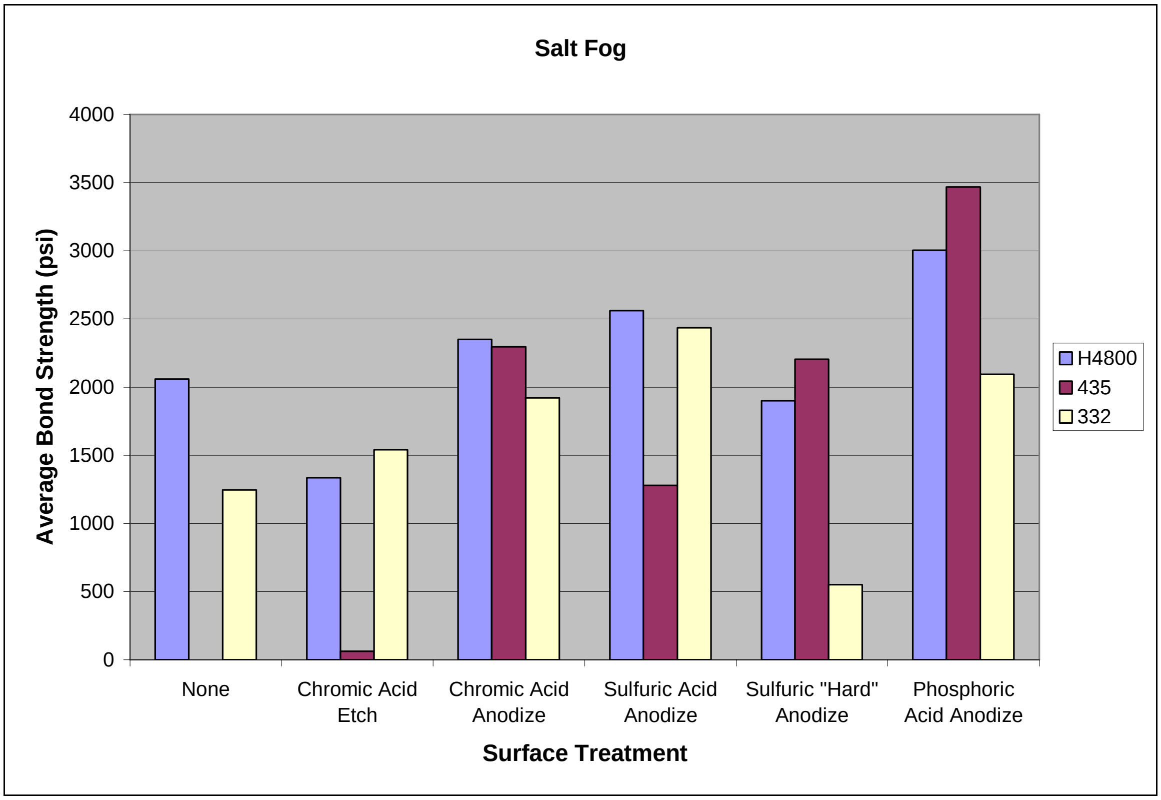


Figure 40: Bond Strength vs. Surface Treatment (Salt Fog)

As shown in **Figure 40**, bond strength varied greatly by not only treatment method, but also by adhesive type. To organize this data, each adhesive type was analyzed separately using Minitab.

2.6.2.1.2.1 Loctite® H4800™

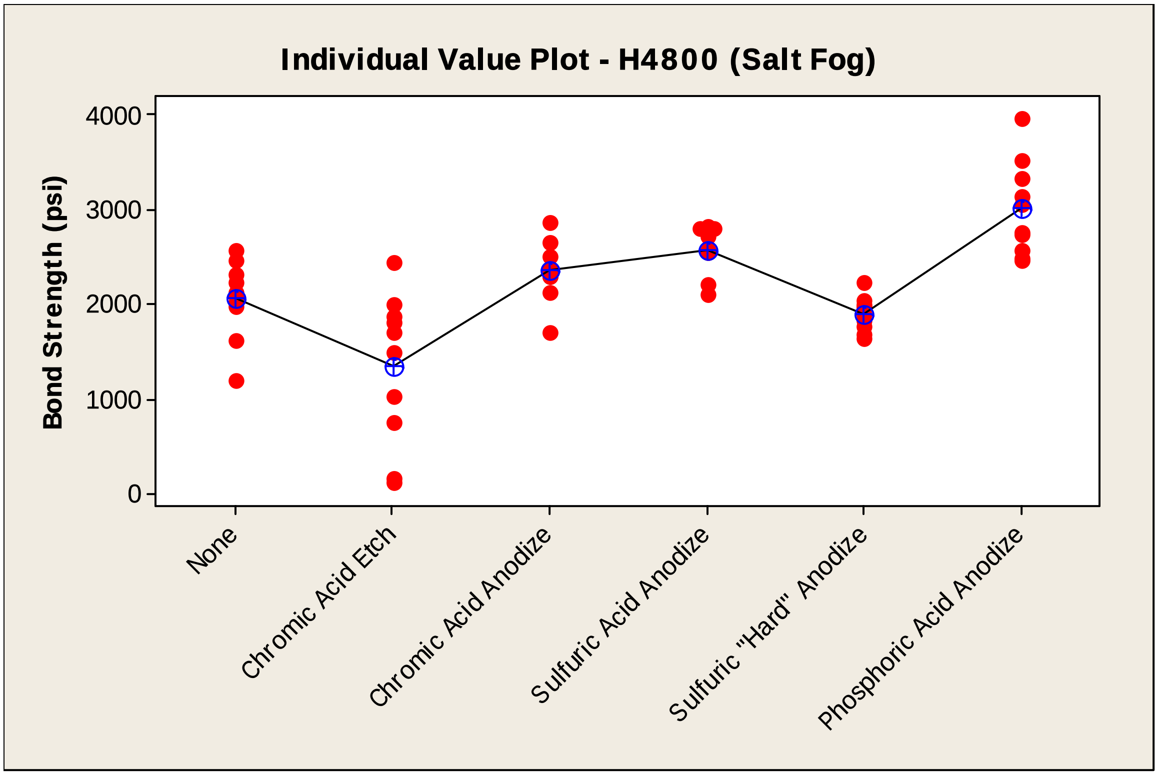


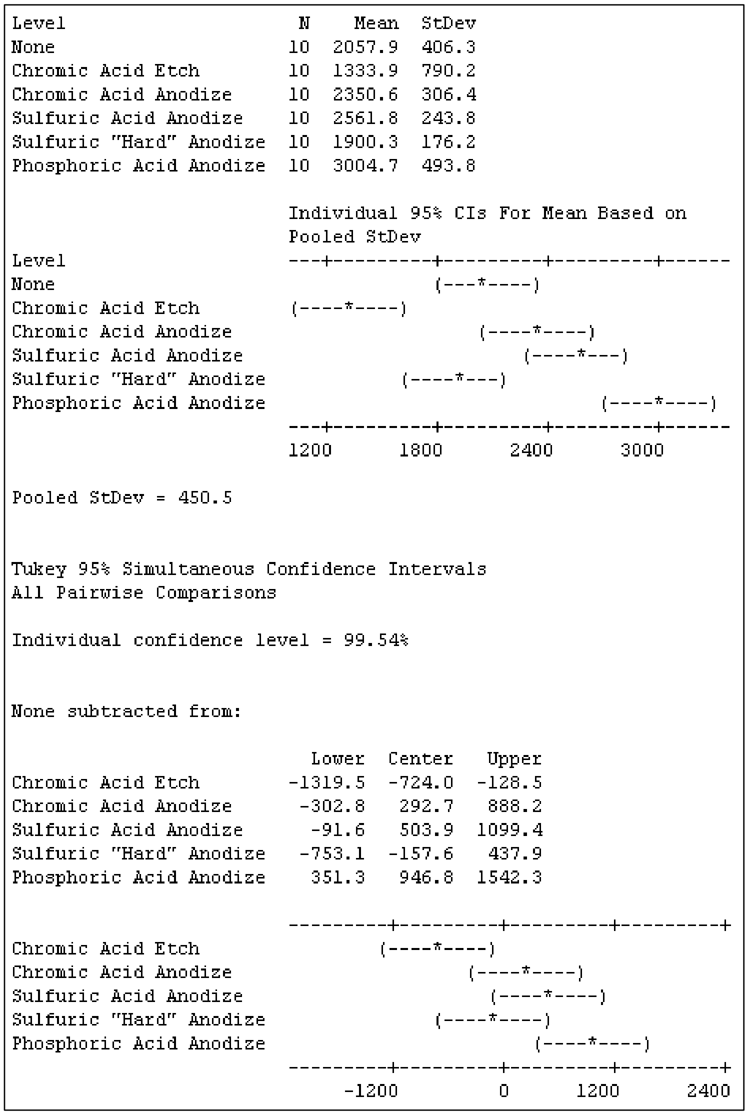
Figure 41: Individual Value Plot - H4800 (Salt Fog)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – H4800 (Salt Fog):

1. Phosphoric Acid Anodize (3005)*
2. Sulfuric Anodize (2562)
3. Chromic Acid Anodize (2351)
4. None (2058)
5. Sulfuric “Hard” Anodize (1900)
6. Chromic Acid Etch (1334)

According to the Tukey analysis **[See Figure 42]**, only phosphoric acid anodize had a greater average bond strength that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                      N    Mean  StDev
None                      10  2057.9  406.3
Chromic Acid Etch         10  1333.9  790.2
Chromic Acid Anodize      10  2350.6  306.4
Sulfuric Acid Anodize     10  2561.8  243.8
Sulfuric "Hard" Anodize   10  1900.3  176.2
Phosphoric Acid Anodize   10  3004.7  493.8

                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level                    ---+---------+---------+---------+------
None                                  (---*----)
Chromic Acid Etch        (----*----)
Chromic Acid Anodize                      (----*----)
Sulfuric Acid Anodize                         (----*---)
Sulfuric "Hard" Anodize            (----*---)
Phosphoric Acid Anodize                              (----*----)
                         ---+---------+---------+---------+------
                         1200      1800      2400      3000

Pooled StDev = 450.5


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                           Lower  Center   Upper
Chromic Acid Etch        -1319.5  -724.0  -128.5
Chromic Acid Anodize      -302.8   292.7   888.2
Sulfuric Acid Anodize      -91.6   503.9  1099.4
Sulfuric "Hard" Anodize   -753.1  -157.6   437.9
Phosphoric Acid Anodize    351.3   946.8  1542.3

                         ---------+---------+---------+---------+
Chromic Acid Etch                (----*----)
Chromic Acid Anodize                     (----*----)
Sulfuric Acid Anodize                      (----*----)
Sulfuric "Hard" Anodize               (----*----)
Phosphoric Acid Anodize                        (----*----)
                         ---------+---------+---------+---------+
                             -1200         0      1200      2400
```

Figure 42: Tukey's Analysis - H4800 (Salt Fog)

2.6.2.1.2.2 Loctite® 435™

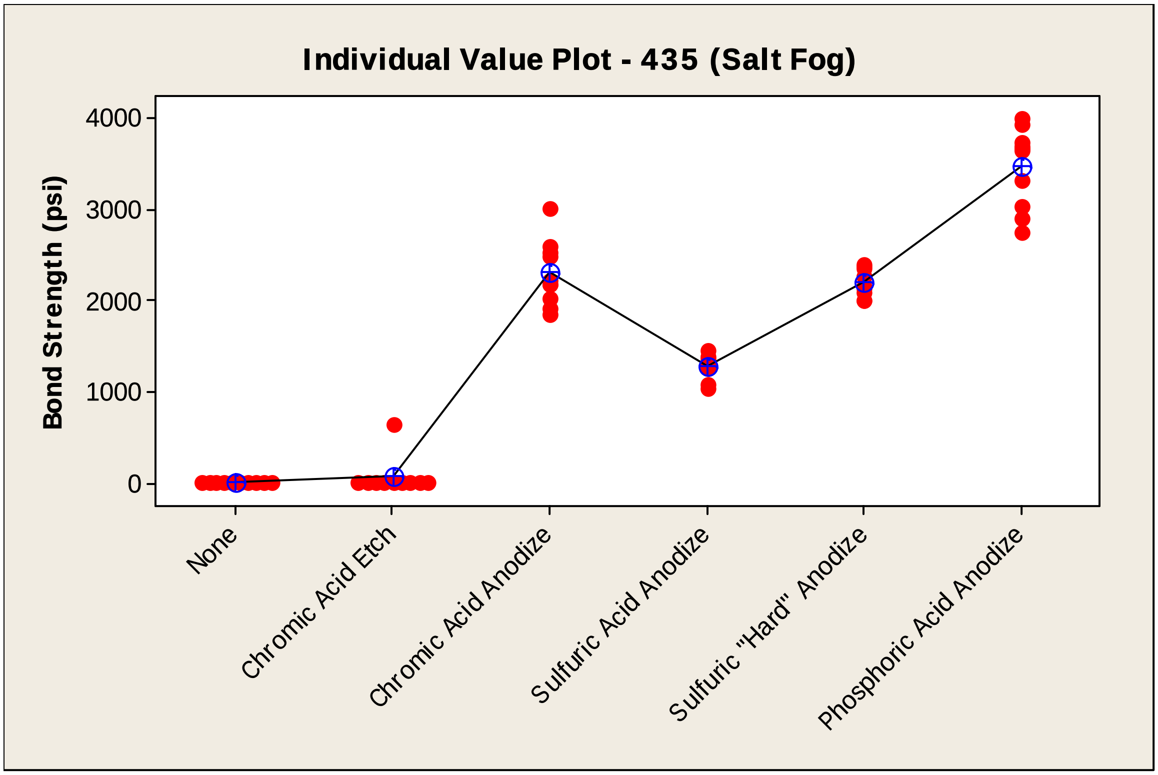


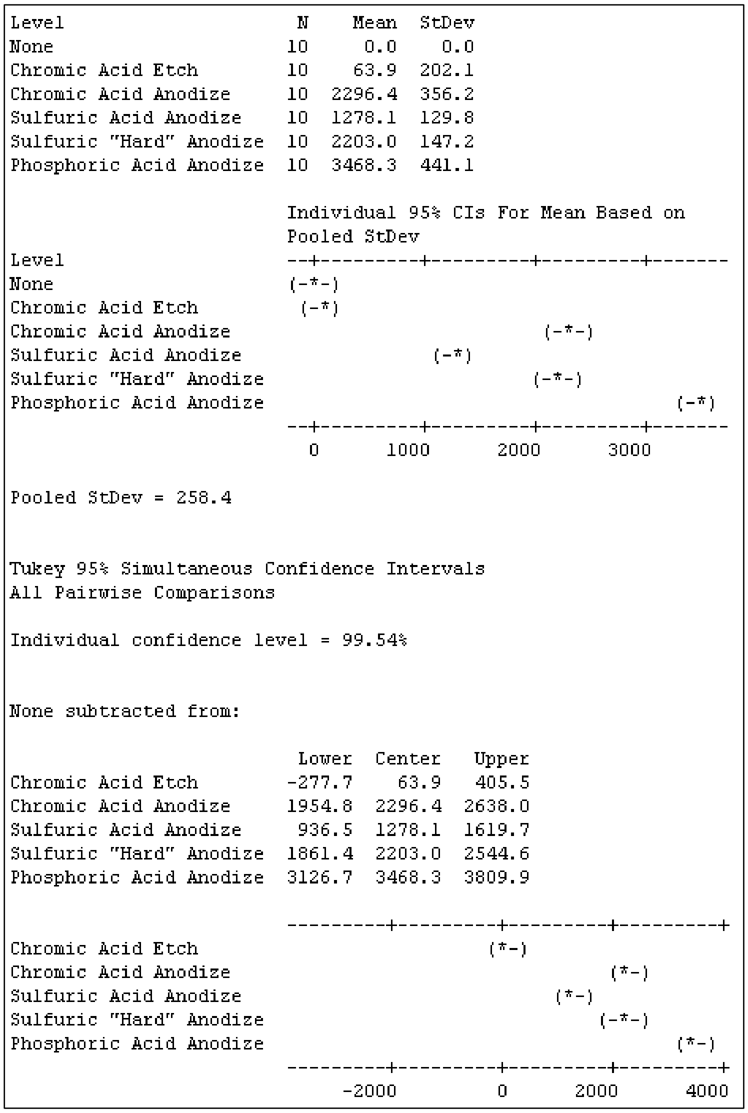
Figure 43: Individual Value Plot - 435 (Salt Fog)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – 435 (Salt Fog):

1. Phosphoric Acid Anodize (3468)*
2. Chromic Acid Anodize (2296)*
3. Sulfuric “Hard” Anodize (2203)*
4. Sulfuric Anodize (1278)*
5. Chromic Acid Etch (64)
6. None (0)

According to the Tukey analysis **[See Figure 44]**, phosphoric acid anodize, chromic acid anodize, sulfuric “hard” anodize & sulfuric anodize all had greater average bond strengths that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                   N      Mean  StDev
None                     10     0.0    0.0
Chromic Acid Etch        10    63.9  202.1
Chromic Acid Anodize     10  2296.4  356.2
Sulfuric Acid Anodize    10  1278.1  129.8
Sulfuric "Hard" Anodize  10  2203.0  147.2
Phosphoric Acid Anodize  10  3468.3  441.1

                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level                    --+---------+---------+---------+-------
None                     (-*-)
Chromic Acid Etch         (-*)
Chromic Acid Anodize                            (-*-)
Sulfuric Acid Anodize                 (-*)
Sulfuric "Hard" Anodize                        (-*-)
Phosphoric Acid Anodize                                     (-*)
                         --+---------+---------+---------+-------
                           0      1000      2000      3000

Pooled StDev = 258.4


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                          Lower  Center   Upper
Chromic Acid Etch        -277.7    63.9   405.5
Chromic Acid Anodize     1954.8  2296.4  2638.0
Sulfuric Acid Anodize     936.5  1278.1  1619.7
Sulfuric "Hard" Anodize  1861.4  2203.0  2544.6
Phosphoric Acid Anodize  3126.7  3468.3  3809.9


                         ---------+---------+---------+---------+
Chromic Acid Etch                          (*-)
Chromic Acid Anodize                                  (*-)
Sulfuric Acid Anodize                            (*-)
Sulfuric "Hard" Anodize                              (-*-)
Phosphoric Acid Anodize                                     (*-)
                         ---------+---------+---------+---------+
                              -2000         0      2000      4000
```

Figure 44: Tukey's Analysis - 435 (Salt Fog)

2.6.2.1.2.3 Loctite® 332™

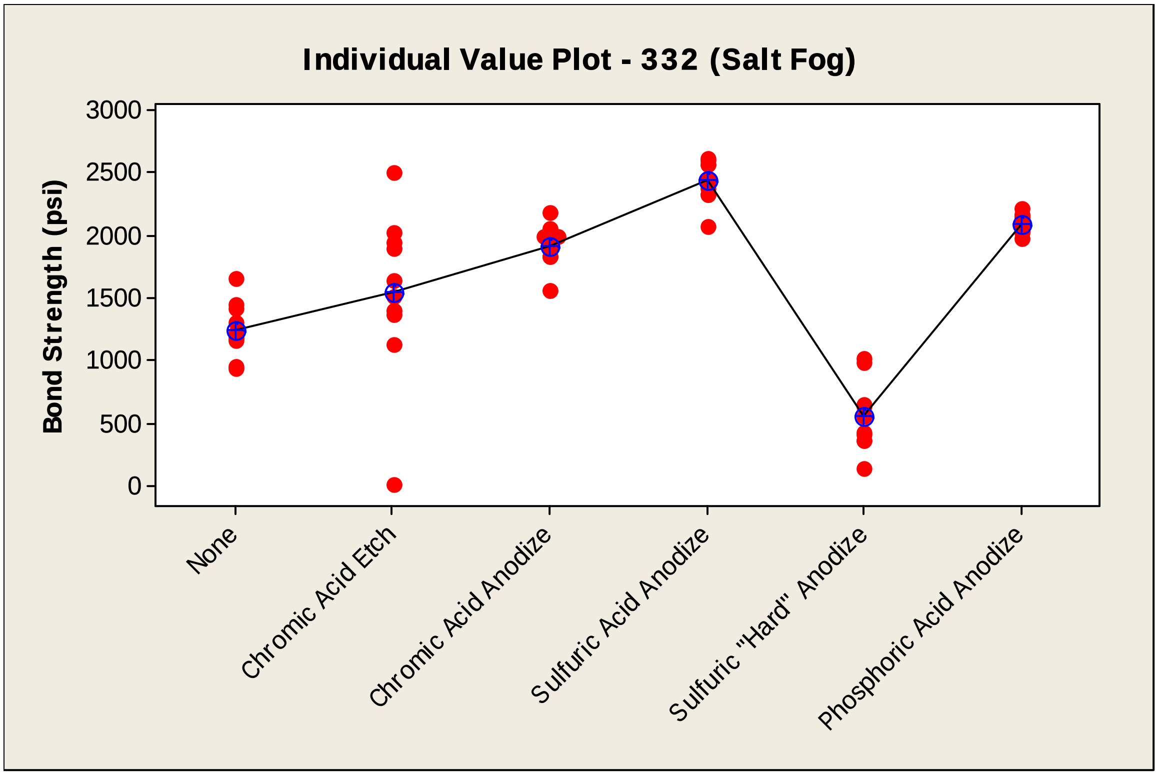


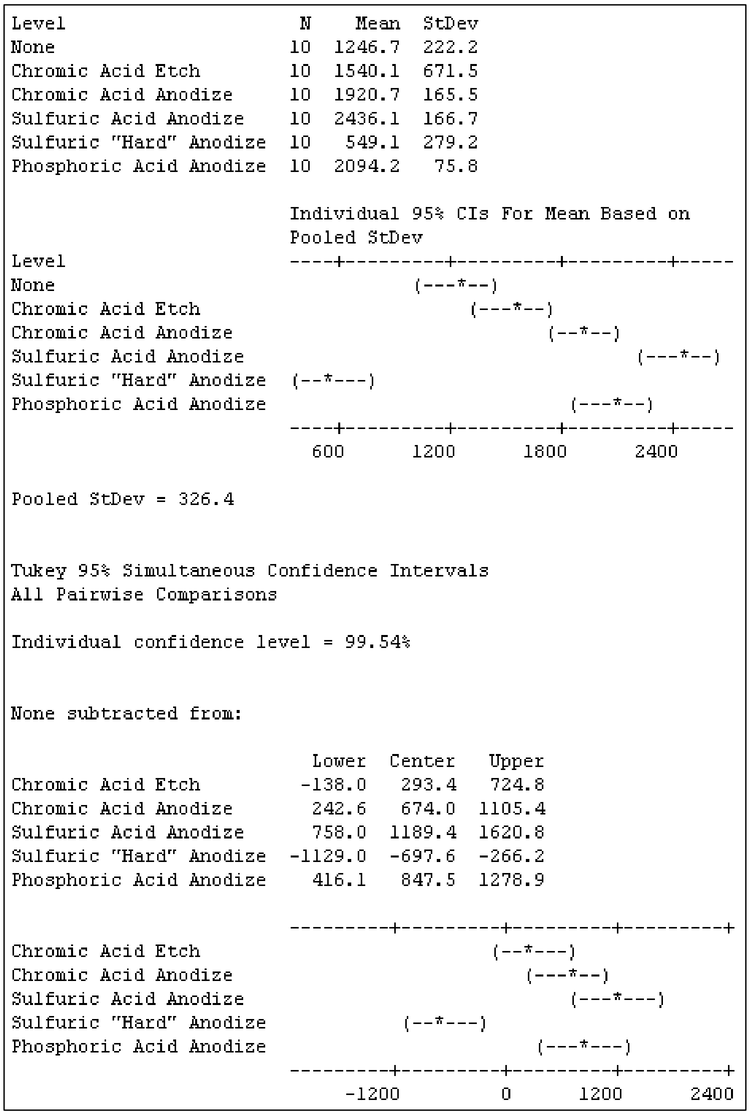
Figure 45: Individual Value Plot - 332 (Salt Fog)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – 332 (Salt Fog):

1. Sulfuric Anodize (2436)*
2. Phosphoric Acid Anodize (2094)*
3. Chromic Acid Anodize (1921)*
4. Chromic Acid Etch (1540)
5. None (1247)
6. Sulfuric “Hard” Anodize (549)

According to the Tukey analysis **[See Figure 46]**, sulfuric anodize, phosphoric acid anodize & chromic acid anodize all had greater average bond strengths that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                     N    Mean  StDev
None                     10  1246.7  222.2
Chromic Acid Etch        10  1540.1  671.5
Chromic Acid Anodize     10  1920.7  165.5
Sulfuric Acid Anodize    10  2436.1  166.7
Sulfuric "Hard" Anodize  10   549.1  279.2
Phosphoric Acid Anodize  10  2094.2   75.8

                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level                    ----+---------+---------+---------+-----
None                                (---*--)
Chromic Acid Etch                        (---*--)
Chromic Acid Anodize                            (--*--)
Sulfuric Acid Anodize                                   (---*--)
Sulfuric "Hard" Anodize  (--*---)
Phosphoric Acid Anodize                           (---*--)
                         ----+---------+---------+---------+-----
                           600      1200      1800      2400

Pooled StDev = 326.4


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                           Lower  Center   Upper
Chromic Acid Etch        -138.0   293.4   724.8
Chromic Acid Anodize      242.6   674.0  1105.4
Sulfuric Acid Anodize     758.0  1189.4  1620.8
Sulfuric "Hard" Anodize -1129.0  -697.6  -266.2
Phosphoric Acid Anodize   416.1   847.5  1278.9


                         ---------+---------+---------+---------+
Chromic Acid Etch                          (--*---)
Chromic Acid Anodize                          (---*--)
Sulfuric Acid Anodize                             (---*---)
Sulfuric "Hard" Anodize            (--*---)
Phosphoric Acid Anodize                        (---*---)
                         ---------+---------+---------+---------+
                              -1200         0      1200      2400
```

Figure 46: Tukey's Analysis - 332 (Salt Fog)

2.6.2.1.3 Condensing Humidity Conditioned Assemblies

Table 20 presents a summary of the results obtained for the condensing humidity assemblies.

Table 20: Condensing Humidity Conditioning Results

Adhesive		Aluminum Surface Treatment					
		None	Chromic Acid Etch	Chromic Acid Anodize	Sulfuric Anodize	Sulfuric "Hard" Anodize	Phosphoric Acid Anodize
H4800	**Average Strength (psi)**	**1684**	**1867**	**1732**	**2347**	**1813**	**2710**
	Stand. Dev.	401	437	155	213	194	325
	COV	0.238	0.234	0.089	0.091	0.107	0.120
	Minimum	1684	1867	1732	2347	1813	2710
435	**Average Strength (psi)**	**1531**	**1629**	**1664**	**950**	**1561**	**3902**
	Stand. Dev.	159	558	163	129	304	341
	COV	0.104	0.343	0.098	0.136	0.195	0.087
	Minimum	1531	1629	1664	950	1561	3902
332	**Average Strength (psi)**	**1303**	**1963**	**1899**	**2337**	**997**	**2213**
	Stand. Dev.	250	397	124	100	374	146
	COV	0.192	0.202	0.065	0.043	0.375	0.066
	Minimum	774	963	1666	2108	546	1910

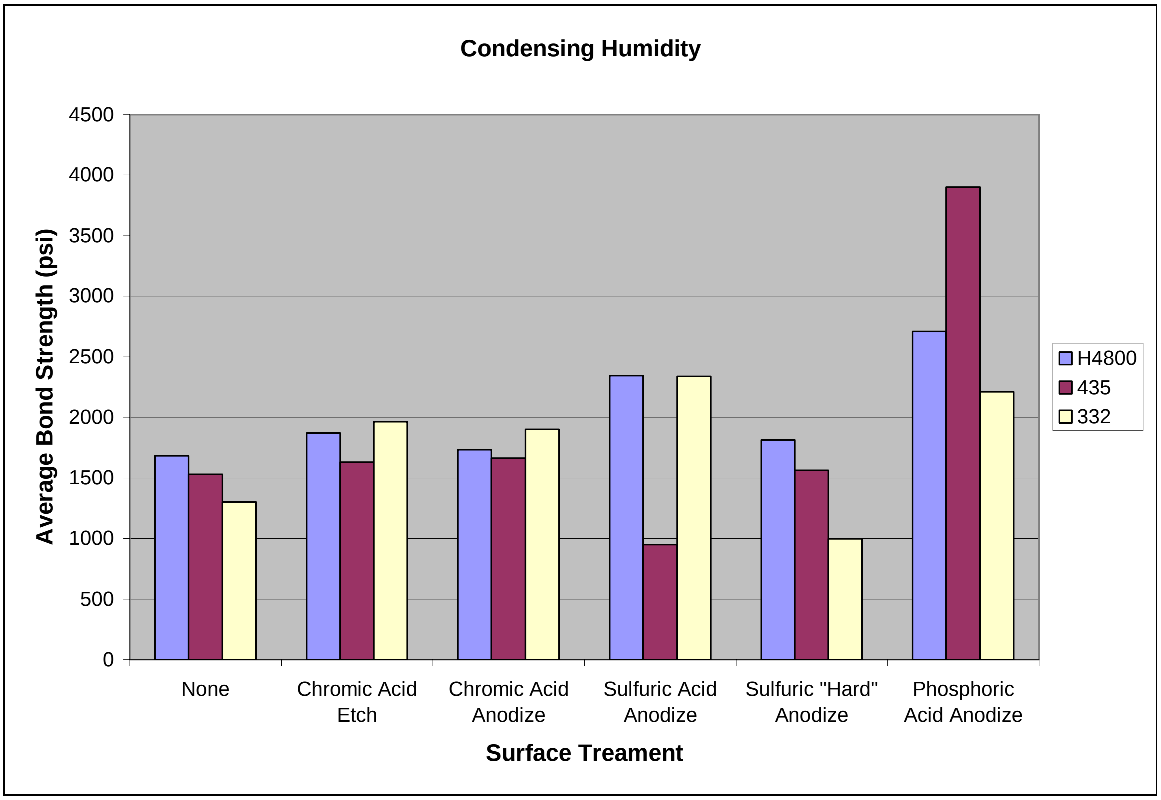


Figure 47: Bond Strength vs. Surface Treatment (Condensing Humidity)

As shown in **Figure 47**, bond strength varied greatly by not only treatment method, but also by adhesive type. To organize this data, each adhesive type was analyzed separately using Minitab.

2.6.2.1.3.1 Loctite® H4800™

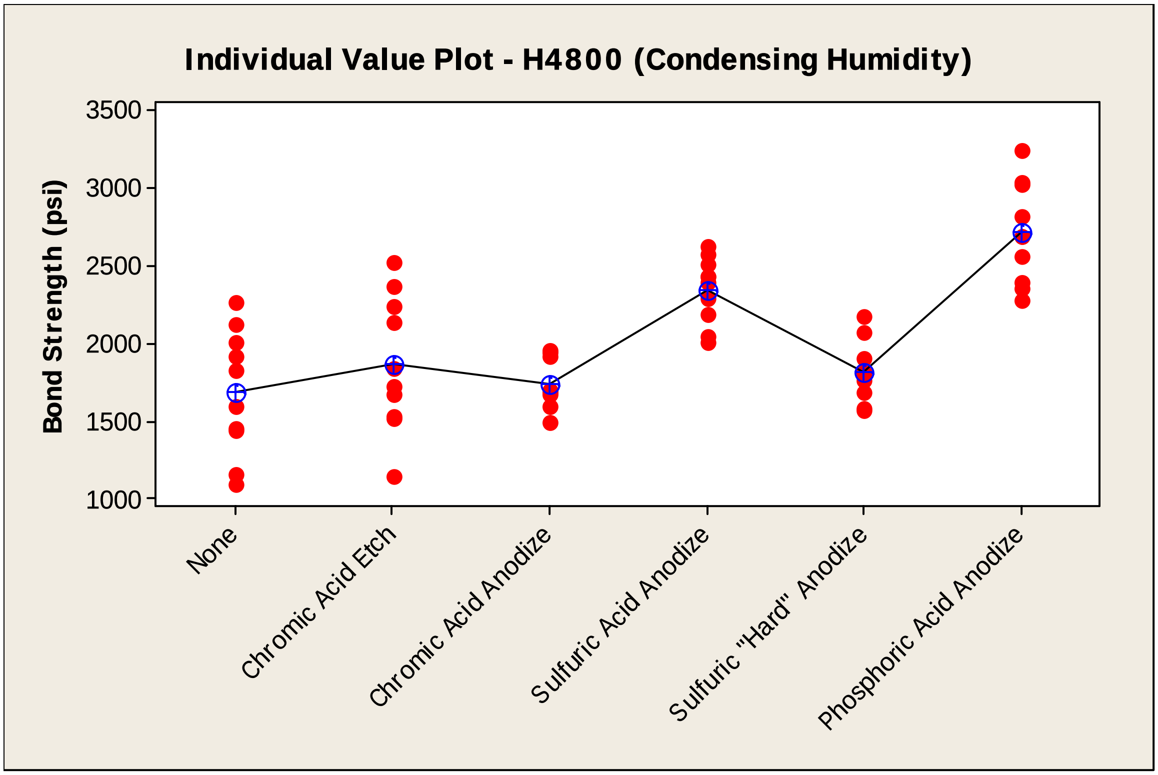


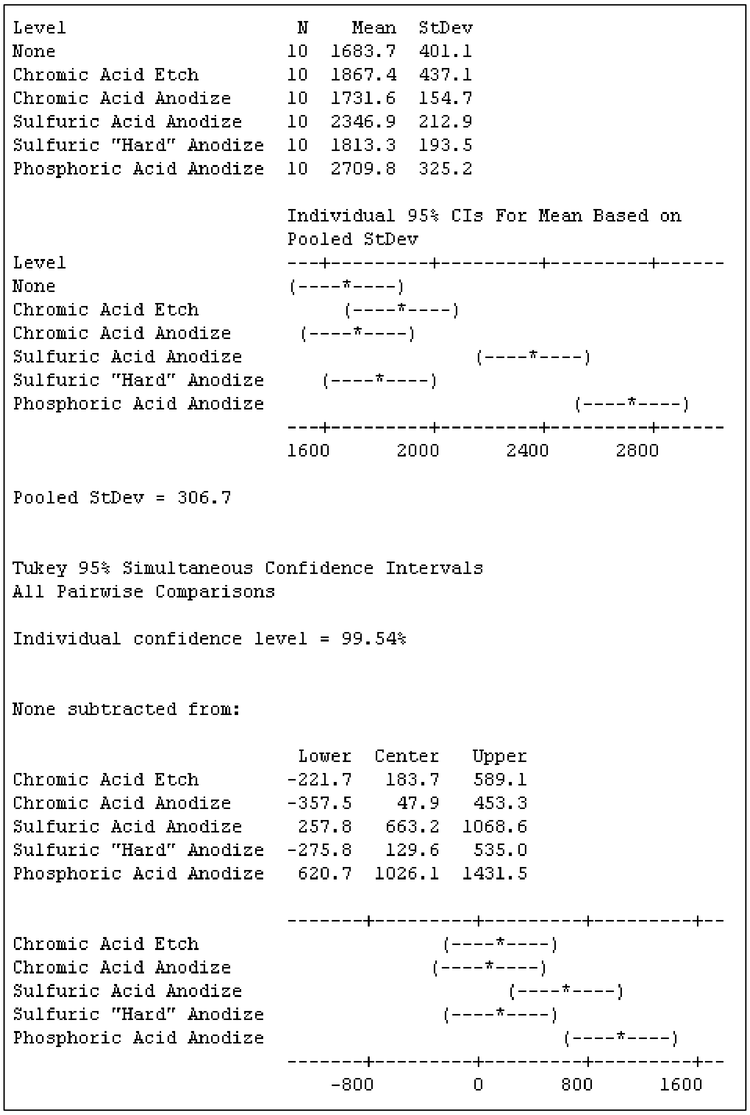
Figure 48: Individual Value Plot - H4800 (Condensing Humidity)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – H4800 (Condensing Humidity):

1. Phosphoric Acid Anodize (2710)*
2. Sulfuric Anodize (2347)*
3. Chromic Acid Etch (1867)
4. Sulfuric “Hard” Anodize (1813)
5. Chromic Acid Anodize (1732)
6. None (1684)

According to the Tukey analysis **[See Figure 49]**, phosphoric acid anodize & sulfuric anodize both had greater average bond strengths that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                     N    Mean  StDev
None                     10  1683.7  401.1
Chromic Acid Etch        10  1867.4  437.1
Chromic Acid Anodize     10  1731.6  154.7
Sulfuric Acid Anodize    10  2346.9  212.9
Sulfuric "Hard" Anodize  10  1813.3  193.5
Phosphoric Acid Anodize  10  2709.8  325.2

                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level                    ---+---------+---------+---------+------
None                     (----*----)
Chromic Acid Etch             (----*----)
Chromic Acid Anodize      (----*----)
Sulfuric Acid Anodize                     (----*----)
Sulfuric "Hard" Anodize     (----*----)
Phosphoric Acid Anodize                            (----*----)
                         ---+---------+---------+---------+------
                         1600      2000      2400      2800

Pooled StDev = 306.7


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                          Lower  Center   Upper
Chromic Acid Etch        -221.7   183.7   589.1
Chromic Acid Anodize     -357.5    47.9   453.3
Sulfuric Acid Anodize     257.8   663.2  1068.6
Sulfuric "Hard" Anodize  -275.8   129.6   535.0
Phosphoric Acid Anodize   620.7  1026.1  1431.5

                         -------+---------+---------+---------+--
Chromic Acid Etch                      (----*----)
Chromic Acid Anodize                  (----*----)
Sulfuric Acid Anodize                       (----*----)
Sulfuric "Hard" Anodize                (----*----)
Phosphoric Acid Anodize                          (----*----)
                         -------+---------+---------+---------+--
                             -800         0       800      1600
```

Figure 49: Tukey's Analysis - H4800 (Condensing Humidity)

2.6.2.1.3.2 Loctite® 435™

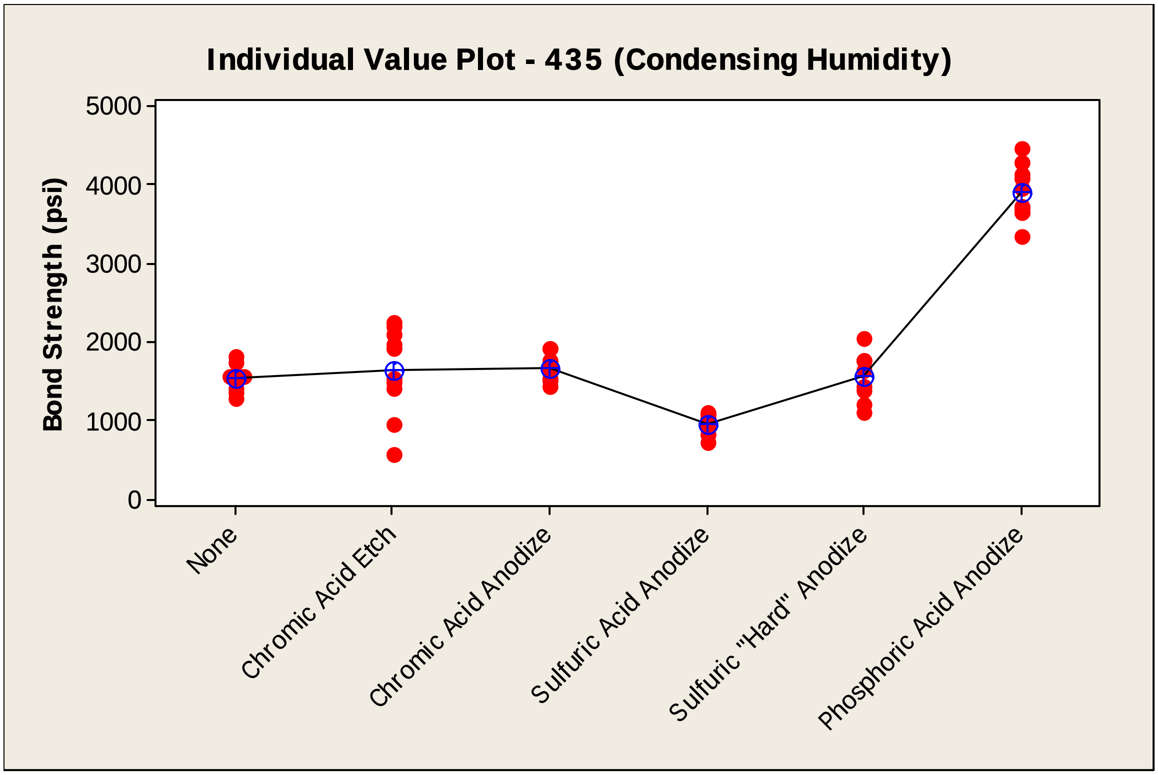


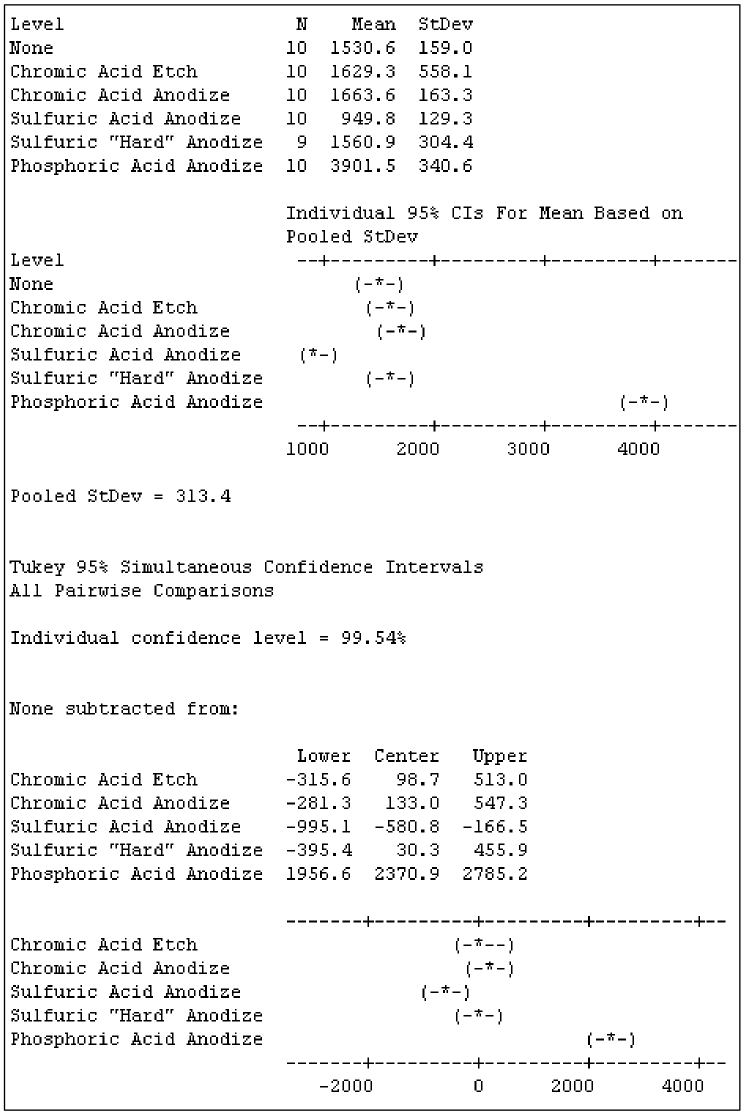
Figure 50: Individual Value Plot - 435 (Condensing Humidity)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – 435 (Condensing Humidity):

1. Phosphoric Acid Anodize (3902)*
2. Chromic Acid Anodize (1664)
3. Chromic Acid Etch (1629)
4. Sulfuric "Hard" Anodize (1561)
5. None (1531)
6. Sulfuric Anodize (950)

According to the Tukey analysis **[Figure 51]**, only phosphoric acid anodize had a greater average bond strength that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                     N    Mean  StDev
None                     10  1530.6  159.0
Chromic Acid Etch        10  1629.3  558.1
Chromic Acid Anodize     10  1663.6  163.3
Sulfuric Acid Anodize    10   949.8  129.3
Sulfuric "Hard" Anodize   9  1560.9  304.4
Phosphoric Acid Anodize  10  3901.5  340.6

                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level                     --+---------+---------+---------+-------
None                           (-*-)
Chromic Acid Etch               (-*-)
Chromic Acid Anodize             (-*-)
Sulfuric Acid Anodize     (*-)
Sulfuric "Hard" Anodize         (-*-)
Phosphoric Acid Anodize                                (-*-)
                          --+---------+---------+---------+-------
                         1000      2000      3000      4000

Pooled StDev = 313.4


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                          Lower  Center   Upper
Chromic Acid Etch        -315.6    98.7   513.0
Chromic Acid Anodize     -281.3   133.0   547.3
Sulfuric Acid Anodize    -995.1  -580.8  -166.5
Sulfuric "Hard" Anodize  -395.4    30.3   455.9
Phosphoric Acid Anodize  1956.6  2370.9  2785.2

                         -------+---------+---------+---------+--
Chromic Acid Etch                       (-*--)
Chromic Acid Anodize                     (-*-)
Sulfuric Acid Anodize                (-*-)
Sulfuric "Hard" Anodize                 (-*-)
Phosphoric Acid Anodize                             (-*-)
                         -------+---------+---------+---------+--
                            -2000         0      2000      4000
```

Figure 51: Tukey's Analysis - 435 (Condensing Humidity)

2.6.2.1.3.3 Loctite® 332™

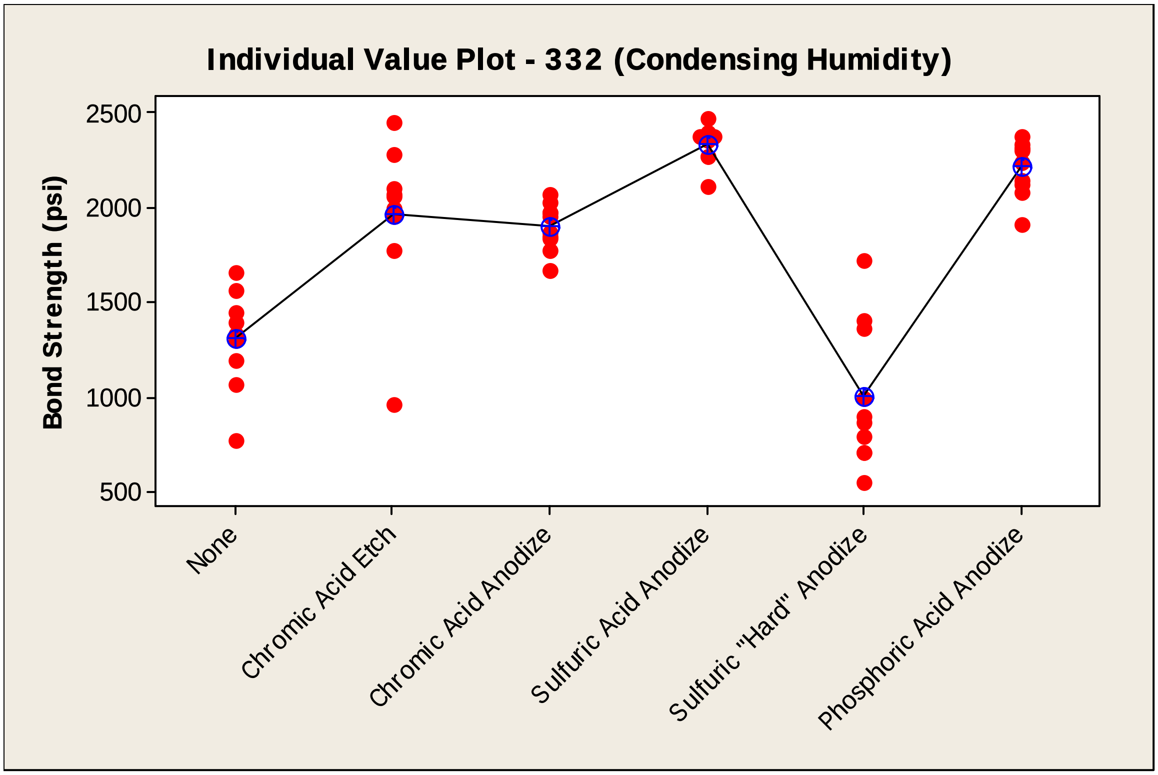


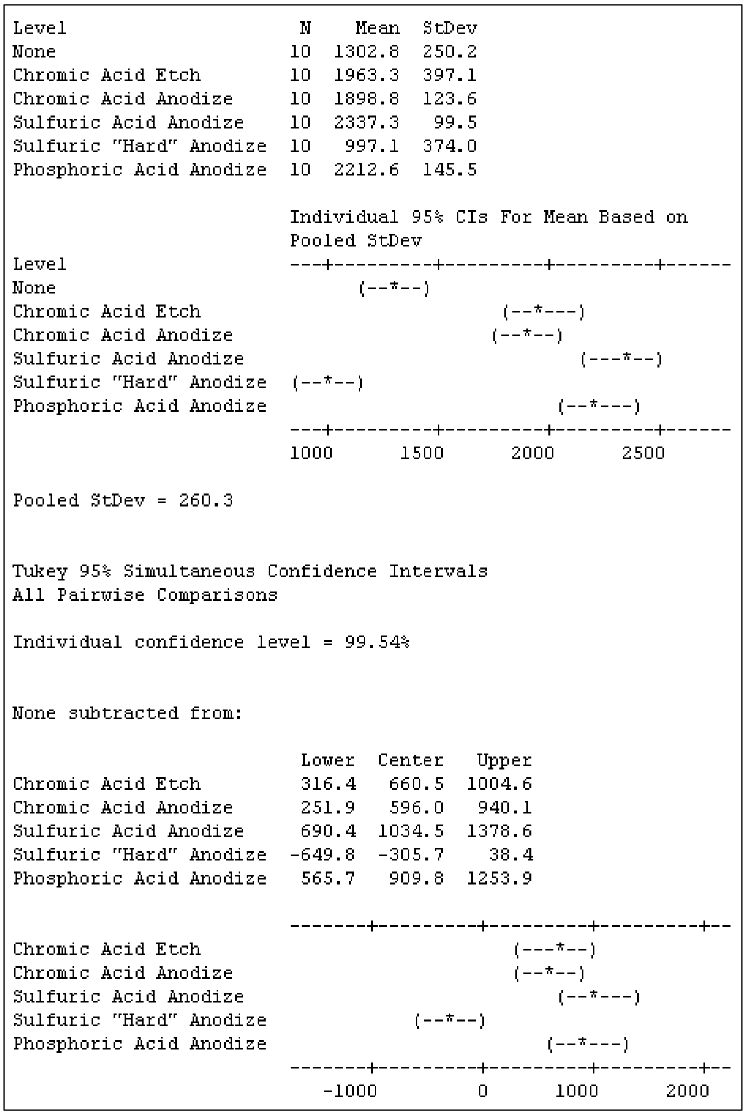
Figure 52: Individual Value Plot - 332 (Condensing Humidity)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – 332 (Condensing Humidity):

1. Sulfuric Anodize (2337)*
2. Phosphoric Acid Anodize (2213)*
3. Chromic Acid Etch (1963)*
4. Chromic Acid Anodize (1899)*
5. None (1303)
6. Sulfuric “Hard” Anodize (997)

According to the Tukey analysis **[See Figure 53],** sulfuric anodize, phosphoric acid anodize, chromic acid etch & chromic acid anodize all had greater average bond strengths that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                     N    Mean  StDev
None                     10  1302.8  250.2
Chromic Acid Etch        10  1963.3  397.1
Chromic Acid Anodize     10  1898.8  123.6
Sulfuric Acid Anodize    10  2337.3   99.5
Sulfuric "Hard" Anodize  10   997.1  374.0
Phosphoric Acid Anodize  10  2212.6  145.5

                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level                    ---+---------+---------+---------+------
None                           (--*--)
Chromic Acid Etch                           (--*---)
Chromic Acid Anodize                       (--*--)
Sulfuric Acid Anodize                              (---*--)
Sulfuric "Hard" Anodize  (--*--)
Phosphoric Acid Anodize                          (--*---)
                         ---+---------+---------+---------+------
                         1000      1500      2000      2500

Pooled StDev = 260.3


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                          Lower  Center   Upper
Chromic Acid Etch         316.4   660.5  1004.6
Chromic Acid Anodize      251.9   596.0   940.1
Sulfuric Acid Anodize     690.4  1034.5  1378.6
Sulfuric "Hard" Anodize  -649.8  -305.7    38.4
Phosphoric Acid Anodize   565.7   909.8  1253.9

                         -------+---------+---------+---------+--
Chromic Acid Etch                            (---*--)
Chromic Acid Anodize                         (--*--)
Sulfuric Acid Anodize                            (--*---)
Sulfuric "Hard" Anodize             (--*--)
Phosphoric Acid Anodize                         (--*---)
                         -------+---------+---------+---------+--
                            -1000         0      1000      2000
```

Figure 53: Tukey's Analysis - 332 (Condensing Humidity)

2.6.2.1.4 Heat 1 Assemblies (100°C for 435, 125°C for H4800 & 332)

Table 21 presents a summary of the results obtained for the heat 1 assemblies.

Table 21: Heat 1 Conditioning Results

Adhesive		Aluminum Surface Treatment					
		None	Chromic Acid Etch	Chromic Acid Anodize	Sulfuric Anodize	Sulfuric “Hard” Anodize	Phosphoric Acid Anodize
H4800	**Average Strength (psi)**	**3800**	**3988**	**3316**	**2320**	**1907**	**3491**
	Stand. Dev.	386	512	386	243	300	432
	COV	0.102	0.128	0.116	0.105	0.157	0.124
	Minimum	3191	3043	2759	1974	1360	2781
435	**Average Strength (psi)**	**1081**	**1300**	**1861**	**813**	**968**	**2381**
	Stand. Dev.	111	142	168	154	120	375
	COV	0.103	0.109	0.090	0.190	0.124	0.157
	Minimum	854	1004	1642	550	776	1892
332	**Average Strength (psi)**	**1981**	**2538**	**2036**	**1729**	**736**	**2061**
	Stand. Dev.	114	281	152	193	352	66
	COV	0.057	0.111	0.075	0.111	0.479	0.032
	Minimum	1837	2028	1848	1419	307	1979

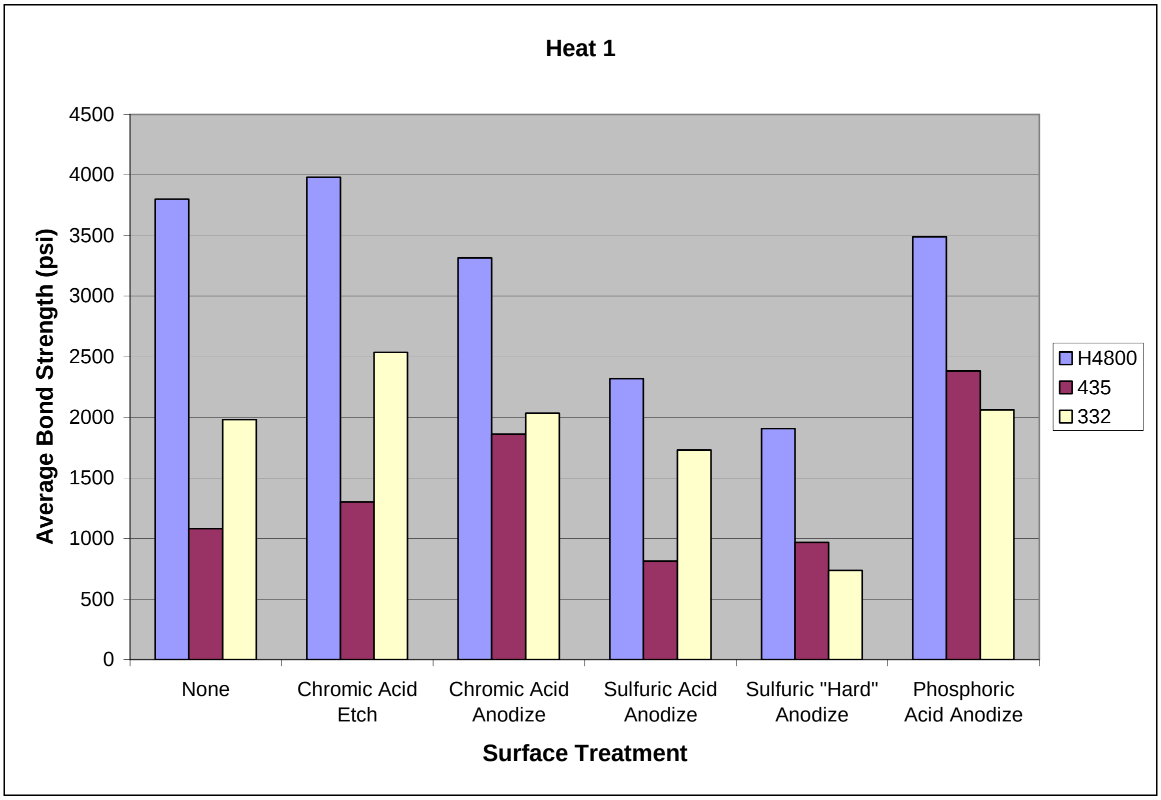


Figure 54: Bond Strength vs. Surface Treatment (Heat 1)

As shown in **Figure 54**, bond strength varied greatly by not only treatment method, but also by adhesive type. To organize this data, each adhesive type was analyzed separately using Minitab.

2.6.2.1.4.1 Loctite® H4800™

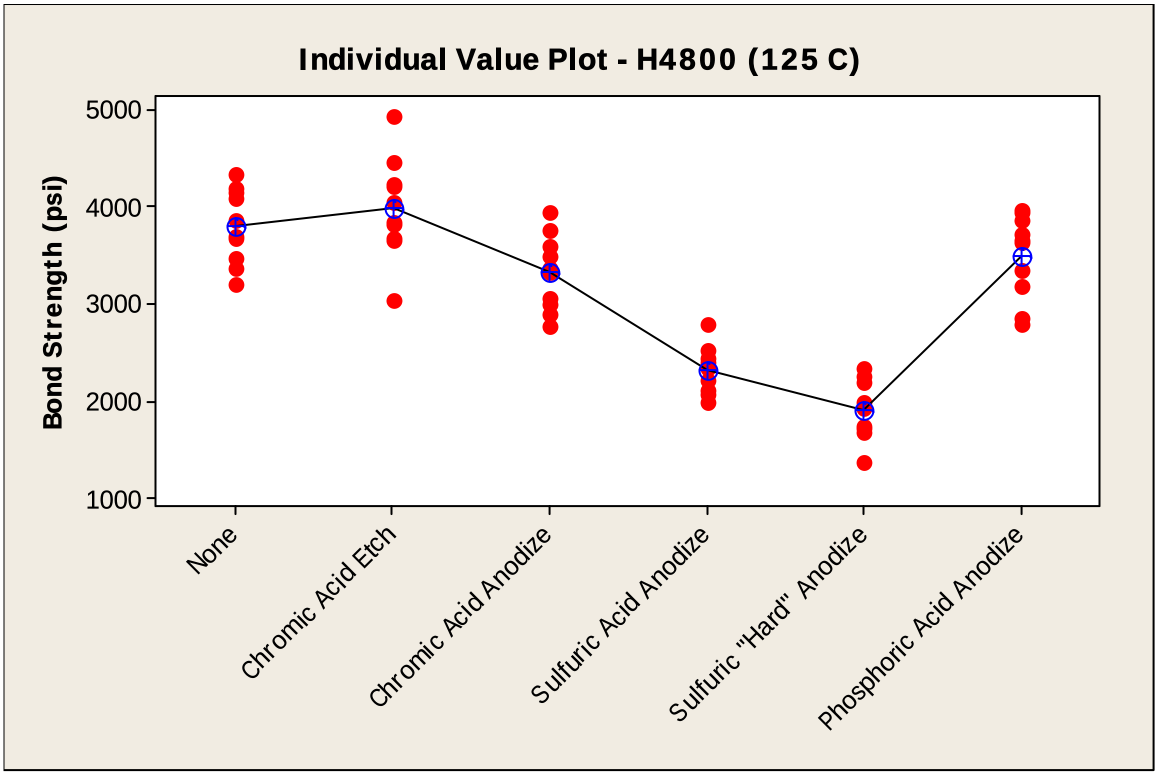


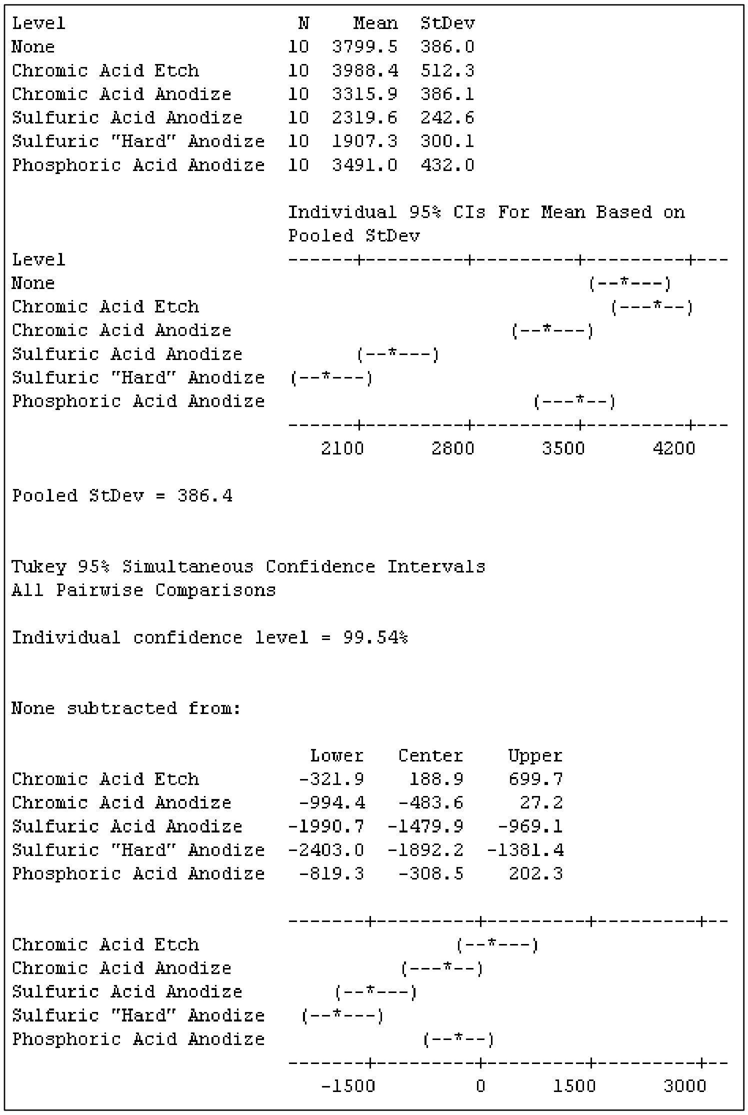
Figure 55: Individual Value Plot - H4800 (125°C)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – H4800 (125°C):

1. Chromic Acid Etch (3988)
2. None (3800)
3. Phosphoric Acid Anodize (3491)
4. Chromic Acid Anodize (3316)
5. Sulfuric Anodize (2320)
6. Sulfuric “Hard” Anodize (1907)

According to the Tukey analysis **[See Figure 56]**, none of the previous surface preparation techniques had a greater average bond strength that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                     N    Mean  StDev
None                     10  3799.5  386.0
Chromic Acid Etch        10  3988.4  512.3
Chromic Acid Anodize     10  3315.9  386.1
Sulfuric Acid Anodize    10  2319.6  242.6
Sulfuric "Hard" Anodize  10  1907.3  300.1
Phosphoric Acid Anodize  10  3491.0  432.0

                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level                    ------+---------+---------+---------+---
None                                                (--*---)
Chromic Acid Etch                                     (---*--)
Chromic Acid Anodize                             (--*---)
Sulfuric Acid Anodize          (--*---)
Sulfuric "Hard" Anodize  (--*---)
Phosphoric Acid Anodize                                (---*--)
                         ------+---------+---------+---------+---
                            2100      2800      3500      4200

Pooled StDev = 386.4


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                           Lower   Center    Upper
Chromic Acid Etch         -321.9    188.9    699.7
Chromic Acid Anodize      -994.4   -483.6     27.2
Sulfuric Acid Anodize    -1990.7  -1479.9   -969.1
Sulfuric "Hard" Anodize  -2403.0  -1892.2  -1381.4
Phosphoric Acid Anodize   -819.3   -308.5    202.3

                         -------+---------+---------+---------+--
Chromic Acid Etch                       (--*---)
Chromic Acid Anodize                 (---*--)
Sulfuric Acid Anodize        (--*---)
Sulfuric "Hard" Anodize   (--*---)
Phosphoric Acid Anodize                (--*--)
                         -------+---------+---------+---------+--
                            -1500         0      1500      3000
```

Figure 56: Tukey's Analysis - H4800 (125°C)

2.6.2.1.4.2 Loctite® 435™

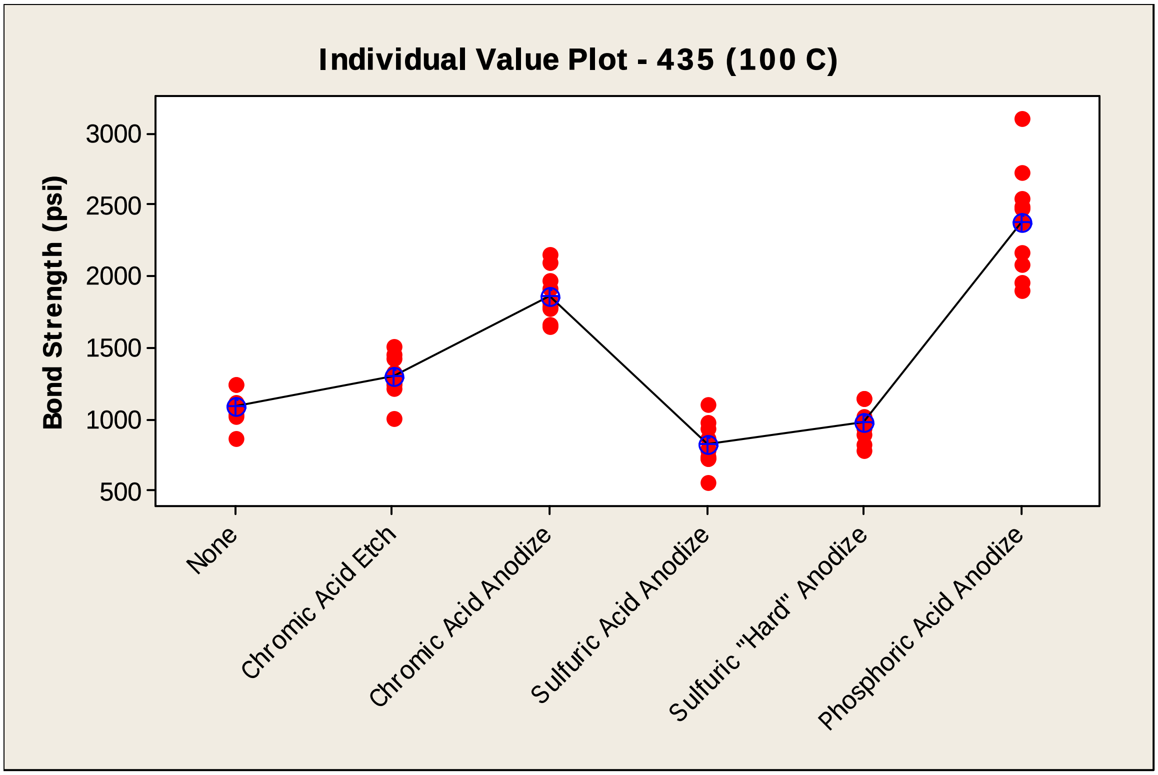


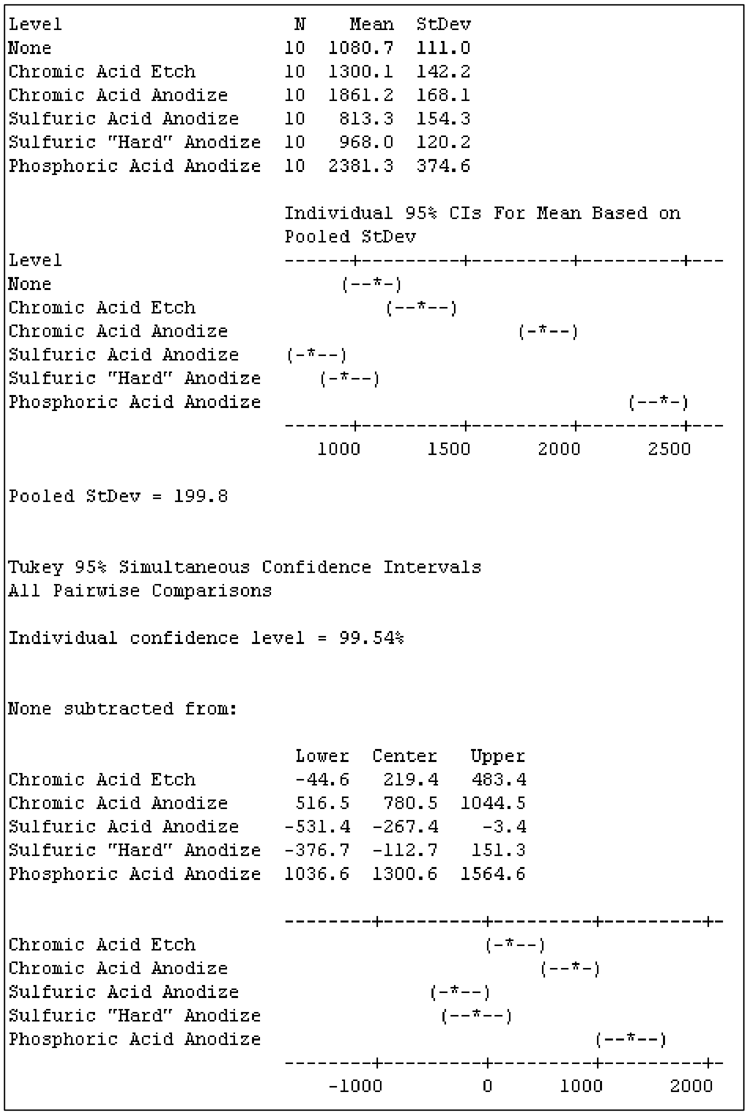
Figure 57: Individual Value Plot - 435 (100°C)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – 435 (100°C):

1. Phosphoric Acid Anodize (2381)*
2. Chromic Acid Anodize (1861)*
3. Chromic Acid Etch (1300)
4. None (1081)
5. Sulfuric “Hard Anodize (968)
6. Sulfuric Anodize (813)

According to the Tukey analysis **[See Figure 58]**, phosphoric acid anodize & chromic acid anodize both had greater average bond strengths that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                    N    Mean  StDev
None                    10  1080.7  111.0
Chromic Acid Etch       10  1300.1  142.2
Chromic Acid Anodize    10  1861.2  168.1
Sulfuric Acid Anodize   10   813.3  154.3
Sulfuric "Hard" Anodize 10   968.0  120.2
Phosphoric Acid Anodize 10  2381.3  374.6

                        Individual 95% CIs For Mean Based on
                        Pooled StDev
Level                   ------+---------+---------+---------+---
None                         (--*-)
Chromic Acid Etch                (--*--)
Chromic Acid Anodize                         (-*--)
Sulfuric Acid Anodize   (-*--)
Sulfuric "Hard" Anodize    (-*--)
Phosphoric Acid Anodize                                (--*-)
                        ------+---------+---------+---------+---
                           1000      1500      2000      2500

Pooled StDev = 199.8


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                         Lower  Center   Upper
Chromic Acid Etch        -44.6   219.4   483.4
Chromic Acid Anodize     516.5   780.5  1044.5
Sulfuric Acid Anodize   -531.4  -267.4    -3.4
Sulfuric "Hard" Anodize -376.7  -112.7   151.3
Phosphoric Acid Anodize 1036.6  1300.6  1564.6

                        --------+---------+---------+---------+-
Chromic Acid Etch                         (-*--)
Chromic Acid Anodize                           (--*-)
Sulfuric Acid Anodize                (-*--)
Sulfuric "Hard" Anodize               (--*--)
Phosphoric Acid Anodize                             (--*--)
                        --------+---------+---------+---------+-
                            -1000         0      1000      2000
```

Figure 58: Tukey's Analysis - 435 (100°C)

2.6.2.1.4.3 Loctite® 332™

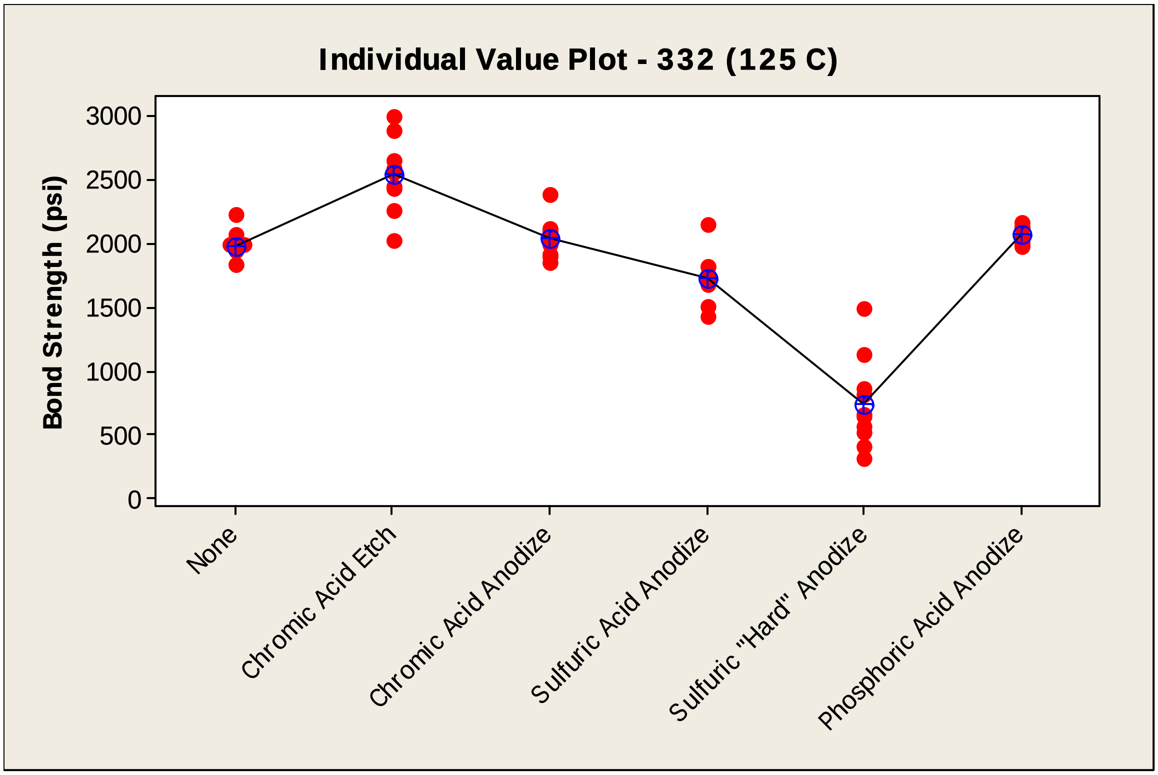


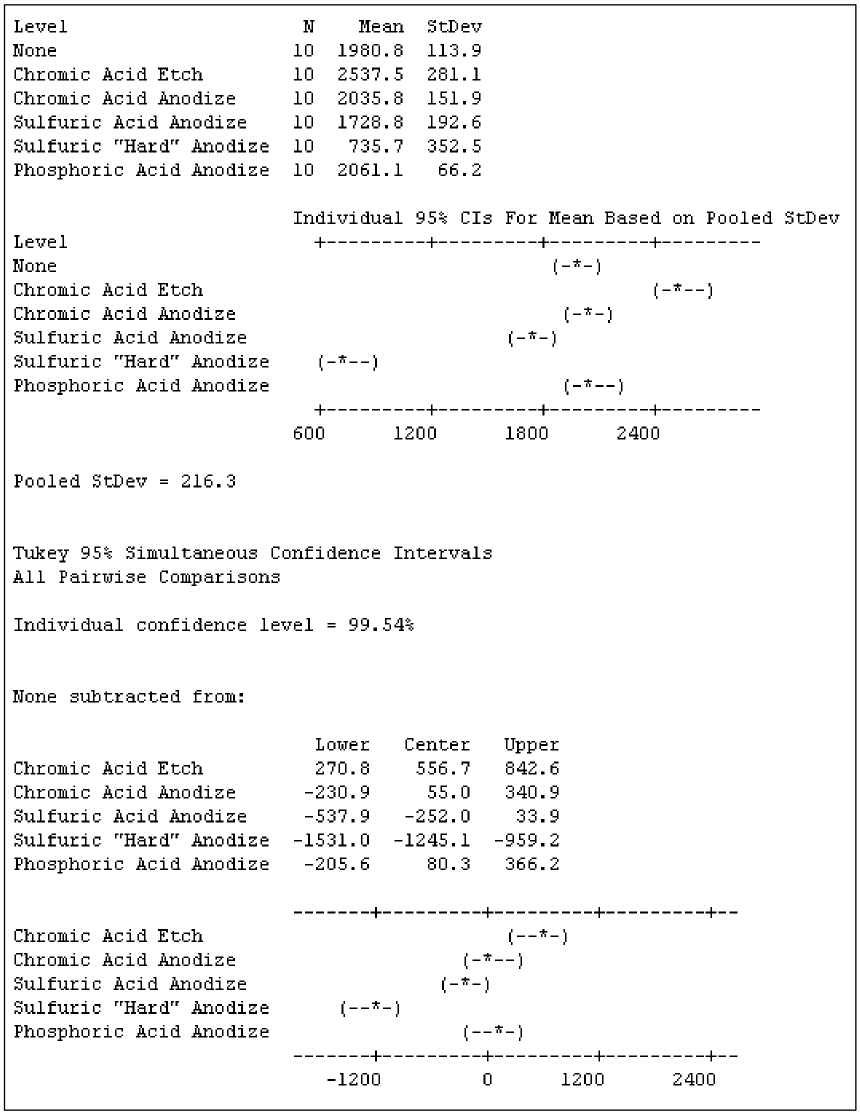
Figure 59: Individual Value Plot - 332 (125°C)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – 332 (125°C):

1. Chromic Acid Etch (2538)*
2. Phosphoric Acid Anodize (2061)
3. Chromic Acid Anodize (2036)
4. None (1981)
5. Sulfuric Anodize (1729)
6. Sulfuric “Hard” Anodize (736)

According to the Tukey analysis **[See Figure 60]**, only chromic acid etch had a greater average bond strength that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                     N    Mean  StDev
None                     10  1980.8  113.9
Chromic Acid Etch        10  2537.5  281.1
Chromic Acid Anodize     10  2035.8  151.9
Sulfuric Acid Anodize    10  1728.8  192.6
Sulfuric "Hard" Anodize  10   735.7  352.5
Phosphoric Acid Anodize  10  2061.1   66.2

                         Individual 95% CIs For Mean Based on Pooled StDev
Level                      +---------+---------+---------+---------
None                                            (-*-)
Chromic Acid Etch                                        (-*--)
Chromic Acid Anodize                             (-*-)
Sulfuric Acid Anodize                       (-*-)
Sulfuric "Hard" Anodize    (-*--)
Phosphoric Acid Anodize                          (-*--)
                           +---------+---------+---------+---------
                         600      1200      1800      2400

Pooled StDev = 216.3


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                           Lower   Center   Upper
Chromic Acid Etch          270.8    556.7   842.6
Chromic Acid Anodize      -230.9     55.0   340.9
Sulfuric Acid Anodize     -537.9   -252.0    33.9
Sulfuric "Hard" Anodize  -1531.0  -1245.1  -959.2
Phosphoric Acid Anodize   -205.6     80.3   366.2

                         -------+---------+---------+---------+--
Chromic Acid Etch                                   (--*-)
Chromic Acid Anodize                            (-*--)
Sulfuric Acid Anodize                         (-*-)
Sulfuric "Hard" Anodize       (--*-)
Phosphoric Acid Anodize                         (--*-)
                         -------+---------+---------+---------+--
                            -1200         0      1200      2400
```

Figure 60: Tukey's Analysis - 332 (125°C)

2.6.2.1.5 Heat 2 Assemblies (125°C for 435, 175°C for H4800 & 332)

Table 22 presents a summary of the results obtained for the heat 2 assemblies.

Table 22: Heat 2 Conditionings Results

Adhesive		**Aluminum Surface Treatment**					
		None	**Chromic Acid Etch**	**Chromic Acid Anodize**	**Sulfuric Anodize**	**Sulfuric "Hard" Anodize**	**Phosphoric Acid Anodize**
H4800	**Average Strength (psi)**	**1564**	**1857**	**1813**	**1539**	**805**	**2049**
	Stand. Dev.	390	778	124	138	152	127
	COV	0.249	0.419	0.069	0.089	0.188	0.062
	Minimum	982	685	1649	1361	578	1835
435	**Average Strength (psi)**	**20**	**252**	**264**	**41**	**1**	**0**
	Stand. Dev.	42	111	133	61	2	0
	COV	2.052	0.441	0.506	1.479	1.563	1.610
	Minimum	0	0	0	0	0	0
332	**Average Strength (psi)**	**2315**	**2992**	**2294**	**1671**	**946**	**2241**
	Stand. Dev.	105	196	134	152	430	115
	COV	0.045	0.065	0.058	0.091	0.455	0.051
	Minimum	2140	2741	2081	1425	402	2045

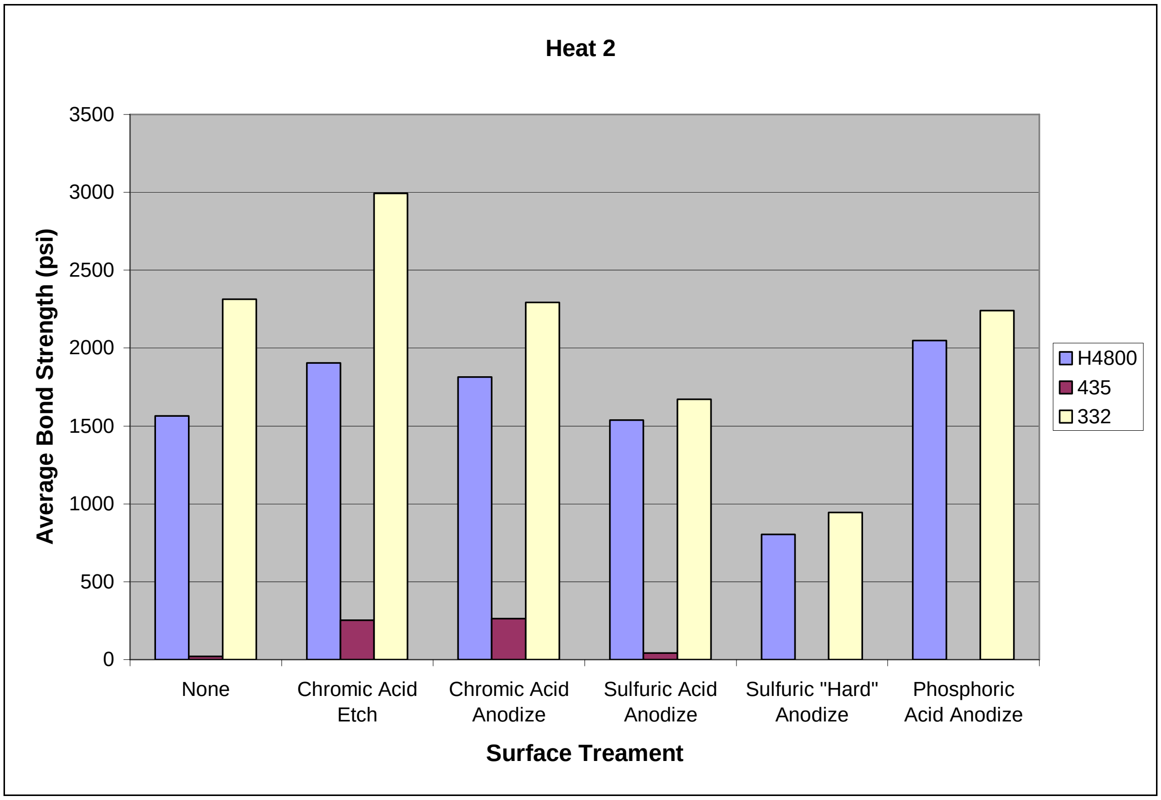


Figure 61: Bond Strength vs. Surface Treatment (Heat 2)

As shown in **Figure 61**, bond strength varied greatly by not only treatment method, but also by adhesive type. To organize this data, each adhesive type was analyzed separately using Minitab.

2.6.2.1.5.1 Loctite® H4800™

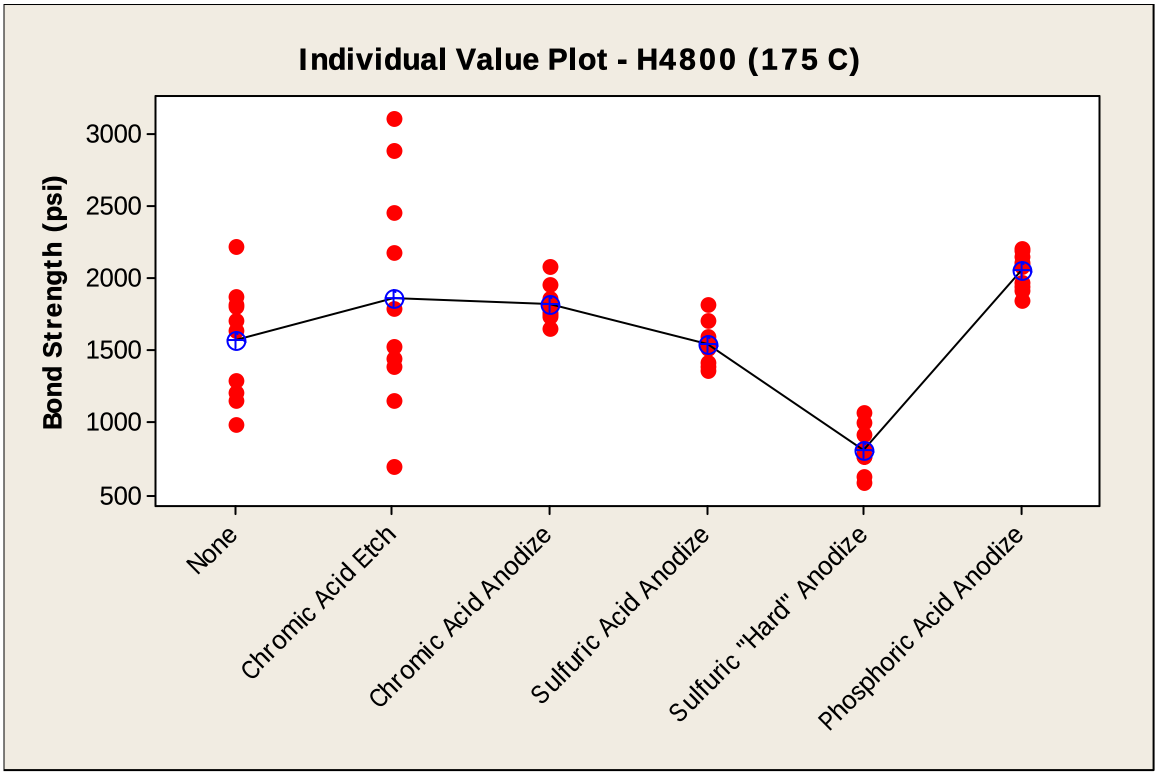


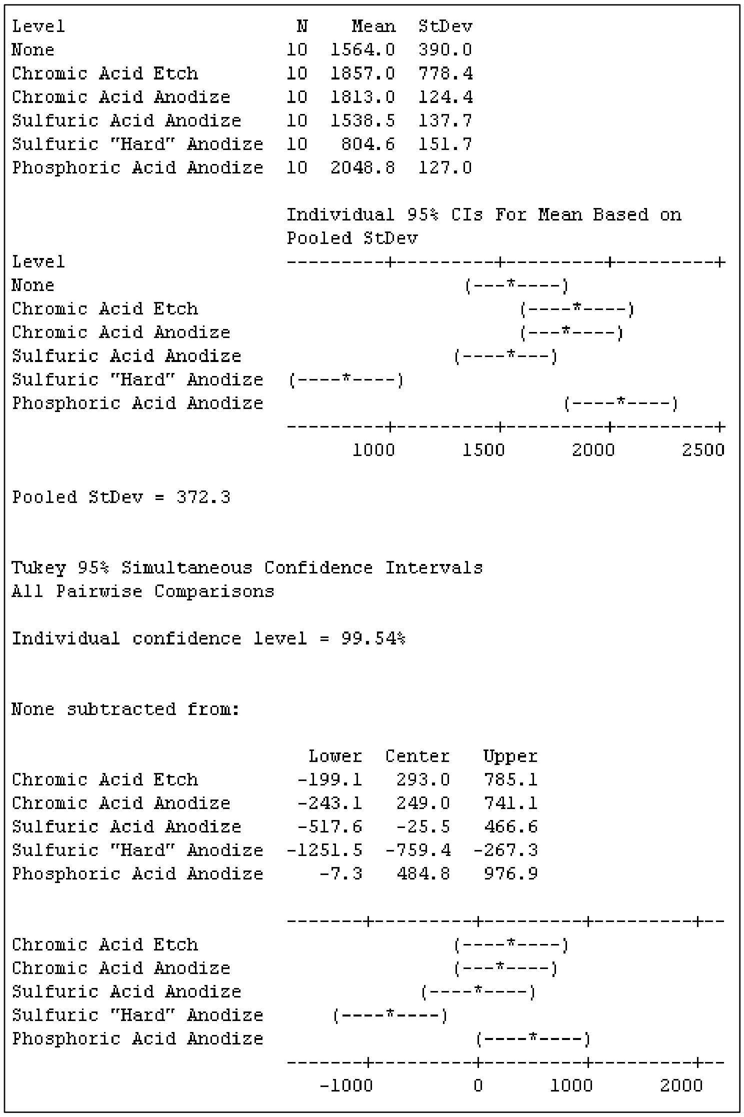
Figure 62: Individual Value Plot - H4800 (175°C)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – H4800 (175°C):

1. Phosphoric Acid Etch (2049)
2. Chromic Acid Etch (1857)
3. Chromic Acid Anodize (1813)
4. None (1564)
5. Sulfuric Anodize (1539)
6. Sulfuric Hard Anodize (805)

According to the Tukey analysis **[See Figure 63]**, none of the previous surface preparation techniques had a greater average bond strength that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                     N    Mean  StDev
None                     10  1564.0  390.0
Chromic Acid Etch        10  1857.0  778.4
Chromic Acid Anodize     10  1813.0  124.4
Sulfuric Acid Anodize    10  1538.5  137.7
Sulfuric "Hard" Anodize  10   804.6  151.7
Phosphoric Acid Anodize  10  2048.8  127.0

                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level                    ---------+---------+---------+---------+
None                                     (---*----)
Chromic Acid Etch                             (----*----)
Chromic Acid Anodize                          (---*----)
Sulfuric Acid Anodize                   (----*---)
Sulfuric "Hard" Anodize  (----*----)
Phosphoric Acid Anodize                           (----*----)
                         ---------+---------+---------+---------+
                               1000      1500      2000      2500

Pooled StDev = 372.3


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                           Lower  Center   Upper
Chromic Acid Etch         -199.1   293.0   785.1
Chromic Acid Anodize      -243.1   249.0   741.1
Sulfuric Acid Anodize     -517.6   -25.5   466.6
Sulfuric "Hard" Anodize  -1251.5  -759.4  -267.3
Phosphoric Acid Anodize     -7.3   484.8   976.9

                         -------+---------+---------+---------+--
Chromic Acid Etch                       (----*----)
Chromic Acid Anodize                    (---*----)
Sulfuric Acid Anodize                (----*----)
Sulfuric "Hard" Anodize      (----*----)
Phosphoric Acid Anodize                  (----*----)
                         -------+---------+---------+---------+--
                            -1000         0      1000      2000
```

Figure 63: Tukey's Analysis - H4800 (175°C)

2.6.2.1.5.2 Loctite® 435™

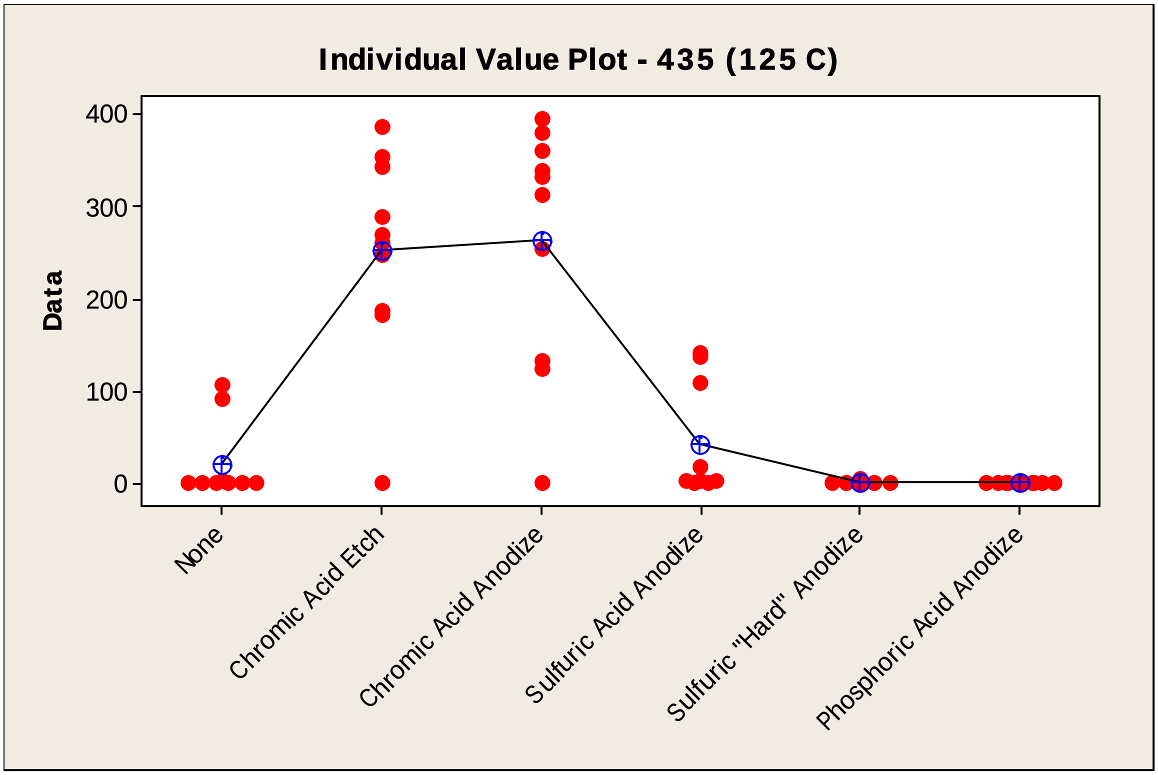


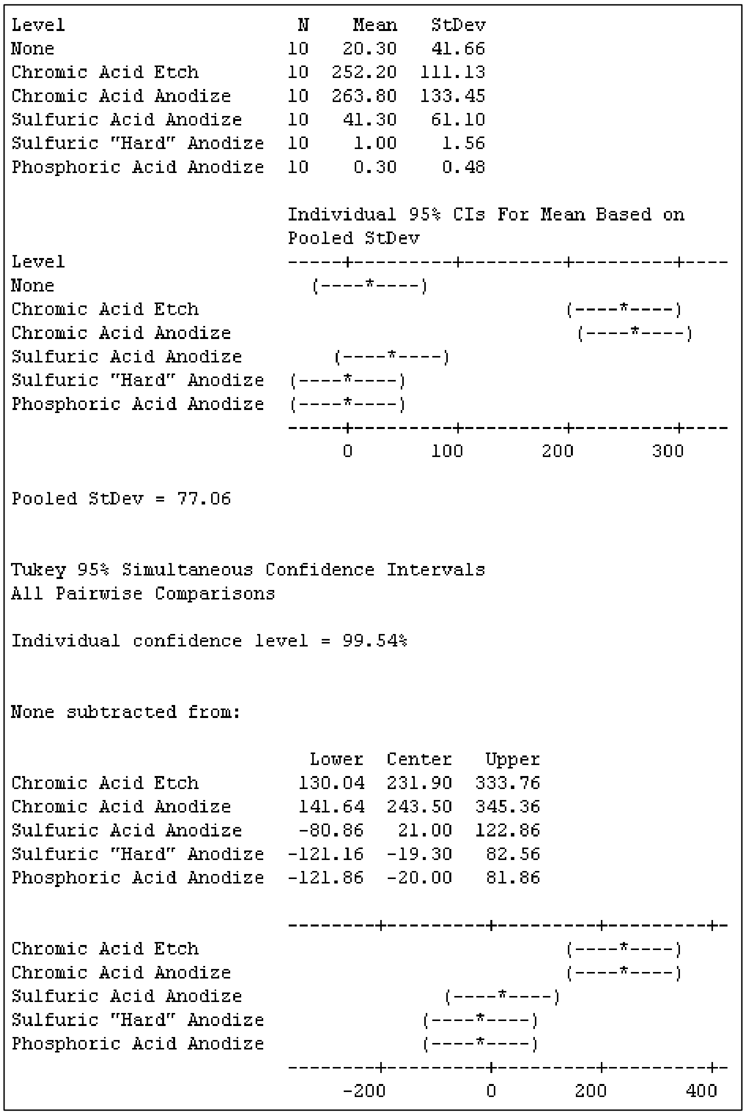
Figure 64: Individual Value Plot - 435 (125°C)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – 435 (125°C):

1. Chromic Acid Anodize (264)*
2. Chromic Acid Etch (252)*
3. Sulfuric Anodize (41)
4. None (20)
5. Sulfuric Hard Anodize (1)
6. Phosphoric Acid Anodize (0)

According to the Tukey analysis **[See Figure 65]**, chromic acid anodize & chromic acid etch both had greater average bond strengths that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                     N    Mean   StDev
None                     10   20.30   41.66
Chromic Acid Etch        10  252.20  111.13
Chromic Acid Anodize     10  263.80  133.45
Sulfuric Acid Anodize    10   41.30   61.10
Sulfuric "Hard" Anodize  10    1.00    1.56
Phosphoric Acid Anodize  10    0.30    0.48

                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level                    -----+---------+---------+---------+----
None                       (----*----)
Chromic Acid Etch                                 (----*----)
Chromic Acid Anodize                               (----*----)
Sulfuric Acid Anodize        (----*----)
Sulfuric "Hard" Anodize  (----*----)
Phosphoric Acid Anodize  (----*----)
                         -----+---------+---------+---------+----
                              0       100       200       300

Pooled StDev = 77.06


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                           Lower  Center   Upper
Chromic Acid Etch         130.04  231.90  333.76
Chromic Acid Anodize      141.64  243.50  345.36
Sulfuric Acid Anodize     -80.86   21.00  122.86
Sulfuric "Hard" Anodize  -121.16  -19.30   82.56
Phosphoric Acid Anodize  -121.86  -20.00   81.86

                         --------+---------+---------+---------+-
Chromic Acid Etch                                 (----*----)
Chromic Acid Anodize                              (----*----)
Sulfuric Acid Anodize                (----*----)
Sulfuric "Hard" Anodize            (----*----)
Phosphoric Acid Anodize            (----*----)
                         --------+---------+---------+---------+-
                              -200         0       200       400
```

Figure 65: Tukey's Analysis - 435 (125°C)

2.6.2.1.5.3 Loctite® 332™

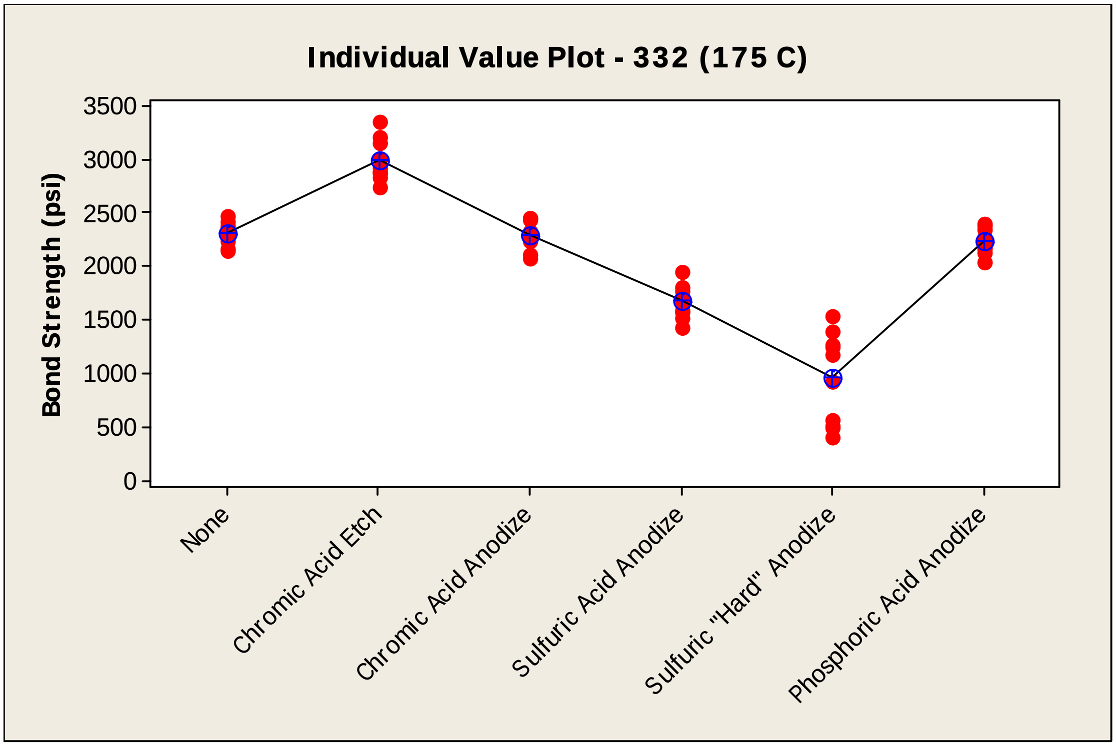


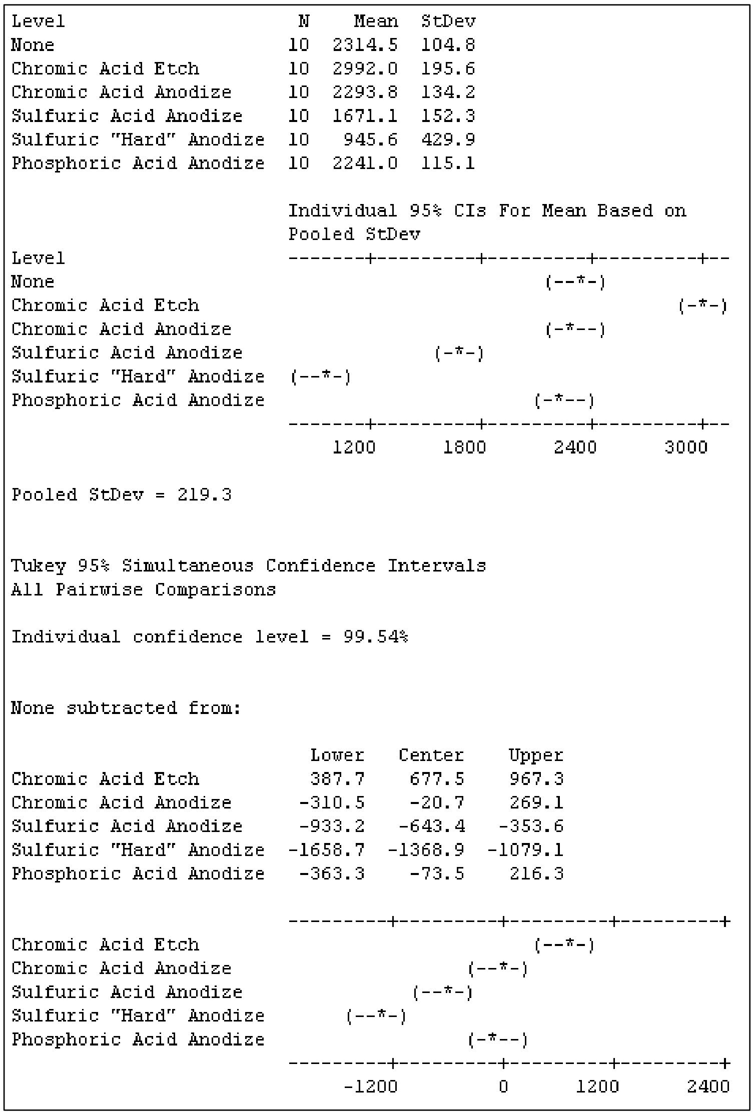
Figure 66: Individual Value Plot - 332 (175°C)

The previous individual value plot presents the difference in the data for all surface treatments evaluated while also identifying the scatter.

Ranked Average Bond Strengths (psi) – 332 (175°C):

1. Chromic Acid Etch (2992)*
2. None (2315)
3. Chromic Acid Anodize (2294)
4. Phosphoric Acid Anodize (2241)
5. Sulfuric Anodize (1671)
6. Sulfuric “Hard” Anodize (946)

According to the Tukey analysis **[See Figure 67]**, only chromic acid etch had a greater average bond strength that proved to be statistically significantly different from the control (None) at a 95% confidence interval.



```
Level                     N    Mean  StDev
None                     10  2314.5  104.8
Chromic Acid Etch        10  2992.0  195.6
Chromic Acid Anodize     10  2293.8  134.2
Sulfuric Acid Anodize    10  1671.1  152.3
Sulfuric "Hard" Anodize  10   945.6  429.9
Phosphoric Acid Anodize  10  2241.0  115.1

                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level                    -------+---------+---------+---------+--
None                                            (--*-)
Chromic Acid Etch                                           (-*-)
Chromic Acid Anodize                            (-*--)
Sulfuric Acid Anodize                 (-*-)
Sulfuric "Hard" Anodize  (--*-)
Phosphoric Acid Anodize                        (-*--)
                         -------+---------+---------+---------+--
                             1200      1800      2400      3000

Pooled StDev = 219.3


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.54%


None subtracted from:

                           Lower   Center    Upper
Chromic Acid Etch          387.7    677.5    967.3
Chromic Acid Anodize      -310.5    -20.7    269.1
Sulfuric Acid Anodize     -933.2   -643.4   -353.6
Sulfuric "Hard" Anodize  -1658.7  -1368.9  -1079.1
Phosphoric Acid Anodize   -363.3    -73.5    216.3

                         ---------+---------+---------+---------+
Chromic Acid Etch                              (--*-)
Chromic Acid Anodize                     (--*-)
Sulfuric Acid Anodize               (--*-)
Sulfuric "Hard" Anodize        (--*-)
Phosphoric Acid Anodize                  (-*--)
                         ---------+---------+---------+---------+
                              -1200         0      1200      2400
```

Figure 67: Tukey's Analysis - 332 (175°C)

2.6.2.2 Results by Surface Treatment

In order for a given surface treatment to be considered successful it must be able to maintain its strength with the bonded adhesive in adverse conditions. Previously we compared the performance of the six surface treatments within the respective conditions that they were exposed to. Now we will investigate how each specific surface treatment reacted to adverse conditions (heat/humidity aging) compared to its unconditioned control.

In the **Table 23** below, within each surface treatment, the unconditioned control was compared to its conditioned counterparts. It was then determined, using Minitab, whether or not the conditioned counterpart was statistically significantly weaker than the unconditioned control at a 95% confidence interval. If so, that particular condition was considered to be a failure. The number in the parentheses is "[average bond strength of the unconditioned control]-[the average bond strength of the respective condition]"

Table 23: Pass/Fail Test for Conditioned Assemblies

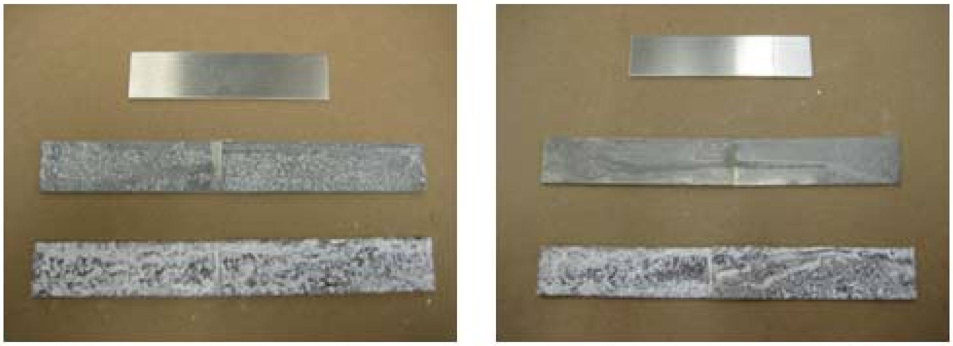
Treatment	**Adhesive**	**Conditioning**			
		Salt Fog	**Condensing Humidity**	**Heat 1**	**Heat 2**
Chromic Acid Etch	**H4800**	Fail (1511)	Fail (977)	Pass (-1144)	Fail (988)
	435	Fail (2458)	Fail (892)	Fail (1222)	Fail (2270)
	332	Fail (1458)	Fail (1035)	Pass (461)	Pass (6)
Chromic Acid Anodize	**H4800**	Pass (212)	Fail (831)	Pass (-753)	Fail (750)
	435	Pass (-33)	Fail (600)	Fail (403)	Fail (2000)
	332	Fail (208)	Fail (230)	Pass (93)	Pass (-165)
Sulfuric Acid Anodize	**H4800**	Pass (147)	Fail (362)	Fail (389)	Fail (1170)
	435	Fail (408)	Fail (737)	Fail (873)	Fail (1645)
	332	Pass (75)	Pass (173)	Fail (782)	Fail (840)
Sulfuric Hard Anodize	**H4800**	Fail (713)	Fail (800)	Fail (706)	Fail (1809)
	435	Pass (191)	Fail (833)	Fail (1426)	Fail (2393)
	332	Pass (285)	Pass (-163)	Pass (98)	Pass (-112)
Phosphoric Acid Anodize	**H4800**	Pass (-95)	Pass (200)	Pass (-581)	Fail (861)
	435	Pass (140)	Pass (-293)	Fail (1227)	Fail (3608)
	332	Pass (79)	Pass (-39)	Pass (113)	Pass (-67)
Untreated	**H4800**	Pass (159)	Fail (534)	Pass (-1582)	Fail (653)
	435	Fail (2104)	Fail (574)	Fail (1024)	Fail (2084)
	332	Fail (624)	Fail (568)	Pass (-110)	Pass (-444)

As was previously mentioned, in order for any one of these surface treatments to be considered successful, regardless of the initial bond strengths that it may achieve, it needs to maintain its strength in adverse conditions. According to the Minitab analyses performed to complete **Table 23**, it was noticed that every single surface treatment failed at the following adhesive and conditioning combination; H4800 at 175°C, 435 at 100°C & 435 at 125°C. Therefore, those three combinations must be excluded from consideration. After excluding those three combinations, there is only one surface treatment that stands out above the rest when it comes to maintaining strength in adverse conditions. That particular surface treatment is phosphoric acid anodizing, passing the 9 remaining adhesive and conditioning combinations. Sulfuric “hard” anodizing and chromic acid anodizing tied for second place, passing 5 of 9 the remaining adhesive and conditioning combinations.

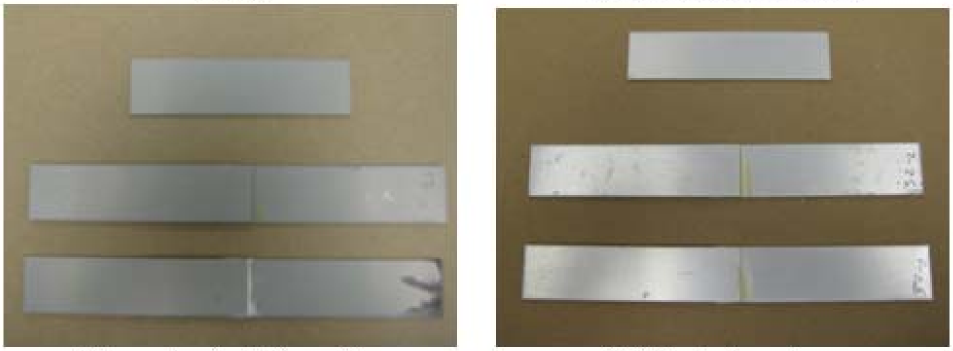
Not only did phosphoric acid anodizing outperform every other surface treatment by maintaining its strength through adverse conditions, it also showed much less variance compared to the current surface treatment that Henkel uses, chromic acid etching. More specifically it did as good, or better, than chromic acid etching for every single adhesive/conditioning combination. For 5 of the 9 adhesive/conditioning combinations it proved to have a statistically significantly lower variance than chromic acid etching at a 95% confidence interval.

2.6.2.2.1 Visual Observations

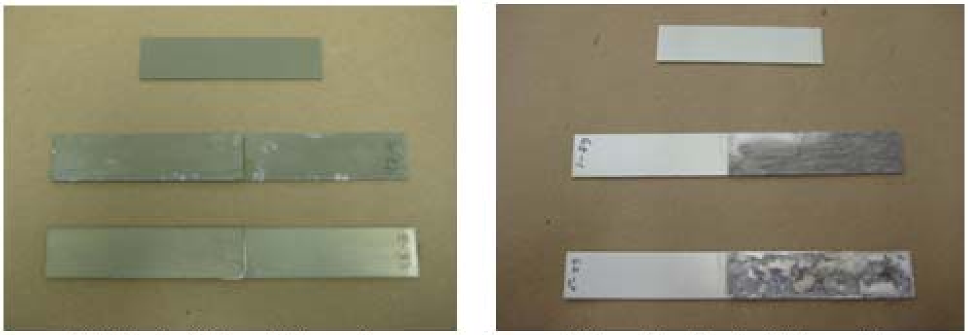
As the testing progressed, it became visually apparent which substrates provided better resistance against humid environments. Below are images **[See Figure 68]** which display each substrate after exposure to 2 weeks of conditioning, in both salt fog and condensing humidity chambers.



None **Chromic Acid Etch**



Chromic Acid Anodize **Sulfuric Anodize**



Sulfuric "Hard" Anodize **Phosphoric Acid Anodize**

Figure 68: Surface Treatment's Resistance to Humid Environments

*Note: Only the left side of the phosphoric acid anodized specimen is representative of how it reacts to humid environments. This is due to the fact that only one side of the treated lap shears was primed with BR-127.

Visual inspection of the treated aluminum assemblies revealed little change in appearance after exposure to the humid environments.

As stated before, only one side of the phosphoric acid anodized specimen was treated with the BR-127 primer. The primed surface, visually, seemed to provide better corrosion resistance than the un-primed side. Also, it was observed that the chromic acid etched specimen had a very similar resistance to the humid environments to untreated specimens. This may very well be because only a small portion of each lap shear was chromic acid etched. Only the bond area of each aluminum lap shear was etched, leaving the rest of the surface area susceptible to corrosion. In turn, the corrosion on the untreated portion may have affected the treated portion of the lap shear, thus, not properly representing it’s resistance in humid environments.

3.0 Conclusions

During the 8 weeks spent here at Henkel, many conclusions were made based on the results obtained during experimental procedures. In this section of the report, these conclusions are presented.

3.1 Chromic Acid Etching Process

Throughout all the experimental procedures completed here at Henkel, using the current chromic acid etching system, some conclusions were made that improved the overall performance of the treated specimens. These conclusions are discussed below.

3.1.1 Design and Assembly of System

The previous chromic acid etching system at Henkel Loctite had several flaws and it was important to correct them by designing and building an entirely new system. A beaker filled with the chromic acid was used and test specimens were hand placed into the beaker then taken out manually. This beaker was heated with a hot plate and the temperature was monitored with a glass thermometer. In order to maintain the required temperature of 70 degrees Celsius, the hot plate had to be hand adjusted, resulting in temperatures greater than or less than the required operating temperature.

The new system used a water bath with an automatic temperature controller and a stand was built surrounding the bath to hold 20 lap shears, thus allowing 20 specimens to be treated at once in uniform. This resulted in more accurate and consisted results from the previous method. Also, it was a much safer method than using a hot plate because the acid bath was secured in the water bath instead of sitting freely. The freshly treated lap shears were able to be cleaned with water before any manual removal from the system, ensuring further safety and more accurate results.

3.1.2 Degradation

It was important for our sponsor to understand whether or not the chromic acid bath degraded after treating a certain amount of test specimen. This could potentially cause a drop in bond strength of the treated specimen, affecting the consistency of data. The chromic acid bath, contrary to what was initially thought, did not degrade after simulating treatment of 1000 aluminum lap shears. After the addition of 0.16 grams of aluminum powder (1000 lap shears), there was no significant difference in bond strength between lap shears treated with the “fresh” bath and those treated with the “degraded” bath. This is an important result, ensuring that bath degradation will not be a concern for all future projects that involve chromic acid etching.

3.1.3 Cleaning Method

It was also important for our sponsor to ensure that the current process in which specimen are treated, obtained the best results possible. One possible area for improvement involved the cleaning after treatment and prior to bonding. The investigation as to whether or not cleaning the treated aluminum surface with isopropyl alcohol prior to bonding had any effect on bond strength proved to be negative. Both the average bond strength and standard deviation between cleaned and non-cleaned samples did not prove to be statistically significantly different. However, wiping the samples with Kimwipes directly after being removed from the chromic acid bath did prove to have a statistically significantly better bond strength compared to drying them in an oven. This too proved to be a very significant result. By modifying the previous process used here at Henkel, we were able to improve bond strength while minimizing variance, which is a result that is always desired.

3.2 Comparative Surface Treatment Analysis

When evaluating a specific surface treatment, there are many important factors one must consider. The most obvious factor is performance; however, there are others that must also be analyzed in order to determine if a specific treatment method is a viable one.

3.2.1 Performance

Below is a list of the three most important factors when evaluating the *performance* of a surface treatment method on aluminum:

1. Achieving high bond strength.
2. Maintaining that bond strength through adverse conditions
3. Minimizing scatter in the bond strength data.

The only surface treatment method that successfully addressed those three performance factors was phosphoric acid anodizing. Therefore, it has been concluded that it is the best *performing* surface treatment method.

3.2.2 Cost

Cost is very important when evaluating which surface treatment that should be incorporated into Henkel's future testing. For example, if a particular surface treatment had superior performing qualities, but was very expensive, it may not be profitable to take for the company to pursue. On the other hand, if a particular surface treatment was rather inexpensive, but performed rather poorly, then it wouldn't be plausible for the company to pursue. So the ideal candidate falls somewhere in the middle of those two scenarios.

Now, further analyzing our particular cases, we can determine a ranked system for all the surface treatments previously evaluated. Chromic Acid Etching has been neglected from the following assessment since it would be rather difficult to determine just how much it costs to treat a given amount of specimen. This is simply because there are too many variables to take into consideration such as, supply cost, laboratory cost (technician's time), and waste disposal. Also, it is the companies desire to eventually steer away from the use of chromic acid etching due to the safety and environmental concerns associated with it. Sulfuric acid anodized specimens were also neglected, since they are a standard test specimen that Henkel currently stocks in their laboratories.

Table 24 below presents the cost of each all surface treatments previously evaluated.

Table 24: Cost of Surface Treatments

Surface Treatment	Cost Per 1 Lap Shear (USD)
Chromic Acid Anodize	1.30$
Sulfuric "Hard" Anodize	2.62$
Phosphoric Acid Anodize	3.00$

Since it isn't our decision on how much money Henkel would be willing to spend for future testing, all we can do is provide the cost. It is of the discretion of our liaison to decide if the performance to price ratio is worth pursuing in the future.

3.2.3 Ease of Use – Safety

It is also very important that the certain surface treatment that Henkel uses in future testing be very safe and relatively easy to use. Since the only surface treatment method that was done "in house" was chromic acid etching, it is the only candidate that is considered to have any safety issues whatsoever. All the other specimens were sent out for treatment, resulting in virtually no concerns.

3.2.4 Use in Industry

A given surface treatment's use in industry is also of importance to Henkel. Since Henkel is a client driven company, they will benefit if they can provide testing on a surface treatment that is widely used in industry. From the previous research done, it was established that the most widely used surface preparation technique on aluminum in industry, is phosphoric acid anodizing. It is the preferred treatment of the aerospace industry because the oxide layer formed is thicker than chromic acid etching, and the "whiskers" (which increase surface area) are much longer in phosphoric acid anodizing process.

4.0 Recommendations

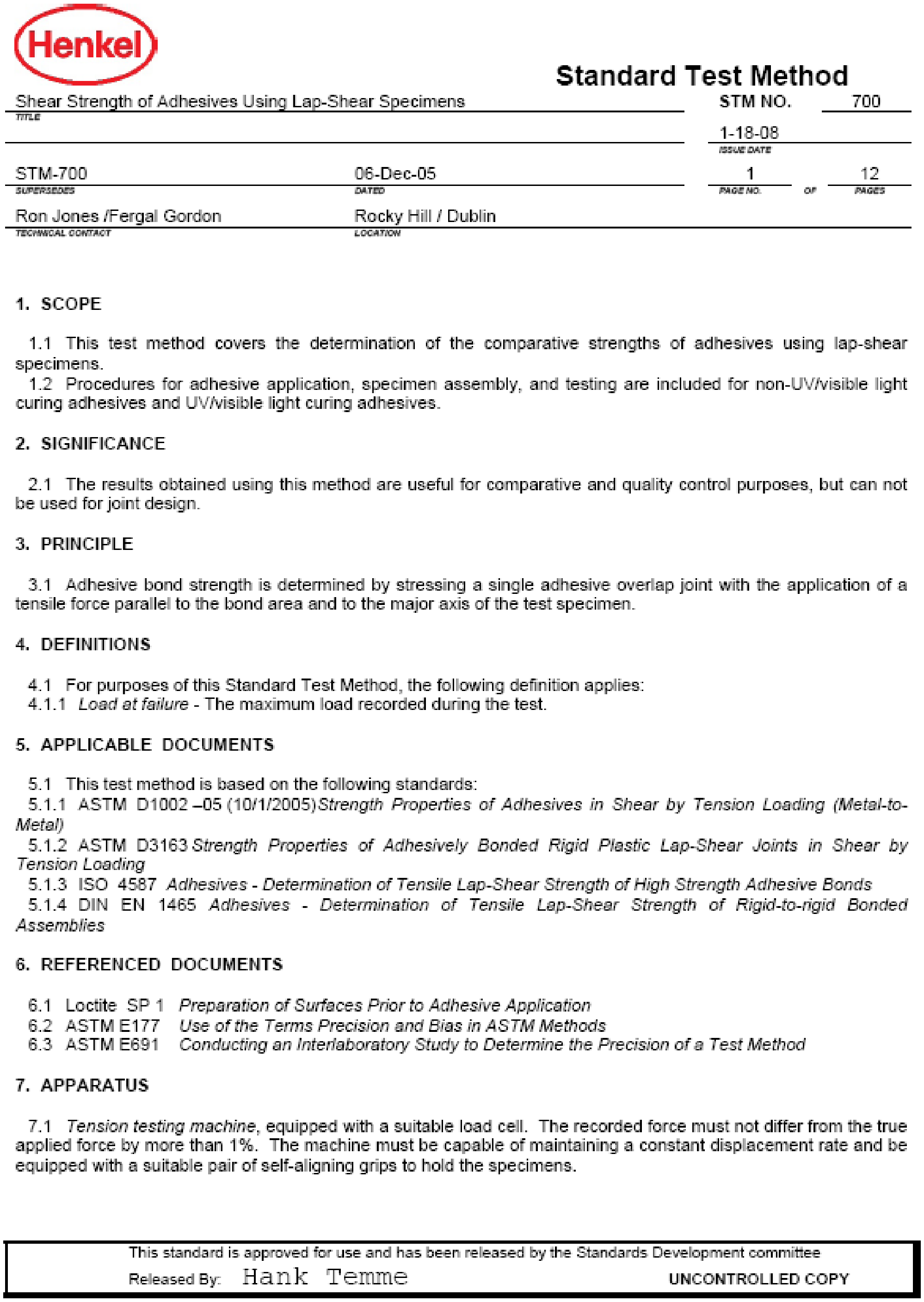
Results obtained from this project reflect short time periods of treating aluminum specimens, bonding them, and testing their bond strengths. It is recommended that additional testing take place with unused treated lap shears to ensure that the data portrayed in this project is completely accurate. A larger water bath was ordered to conduct future chromic acid etching for the sponsor. Because the water bath used in all experiments in this project was rather small, a limited number of aluminum lap shears could be treated at once. A larger water bath will allow more specimens to be treated in one batch, possibly producing more accurate results and requiring less time. After testing was completed, certain conclusions were drawn due to the success of our designed system. A larger water bath was purchased to accommodate various test specimens and can be seen below in **Figure 69.**

Figure 69: Large Water Bath

It is also recommended that the environmental conditions be changed slightly to fully ensure that a certain type of surface treatment method performs better in some conditions and worse in others. For this project, the lap shears were placed in salt fog chambers, regular fog chambers, and heated ovens for exactly two weeks. Placing assemblies in these chambers for longer periods of time and at different temperatures would give a very wide and descriptive range of results.

Also, shear strength was the only variable tested in these experiments. To get a better idea of how strong the bond really is, it would be beneficial to perform other test methods, such as peel strength, in which the entire lap shear is bonded then peeled off using the Instron machine. Looking at the bond strength from multiple angles will give Loctite more detailed information on each surface treatment with a particular adhesive.

Appendix A: STM 700



Henkel

Standard Test Method

Shear Strength of Adhesives Using Lap-Shear Specimens
TITLE

STM NO. 700

1-18-08
ISSUE DATE

STM-700
SUPERSEDES

06-Dec-05
DATED

1
PAGE NO.
OF
12
PAGES

Ron Jones /Fergal Gordon
TECHNICAL CONTACT

Rocky Hill / Dublin
LOCATION

1. SCOPE

1.1 This test method covers the determination of the comparative strengths of adhesives using lap-shear specimens.
1.2 Procedures for adhesive application, specimen assembly, and testing are included for non-UV/visible light curing adhesives and UV/visible light curing adhesives.

2. SIGNIFICANCE

2.1 The results obtained using this method are useful for comparative and quality control purposes, but can not be used for joint design.

3. PRINCIPLE

3.1 Adhesive bond strength is determined by stressing a single adhesive overlap joint with the application of a tensile force parallel to the bond area and to the major axis of the test specimen.

4. DEFINITIONS

4.1 For purposes of this Standard Test Method, the following definition applies:
4.1.1 *Load at failure* - The maximum load recorded during the test.

5. APPLICABLE DOCUMENTS

5.1 This test method is based on the following standards:
5.1.1 ASTM D1002 –05 (10/1/2005) *Strength Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal)*
5.1.2 ASTM D3163 *Strength Properties of Adhesively Bonded Rigid Plastic Lap-Shear Joints in Shear by Tension Loading*
5.1.3 ISO 4587 *Adhesives - Determination of Tensile Lap-Shear Strength of High Strength Adhesive Bonds*
5.1.4 DIN EN 1465 *Adhesives - Determination of Tensile Lap-Shear Strength of Rigid-to-rigid Bonded Assemblies*

6. REFERENCED DOCUMENTS

6.1 Loctite SP 1 *Preparation of Surfaces Prior to Adhesive Application*
6.2 ASTM E177 *Use of the Terms Precision and Bias in ASTM Methods*
6.3 ASTM E691 *Conducting an Interlaboratory Study to Determine the Precision of a Test Method*

7. APPARATUS

7.1 *Tension testing machine*, equipped with a suitable load cell. The recorded force must not differ from the true applied force by more than 1%. The machine must be capable of maintaining a constant displacement rate and be equipped with a suitable pair of self-aligning grips to hold the specimens.

This standard is approved for use and has been released by the Standards Development committee
Released By: Hank Temme
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7.2 *Temperature Chamber*, designed for use with the tension testing machine for testing at low and elevated temperatures.

7.3 *Measuring device*, suitable for measuring out an overlap area.

7.4 *Clamps*, capable of applying a clamp load of 45 to 90 N (10 to 20 lbs.) such as Hargrave No. 1 spring clamps.

7.5 *Weight blocks*, weighing approximately 170 g. each and having approximate dimensions of 44.5 by 24.5 by 19.1 mm (1.75 by 1 by 0.75 in.) such as the lower half of an impact block set.

7.6 *Timing device*, appropriate for measuring specified times.

7.7 *Light source,* for UV/visible light curing, capable of producing the required intensity at the appropriate wave length as specified in the quality specification, product profile, or test program.

7.8 *Light meter and probe,* for UV/visible light curing, capable of accurately measuring the specified irradiance at the appropriate wave length.

7.9 *Assembly/cure fixture*, as shown in Figure 6, or equivalent, for use in assembling and curing specimens with UV/visible light curing adhesives .

8. TEST SPECIMENS

8.1 *Lap-shear specimens*, as specified in the quality specification, product profile, or test program. Use Loctite Standard Practice 1 for preparing the surface of the lap-shear specimens as specified in the quality specification, product profile, or test program.

8.2 *Gap spacers*, having the appropriate thickness suitable for inducing gaps in the lap-shear assemblies as specified in the quality specification, product profile, or test program. All gap spacers used must be listed on the approved test specimen list.

9. ASSEMBLY PROCEDURE FOR NON-UV/VISIBLE LIGHT CURING ADHESIVES

9.1 Assemble and test five test specimens for each test point unless additional specimens are specified in the quality specification, product profile, or test program.

9.2 If an activator or primer is specified in the quality specification, product profile, or test program, refer to Loctite Standard Practice 1 for application and proper handling of activators and primers.

9.3 Isopropyl alcohol wipe all specimens in accordance with Loctite Standard Practice 1.

9.4 The assembly procedures that follow are recommended for non-UV/visible light curing adhesives, and have been shown to give reasonably consistent results. However, it is recognized that there may be procedures that may yield equivalent results. Comparable procedures may be used if the procedures ensure that the test specimens are properly aligned, and the results are not influenced by the introduction of additional variables associated with the procedures.

9.4.1 While the assembly procedures may be varied if the criteria detailed in 9.4 is met, deviations from the techniques described for the application of the adhesive are not permitted. It is also not permissible to "swirl" or rub mating lap-shear specimens together.

9.5 Assemble **non-induced gap** specimens as follows:

9.5.1 Position lap-shear specimens as shown in Figure 1 with the prepared surfaces up.

9.5.2 For cyanoacrylate adhesive cures of ≤5 minutes, apply a small drop of adhesive to the prepared surface of one lap-shear specimen.

9.5.3 For two-part adhesive systems that are not mixed prior to application, apply as follows:

9.5.3.1 *Bead-on-bead* - Apply a bead of Part A to the prepared surface of one lap-shear specimen and a bead of Part B to the prepared surface of the mating lap-shear specimen such that when the lap-shear specimens are mated the two beads contact each other fully. Apply sufficient quantities of each part so as to ensure complete coverage of a 322.6 mm^2 (0.5 in.^{2}) area.

9.5.3.2 *Bead-by-bead* - Apply a bead of Part A to the prepared surface of one lap-shear specimen and a bead of Part B next to the bead of Part A on the same lap-shear specimen. Apply sufficient quantities of each part so as to ensure complete coverage of a 322.6 mm^2 (0.5 in.^{2}) area.

9.5.4 For all other adhesives apply a bead of adhesive to the prepared surface of one lap-shear specimen of sufficient quantity such that when the lap-shear specimens are mated a 322.6 mm^2 (0.5 in.^{2}) area will be completely covered. If necessary, spread the adhesive using an appropriate utensil (applicator stick, tongue depressor, etc.) so as to ensure complete coverage of the bond area.

Note 1 - Excess cyanoacrylate adhesive in the bond area may have an adverse effect on cured performance.

9.5.5 Taking care so as not to lift the lap-shear specimens off the work surface, turn both lap-shear specimens at once onto their inside edges such that a 12.7 mm (0.5 in.) overlap will result when the bonding surfaces are mated.

Note 2 - When plastic lap-shear specimens are used, it is permissible to decrease the overlap length in order to ensure that failure occurs in the adhesive joint rather than in the substrate.

9.5.6 Press the mating surfaces together using the thumb and index finger and clamp the assembly on each side of the bond area approximately 6.4 mm (0.25 in.) from each edge making sure that proper alignment of the lap-shear specimens is achieved.

Note 3 - When using cyanoacrylate adhesives or if a two-side primed assembly is specified, failure to assemble the bond within the minimum time period may result in inconsistent results due to premature curing of the adhesive.

9.6 Assemble **induced gap** specimens using the clamp method described in 9.6.1. If after testing, cured material is evident only in the area around the gap spacers, repeat the test following the block method described in 9.6.2.

9.6.1 **Clamp Method**

9.6.1.1 Apply a sufficient quantity of adhesive to the prepared surface of one lap-shear specimen such that when the mating lap-shear specimen is placed on top of the adhesive a 322.6 mm^2 (0.5 in.^{2}) area will be completely covered.

9.6.1.2 Place two appropriate gap spacers into the adhesive approximately 6.4 mm (0.25 in.) in from each edge such that they extend through the bond area as shown in Figure 2.

9.6.1.3 Place the mating lap-shear specimen onto the adhesive and clamp the assembly on each side of the bond area approximately 6.4 mm (0.25 in.) from each edge making sure that proper alignment of the lap-shear specimens is achieved.

9.6.2 **Block Method**

9.6.2.1 Bend an appropriate gap spacer into a "V" shape and place it onto the prepared surface of one lap-shear specimen such that the two ends of the "V" shaped gap spacer protrude approximately 1.6 mm (.0625 in.) into the 322.6 mm^2 (0.5 $in.^2$) bond area . Place an additional gap spacer onto a spacer lap-shear specimen as shown in Figure 3 (spacer lap-shear specimen must be the same thickness as the lap-shear test specimen).

9.6.2.2 Apply a sufficient quantity of adhesive such that when the mating lap-shear specimen is placed on top of the adhesive, a 322.6 mm^2 (0.5 $in.^2$) area will be completely covered (See Figure 4).

9.6.2.3 Place one end of the prepared surface side of the mating lap-shear specimen onto the adhesive, with the other end resting on the gap spacer on the spacer lap-shear specimen and press the mating lap-shear specimen gently until resistance from the gap spacer in the adhesive is felt.

9.6.2.4 If the gap spacer in the adhesive begins slipping out of the bond area, push it back into the bond area to the required distance using a stability stick and hold it there until resistance is felt.

9.6.2.5 Place a weight block on top of the mating lap-shear specimen over the bond area to achieve a final assembly as shown in Figure 5 taking care to ensure proper alignment of the lap-shear specimens.

9.7 Cure the adhesive assemblies as specified in accordance with the quality specification, product profile, or test program. Use an appropriate timing device to ensure that the cure time is not less than the time specified, nor greater than 110% of the time specified.

9.8 Remove all clamps or weight blocks after the specified cure time unless otherwise specified in the quality specification, product profile, or test program.

10. ASSEMBLY PROCEDURE FOR UV/VISIBLE LIGHT CURING ADHESIVES

10.1 Assemble and test five test specimens for each test point unless additional specimens are specified in the quality specification, product profile, or test program.

10.2 If an activator or primer is specified in the quality specification, product profile, or test program, refer to Loctite Standard Practice 1 for application and proper handling of activators and primers.

10.3 Isopropyl alcohol wipe all specimens in accordance with Loctite Standard Practice 1.

10.4 The assembly procedures that follow are recommended for UV/visible light curing adhesives, and have been shown to give reasonably consistent results. However, it is recognized that there may be procedures that may yield equivalent results. Comparable procedures may be used if the procedures ensure that the test specimens are properly aligned, and the results are not influenced by the introduction of additional variables associated with the procedures.

10.4.1 While the assembly procedures may be varied if the criteria detailed in 10.4 is met, deviations from the techniques described for the application of the adhesive are not permitted. It is also not permissible to "swirl" or rub mating lap-shear specimens together.

10.5 Set the light for the proper intensity at the proper wave length and map out the area where the irradiance at the bond line (through the specimen) is +10% -0% of that specified. This area is referred to as the exposure area.

Note 4 - For lights without an automatic shutter and for fixture times under 15 seconds it is strongly suggested that a sheet of non-light transmitting material is placed over the assemblies and fixture to block the light as it is positioned under the light source. The non-light transmitting sheet is then used as a shutter allowing accurate exposure times to be achieved.

10.6 Assemble **non-induced gap** specimens on an assembly/cure fixture as follows:

10.6.1 Apply a bead of adhesive to the prepared surface of one lap-shear specimen of sufficient quantity such that when the lap-shear specimens are mated a 322.6 mm^2 (0.5 $in.^2$) area will be completely covered.

10.6.2 Place one end of the prepared surface side of the mating lap-shear specimen onto the adhesive with the other end resting on the spacer lap-shear specimen (see Fig 6), and press the mating lap-shear specimen gently until resistance from the lap-shears coming together is felt.

10.6.3 Place a weight block on top of the mating lap-shear specimen to achieve a final assembly as shown in Figure 6 taking care to ensure proper alignment of the lap-shear specimens. Make sure the block is behind the bond area so as not to block any of the light during exposure.

10.6.4 Cure the lap-shear specimen(s) on the fixture under the light in the exposure area for the required exposure time specified in the quality specification, product profile, or test program.

10.7 Assemble **induced gap specimens** on an assembly/cure fixture as follows:

10.7.1 Bend an appropriate gap spacer into a "V" shape and place it onto the prepared surface of the lap-shear specimen such that the two ends of the "V" shaped spacer protrude approximately 2 mm (.0625 in.) into the 322.6 mm^2 (0.5in.^{2}) bond area. Place an additional gap spacer onto a spacer lap-shear specimen as shown in Figure 7 (spacer lap-shear specimen must be the same thickness as the lap-shear test specimen).

10.7.2 Apply a sufficient quantity of adhesive to the prepared surface of the lap-shear specimen such that when the mating lap-shear specimen is placed on top of the adhesive, a 323 mm^2 (0.5 in.^{2}) area will be completely covered.

10.7.3 Place one end of the prepared surface side of the mating lap-shear specimen onto the adhesive with the other end resting on the gap spacer on the spacer lap-shear specimen, and press the mating lap-shear specimen gently until resistance from the gap spacer in the adhesive is felt.

10.7.4 If the gap spacer in the adhesive begins slipping out of the bond area, push it back into the bond area to the required distance using a stability stick and hold it there until resistance is felt.

10.7.5 Place a weight block on top of the mating lap-shear specimen behind the bond area to achieve a final assembly as shown in Figure 8 taking care to ensure proper alignment of the lap-shear specimens. Make sure the block is behind the bond area so as not to block any of the light during cure.

10.7.6 Cure the lap-shear specimen(s) on the fixture under the light in the exposure area for the required exposure time specified in the quality specification, product profile, or test program.

11. TEST PROCEDURE

11.1 If adhesive assemblies are cured or aged under conditions other than ambient, allow the assemblies to return to room temperature for a period of one hr. ± 5 min. prior to testing unless otherwise specified in the quality specification, product profile, or test program.

11.2 Carry out hot and cold strength testing at the temperature specified in the quality specification, product profile, or test program in a chamber designed for use with the tension testing machine. If this type of chamber is not available, use a standard oven/chamber for the temperature soaking of the assemblies and the jaws of the testing machine, and test the assemblies within 30 seconds of removal from the oven/chamber.

11.3 After allowing for cure, and any environmental conditioning (heat aging, salt fog,etc.), as specified in the quality specification, product profile, or test program, determine the shear strength as follows:

11.3.1 Place the test specimen in the grips of the testing machine so that the outer 25.4 mm (1 in.) of each end are grasped by the jaws and so that the long axis of the test specimen coincides with the direction of applied tensile force through the center line of the grip assembly.

11.3.2 Test the assembly at a crosshead speed of 2.0 mm/min or 0.05 in./min., unless otherwise specified in the quality specification, product profile, or test program, until the assembly can no longer support a load.

Note 5 - When testing plastic substrates, if the tension testing machine is capable of testing using a rate of loading, the assemblies may be tested at a rate of 8.3 to 9.7 MPa (1200 to 1400 psi) of shear area per minute.

11.3.3 Record the load at failure.
11.3.4 Record the failure mode when required by the quality specification, product profile, or test program.

12. CALCULATIONS

12.1 Determine the bond area as follows:
12.1.1 For a **rectangular** shaped bond area;

$$A = lw$$

Where
A = bond area in mm^2 (in^2)
l = length of the bond in mm (in)
w = width of the bond in mm (in)

12.1.2 For a **circular** or **oval/elliptical** shaped bond area;

circle $A = \pi R^2$

where
A = bond area in mm^2 (in^2)
π = 3.1416
R = radius of the circle in mm (in)

oval/ellipse $A = \pi ab$

where
A = bond area in mm^2 (in^2)
π = 3.1416
a = ½ length of major axis in mm (in)
b = ½ length of minor axis in mm (in)

12.2 Calculate the lap-shear strength as follows:

$$S = L / A$$

Where
S = lap-shear strength in N/mm^2 (psi)
L = load at failure in N (lbs)
A = bond area in mm^2 (in^2)

13. RECORDS

13.1 Record the following information:
13.1.1 Identification of the adhesive including name or number, and lot number,
13.1.2 Identification of the lap-shear specimen used including substrate and dimensions,
13.1.3 Surface preparation used to prepare the lap-shear specimens,
13.1.4 Induced gaps, if any,
13.1.5 Cure conditions,
13.1.6 Test conditions,

13.1.7 Environmental conditioning, if any,
13.1.8 Number of specimens tested, if other than 5,
13.1.9 Results for each specimen,
13.1.10 Average lap-shear strength for all replicates,
13.1.11 Exceptions to the use of clamps, when testing non-UV/visible light curing adhesives,
13.1.12 Overlap length used, if other than 12.7 mm (0.5 in.),
13.1.13 Failure mode for each specimen when required by the quality specification, product profile, or test program,
13.1.14 Any deviation from this method.

14. PRECISION

14.1 An interlaboratory study was conducted, in accordance with ASTM E691, using 1 inch by 4 inch by 0.063 inch gritblasted steel lap-shear specimens. Six laboratories tested three adhesives using five replicates per adhesive. All specimens were cured for 24 hours @ 70 to 74° F and 45 to 50% relative humidity. Specimens were tested using a calibrated tensile testing machine with a 10,000 pound load cell. Values are in psi, unless otherwise noted. The following precision parameters, as defined in ASTM E177 were generated as a result of the study:

Summary of Precision Parameters

Matl	Avg	S_r	$CV\%_r$	S_R	$CV\%_R$	r	R
A	2663	236	8.9	399	15.0	662	1118
B	2003	200	10.0	299	14.9	561	838
C	2538	161	6.3	249	9.8	450	696

Where Avg = Average for the Six Laboratories
S_r = Repeatability Standard Deviation
$CV\%_r$ = Repeatability Coefficient of Variation
S_R = Reproducibility Standard Deviation
$CV\ \%_R$ = Reproducibility Coefficient of Variation
r = 95% Repeatability Limit
R = 95% Reproducibility Limit

Standard Test Method

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STM-700 SUPERSEDES	06-Dec-05 DATED	8 PAGE NO. OF	12 PAGES
Ron Jones /Fergal Gordon TECHNICAL CONTACT	Rocky Hill / Dublin LOCATION		

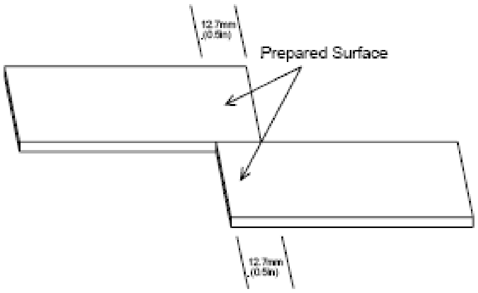


Figure 1
Position of Lap-Shear Specimens
Non-induced Gap

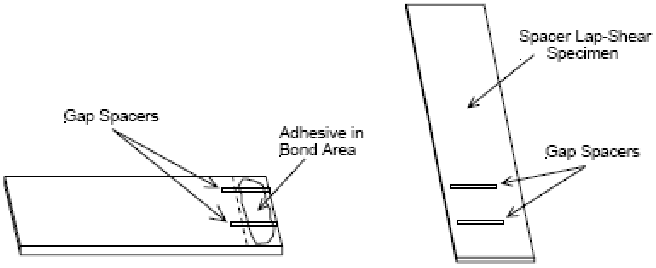


Figure 2
Gap Spacer Position
Clamp Method

This standard is approved for use and has been released by the Standards Development committee
Released By: Hank Temme **UNCONTROLLED COPY**

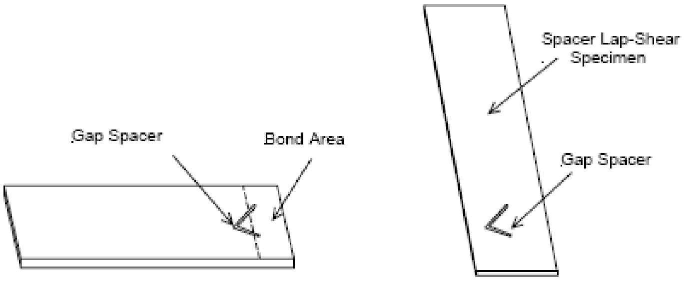


Figure 3
Gap Spacer Position
Block Method

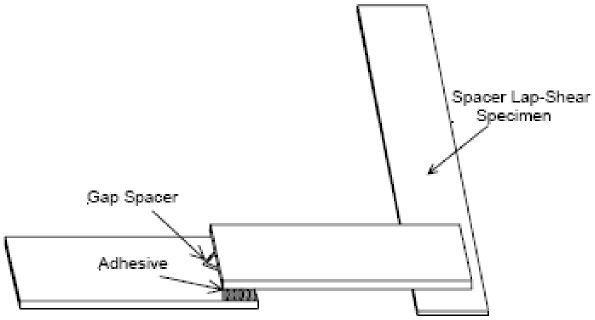


Figure 4
Mated - Gap Induced
Block Method

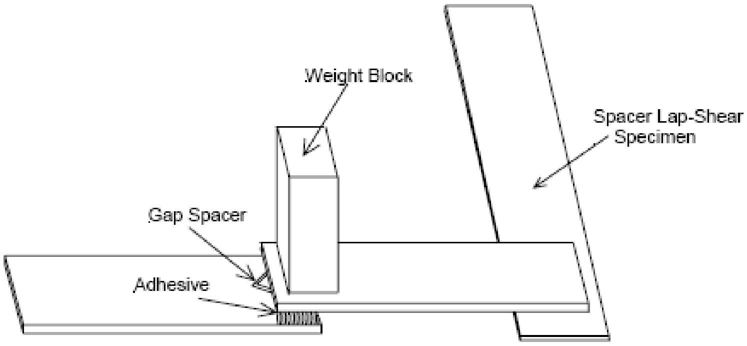


Figure 5
Gap Induced - Final Assembly
Block Method

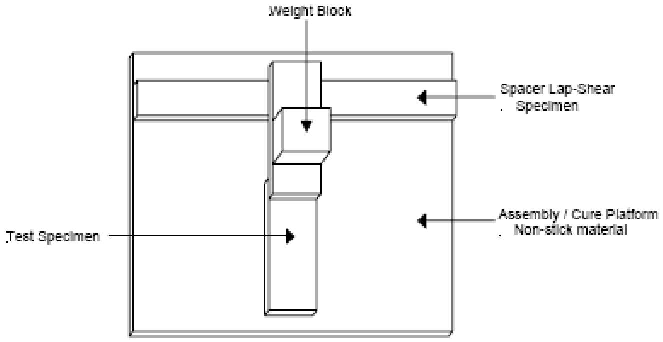


Figure 6
Assembly / Cure Fixture

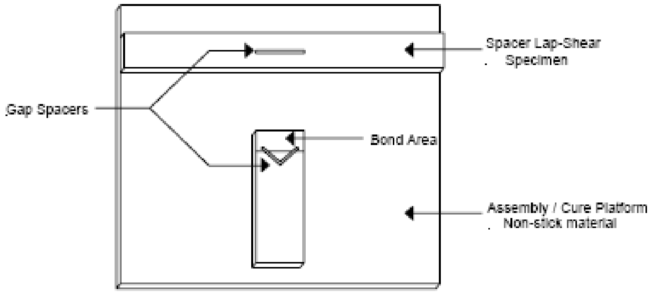


Figure 7
Gap Spacer Position

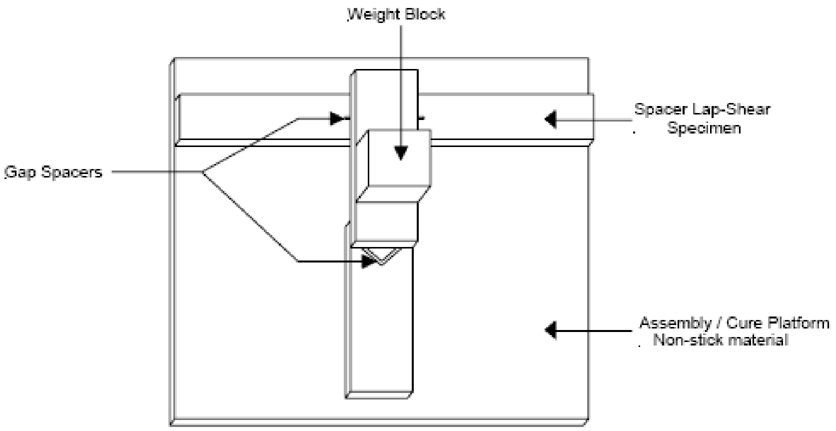


Figure 8
Gap Induced - Final Assembly

Appendix B: Chromic Acid Bath Calculations

Composition of Chromic Acid Bath:

10 parts by weight sulfuric acid (H_2SO_4)
1 part by weight sodium dichromate ($Na_2Cr_2O_7$)
30 parts by weight water (H_2O)

Molecular Mass of Bath:

H_2SO_4: 98 g/mol
$Na_2Cr_2O_7$: 298 g/mol
H_2O: 18 g/mol

Density of Bath:

H_2SO_4: 1.84 g/mL
$Na_2Cr_2O_7$: 2.52 g/mL
H_2O: 1 g/mL

Assuming 10 g H_2SO_4, 1 g $Na_2Cr_2O_7$, and 30 g H_2O, total volume can be calculated

$$10g \cdot 1.84\frac{g}{mL} = 5.43mL$$

$$1g \cdot 2.52\frac{g}{mL} = 0.40mL$$

$$30g \cdot 1\frac{g}{mL} = 30mL$$

5.43 mL H_2SO_4: 15.2 % by volume
0.40 mL $Na_2Cr_2O_7$: 1.12 % by volume
30 mL H_2O: 83.7 % by volume

$$540mL \cdot .152 = 82.08mL$$

$$540mL \cdot .0112 = 6.05mL$$

$$540mL \cdot .837 = 451.98mL$$

$$6.05mL \cdot 2.52\frac{g}{mL} = 15.25g$$

Chromic Acid Bath Contains:

82.08 mL H_2SO_4
15.25 g $Na_2Cr_2O_7$
451.98 mL H_2O

Appendix C: Adhesive Selection Testing – Raw Data

Results																			
Adhesive																			
E-60HP		E-30UT		H8010		E-40FL		H4800		H8000		480		435		331		332	
Strength [psi]	Failure Mode	Strength [psi]	Failure Mode	Strength [psi]	Failure Mode	Strength [psi]	Failure Mode	Strength [psi]	Failure Mode	Strength [psi]	Failure Mode	Strength [psi]	Failure Mode	Strength [psi]	Failure Mode	Strength [psi]	Failure Mode	Strength [psi]	Failure Mode
2447	Adh/Coh	2582	Adh/Coh	2629	Cohesive	736	Adhesive	1963	Adh/Coh	2939	Cohesive	2199	Adh/Coh	1785	Adh/Coh	2431	Cohesive	1607	Cohesive
2193	Adh/Coh	2330	Adh/Coh	2545	Cohesive	552	Adhesive	2461	Adh/Coh	2954	Cohesive	2260	Adh/Coh	647	Adhesive	2409	Cohesive	1743	Cohesive
2476	Adh/Coh	2061	Adh/Coh	2922	Cohesive	568	Adhesive	2214	Adh/Coh	2919	Cohesive	2031	Adh/Coh	543	Adhesive	2150	Adh/Coh	1743	Cohesive
2139	Adh/Coh	1656	Adh/Coh	2588	Cohesive	489	Adhesive	2182	Adh/Coh	2755	Cohesive	1929	Adh/Coh	982	Adh/Coh	2170	Adh/Coh	1656	Cohesive
2022	Adh/Coh	1622	Adh/Coh	3053	Cohesive	437	Adhesive	2222	Adh/Coh	2852	Cohesive	2407	Adh/Coh	848	Adh/Coh	1714	Adh/Coh	1519	Cohesive
2109	Adh/Coh	2462	Adh/Coh	2587	Cohesive	442	Adhesive	2110	Adh/Coh	2880	Cohesive	2077	Adh/Coh	1233	Adh/Coh	2237	Adh/Coh	1433	Cohesive
	Adh/Coh	2198	Adh/Coh	2504	Cohesive	394	Adhesive	2365	Adh/Coh	2826	Cohesive	2172	Adh/Coh	1745	Adh/Coh	2105	Adh/Coh	1481	Cohesive
	Adh/Coh	2074	Adh/Coh	2604	Cohesive	390	Adhesive	2445	Adh/Coh	2764	Cohesive	2331	Adh/Coh	1119	Adh/Coh	1385	Adh/Coh	1605	Cohesive
	Adh/Coh	1973	Adh/Coh	3164	Cohesive	465	Adhesive	1567	Adh/Coh	2603	Cohesive	2256	Adh/Coh	1250	Adh/Coh	1440	Adh/Coh	1680	Cohesive
	Adh/Coh	1921	Adh/Coh	2382	Cohesive	462	Adhesive	2330	Adh/Coh	2667	Cohesive	2407	Adh/Coh	913	Adh/Coh	1272	Adh/Coh	1725	Cohesive
2231		**2088**		**2698**		**494**		**2186**		**2816**		**2207**		**1107**		**1931**		**1619**	
187		316		257		103		266		118		159		415		438		111	
0.084		0.151		0.095		0.209		0.122		0.042		0.072		0.375		0.227		0.069	
2022		1622		2382		390		1567		2603		1929		543		1272		1433	
1060	Adhesive	2328	Cohesive	3153	Cohesive	184	Adhesive	3133	Adh/Coh	3051	Adh/Coh	866	Adhesive	1336	Adh/Coh	2305	Adh/Coh	2264	Adh/Coh
2502	Adhesive	1623	Adh/Coh	2400	Adh/Coh	592	Adhesive	3377	Adh/Coh	3123	Adh/Coh	1329	Adh/Coh	1619	Adh/Coh	1966	Adh/Coh	2029	Adh/Coh
1389	Adhesive	1578	Adh/Coh	2531	Adh/Coh	698	Adh/Coh	2933	Adh/Coh	2649	Adh/Coh	1873	Adh/Coh	2751	Adh/Coh	1225	Adhesive	1631	Adh/Coh
964	Adh/Coh	528	Adhesive	3150	Cohesive	541	Adhesive	3431	Adh/Coh	2184	Adh/Coh	2386	Adh/Coh	948	Adhesive	1437	Adh/Coh	1101	Adh/Coh
1376	Adh/Coh	838	Adhesive	2178	Adh/Coh	687	Adhesive	3542	Adh/Coh	2178	Adh/Coh	2267	Adh/Coh	1323	Adh/Coh	1263	Adh/Coh	1829	Adh/Coh
2032	Adh/Coh	3148	Adh/Coh	2108	Adh/Coh	681	Adhesive	2966	Adh/Coh	2728	Cohesive	2244	Adh/Coh	1236	Adh/Coh	1724	Adhesive	1678	Adh/Coh
789	Adhesive	590	Adhesive	2335	Adh/Coh	526	Adhesive	3447	Adh/Coh	2986	Adh/Coh	2312	Adh/Coh	1139	Adh/Coh	1396	Adh/Coh	1531	Adh/Coh
1265	Adh/Coh	634	Adhesive	2802	Adh/Coh	731	Adhesive	3573	Cohesive	2849	Cohesive	1408	Adhesive	2738	Adh/Coh	1631	Adh/Coh	2523	Adh/Coh
468	Adhesive	1508	Adh/Coh	3163	Cohesive	285	Adhesive	3711	Cohesive	2515	Cohesive	2577	Adh/Coh	1574	Adh/Coh	981	Adhesive	2071	Adh/Coh
1903	Adh/Coh	3507	Cohesive	2977	Adh/Coh	702	Adhesive	3085	Adh/Coh	2348	Adh/Coh	1361	Adh/Coh	2054	Adh/Coh	2109	Adh/Coh	3125	Adh/Coh
1375		**1628**		**2680**		**563**		**3320**		**2661**		**1862**		**1672**		**1604**		**1978**	
617		1067		419		188		271		348		580		640		423		568	
0.449		0.655		0.156		0.334		0.082		0.131		0.312		0.383		0.264		0.287	
468		528		2108		184		2933		2178		866		948		981		1101	
2465	Adh/Coh																		
2723	Adh/Coh																		
1594	Adh/Coh																		
2361	Adh/Coh																		
2607	Adh/Coh																		
1659	Adhesive																		
2377	Adh/Coh																		
2603	Adh/Coh																		
2830	Cohesive																		
1512	Adh/Coh																		
2273																			
495																			
0.218																			
1512																			

Appendix D: DOE Full Minitab Results

Factorial Fit: Avg versus Treatment, Cleaning

```
Estimated Effects and Coefficients for Avg (coded units)

Term                Effect     Coef  SE Coef      T      P
Constant                    2262.63    92.65  24.42  0.000
Treatment           831.25   415.62    92.65   4.49  0.011
Cleaning            119.75    59.87    92.65   0.65  0.553
Treatment*Cleaning   61.75    30.88    92.65   0.33  0.756


S = 262.060     PRESS = 1098810
R-Sq = 83.77%   R-Sq(pred) = 35.10%   R-Sq(adj) = 71.60%
```

The following Minitab analysis proves that, at a 95% confidence interval, the difference in bond strengths from treated to untreated assemblies is statistically significantly different.

Factorial Fit: Std Dev versus Treatment, Cleaning

```
Estimated Effects and Coefficients for Std Dev (coded units)

Term                 Effect    Coef  SE Coef      T      P
Constant                     333.63    74.75   4.46  0.011
Treatment            379.75  189.87    74.75   2.54  0.064
Cleaning            -173.75  -86.87    74.75  -1.16  0.310
Treatment*Cleaning  -132.25  -66.13    74.75  -0.88  0.426


S = 211.428     PRESS = 715230
R-Sq = 68.22%   R-Sq(pred) = 0.00%   R-Sq(adj) = 44.38%
```

The following Minitab analysis proves that, at a 93.6% confidence interval, the difference in standard deviations from treated to untreated assemblies is statistically significantly different.

Appendix E: Aluminum Powder Addition Calculations

Depth of Aluminum Oxide Layer for Chromic Acid Etching:

$$4.5\times10^{-6}\,cm$$

Density of Aluminum:

$$2.7\frac{g}{cm^3}$$

Average Radius of Aluminum Powder Particle:

$$0.0006cm$$

Surface Area of Aluminum Powder Particle:

$$4\cdot\pi\cdot r^2 = 4\cdot\pi\cdot 0.0006^2 = 3.7\times10^{-6}\,cm^2$$

Volume of Aluminum Powder Particle:

$$\frac{4}{3}\cdot\pi\cdot r^3 = \frac{4}{3}\cdot\pi\cdot 0.0006^3 = 9.05\times10^{-10}\,cm^3$$

Grams per Particle:

$$9.05\times10^{-10}\,cm^3\cdot\frac{2.7g}{cm^3} = 2.44\times10^{-9}\,\frac{g}{particle}$$

Centimeters Cubed per Particle:

$$\frac{9.05\times10^{-10}\,cm^3}{particle}\cdot\frac{particle}{2.44\times10^{-9}\,g} = 0.371\frac{cm^3}{g}$$

Dimensions of Treated Surface on Aluminum Lap Shear:

$$2.54cm\times2.54cm\times.16cm$$

Surface Area of Treated Surface on Aluminum Lap Shear:

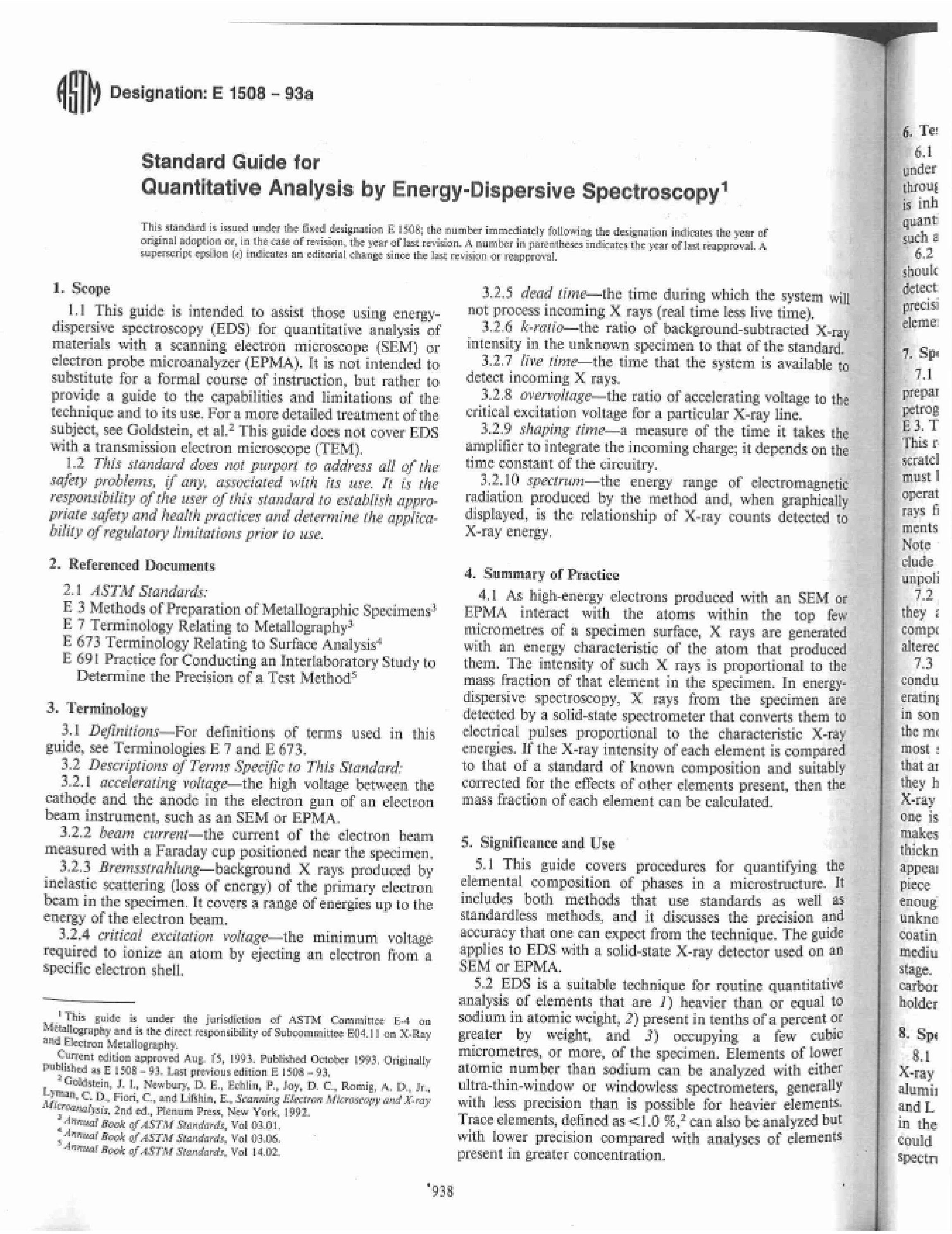
$$13.38cm^2$$

Mass of Aluminum Powder Equivalent to Treating 1000 Lap Shears:

$$4.5\times10^{-6}\,cm\cdot13.38cm^2 = 0.00006cm^3\cdot1000laps = 0.06cm^3$$

$$0.12042cm^3\cdot\frac{1g}{0.371cm^3} = 0.162g$$

Appendix F: ASTM E 1508-93a



Designation: E 1508 – 93a

Standard Guide for Quantitative Analysis by Energy-Dispersive Spectroscopy[1]

This standard is issued under the fixed designation E 1508; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide is intended to assist those using energy-dispersive spectroscopy (EDS) for quantitative analysis of materials with a scanning electron microscope (SEM) or electron probe microanalyzer (EPMA). It is not intended to substitute for a formal course of instruction, but rather to provide a guide to the capabilities and limitations of the technique and to its use. For a more detailed treatment of the subject, see Goldstein, et al.[2] This guide does not cover EDS with a transmission electron microscope (TEM).

1.2 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 3 Methods of Preparation of Metallographic Specimens[3]
E 7 Terminology Relating to Metallography[3]
E 673 Terminology Relating to Surface Analysis[4]
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[5]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide, see Terminologies E 7 and E 673.

3.2 *Descriptions of Terms Specific to This Standard:*

3.2.1 *accelerating voltage*—the high voltage between the cathode and the anode in the electron gun of an electron beam instrument, such as an SEM or EPMA.

3.2.2 *beam current*—the current of the electron beam measured with a Faraday cup positioned near the specimen.

3.2.3 *Bremsstrahlung*—background X rays produced by inelastic scattering (loss of energy) of the primary electron beam in the specimen. It covers a range of energies up to the energy of the electron beam.

3.2.4 *critical excitation voltage*—the minimum voltage required to ionize an atom by ejecting an electron from a specific electron shell.

3.2.5 *dead time*—the time during which the system will not process incoming X rays (real time less live time).

3.2.6 *k-ratio*—the ratio of background-subtracted X-ray intensity in the unknown specimen to that of the standard.

3.2.7 *live time*—the time that the system is available to detect incoming X rays.

3.2.8 *overvoltage*—the ratio of accelerating voltage to the critical excitation voltage for a particular X-ray line.

3.2.9 *shaping time*—a measure of the time it takes the amplifier to integrate the incoming charge; it depends on the time constant of the circuitry.

3.2.10 *spectrum*—the energy range of electromagnetic radiation produced by the method and, when graphically displayed, is the relationship of X-ray counts detected to X-ray energy.

4. Summary of Practice

4.1 As high-energy electrons produced with an SEM or EPMA interact with the atoms within the top few micrometres of a specimen surface, X rays are generated with an energy characteristic of the atom that produced them. The intensity of such X rays is proportional to the mass fraction of that element in the specimen. In energy-dispersive spectroscopy, X rays from the specimen are detected by a solid-state spectrometer that converts them to electrical pulses proportional to the characteristic X-ray energies. If the X-ray intensity of each element is compared to that of a standard of known composition and suitably corrected for the effects of other elements present, then the mass fraction of each element can be calculated.

5. Significance and Use

5.1 This guide covers procedures for quantifying the elemental composition of phases in a microstructure. It includes both methods that use standards as well as standardless methods, and it discusses the precision and accuracy that one can expect from the technique. The guide applies to EDS with a solid-state X-ray detector used on an SEM or EPMA.

5.2 EDS is a suitable technique for routine quantitative analysis of elements that are *1*) heavier than or equal to sodium in atomic weight, *2*) present in tenths of a percent or greater by weight, and *3*) occupying a few cubic micrometres, or more, of the specimen. Elements of lower atomic number than sodium can be analyzed with either ultra-thin-window or windowless spectrometers, generally with less precision than is possible for heavier elements. Trace elements, defined as <1.0 %,[2] can also be analyzed but with lower precision compared with analyses of elements present in greater concentration.

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[1] This guide is under the jurisdiction of ASTM Committee E-4 on Metallography and is the direct responsibility of Subcommittee E04.11 on X-Ray and Electron Metallography.

Current edition approved Aug. 15, 1993. Published October 1993. Originally published as E 1508 – 93. Last previous edition E 1508 – 93.

[2] Goldstein, J. I., Newbury, D. E., Echlin, P., Joy, D. C., Romig, A. D., Jr., Lyman, C. D., Fiori, C., and Lifshin, E., *Scanning Electron Microscopy and X-ray Microanalysis*, 2nd ed., Plenum Press, New York, 1992.

[3] *Annual Book of ASTM Standards*, Vol 03.01.

[4] *Annual Book of ASTM Standards*, Vol 03.06.

[5] *Annual Book of ASTM Standards*, Vol 14.02.

6. Test Specimens

6.1 Suitable specimens are those that are normally stable under an electron beam and vacuum and are homogeneous throughout the volume of X-ray production. If the specimen is inhomogeneous at the micrometre level, then a truly quantitative analysis is not possible, and a bulk technique such as X-ray fluorescence should be used.

6.2 The concentration of each element to be analyzed should equal or exceed about 0.1 wt %. Lower limits of detection are possible with longer counting times, but the precision of trace element analysis is poorer than when the element is present at the percent level.

7. Specimen Preparation

7.1 Specimens for quantitative EDS analysis should be prepared in accordance with standard metallographic or petrographic techniques. Guidelines are given in Methods E 3. The specimen must be flat in the region to be analyzed. This requirement does not preclude scratches; however, any scratches in the immediate vicinity of the analyzed region must be insignificant with respect to the X-ray volume. The operator must also be aware of the possibility of spurious X rays from parts of the chamber, polishing compound elements, or from adjacent phases or a combination thereof. Note that these requirements for surface preparation preclude the quantitative analysis of casual samples, such as unpolished surfaces like fracture surfaces.

7.2 Unetched or lightly etched specimens are preferred. If they are etched, the operator must make sure that the composition in the region to be analyzed has not been altered and that the region to be analyzed is flat.

7.3 Nonconducting specimens should be coated with a conductive material to prevent charging. Lowering the accelerating voltage may reduce or eliminate the effect of charging in some samples, but applying a conductive coating is still the most common method. Evaporated carbon is usually the most suitable coating material. Heavy metals such as gold that are often used for SEM imaging are less suitable because they heavily absorb X rays; if the coating is thick enough, X-ray lines from those metals will be seen in the spectrum. If one is analyzing carbon in the specimen, then aluminum makes a good coating. The coatings are usually applied in thicknesses of several tens of nanometres. Carbon that appears to be tan in color on the specimen surface, or on a piece of filter paper in the evaporator, is probably thick enough. For the most accurate analysis, standards and unknowns should be coated at the same time to assure equal coating thicknesses. Specimens mounted in a nonconducting medium must make electrical contact with the microscope stage. This is often accomplished by painting a stripe of carbon or silver paint from the specimen to the specimen holder.

8. Spectrum Collection

8.1 *Calibration*—The analyzer must be calibrated on two X-ray peaks to set the amplifier gain and offset. Often aluminum and copper are used, and sometimes both the K and L lines of copper are used. The two elements need not be in the same specimen. A spectrum from pure aluminum could be collected followed by pure copper in the same spectrum. Software is usually available to calibrate the EDS system, and one should consult the system manual for the details of operation. To ensure reproducible results, calibration should be checked periodically.

8.2 *Operating Parameters:*

8.2.1 The accelerating voltage of the SEM must be chosen to provide an adequate overvoltage to excite the X-ray lines of interest. An overvoltage that is too low will not sufficiently excite X rays; one that is too high yields low spatial resolution and causes absorption as X rays escape from deep within the specimen. An overvoltage of at least 1.5 times the critical excitation potential of the highest energy X-ray line analyzed is recommended. When analyzing hard and soft X rays in the same specimen, analyses at two voltages may be necessary. For materials such as minerals and ceramics, which contain light elements (that is, of low atomic number), 15 kV is usually a good compromise. For many metals containing medium atomic number elements, 20 to 30 kV is a good choice. Heavy elements (those of higher atomic number) may be analyzed using L or M lines, and so higher voltages are not necessary. The actual accelerating voltage of the electron beam does not always correspond with the voltage selected on the instrument. It can be determined by expanding the vertical scale of the EDS spectrum and observing the energy above which continuum X rays do not occur.

8.2.2 Almost all elements can be analyzed using characteristic X-ray lines in the range of 0–10 keV. This range contains K lines of the first transition series (scandium–zinc (Sc-Zn)), L lines of the second transition series plus the lanthanides, and M lines of the third transition series plus the actinides. Accordingly, most operators choose a 0–10 keV display at higher display resolution rather than a 0–20 keV display at lower resolution. Tables of X-ray energies can be found in various texts, such as Goldstein, et al[2] or Johnson and White.[6]

8.2.3 X-ray spatial resolution degrades with overvoltage, because as the electrons penetrate deeper into the specimen, X rays are generated from a larger volume. An approximation of the diameter of this tear-drop-shaped excitation volume, referred to as the X-ray range, can be obtained using the following equation.[7]

$$R = 0.064(E_o^{1.68} - E_c^{1.68})/\rho \qquad (1)$$

where:

R = the range in μm,
E_o = the accelerating voltage in kV,
E_c = the critical excitation potential in keV, and
ρ = the density in g/cm^3.

More accurate interaction volumes can be computed by Monte Carlo computer methods to generate random electron trajectories, but Eq 1 provides a reasonable estimate for most purposes.

8.2.4 The beam can be placed in the spot mode to form a probe to analyze the minimum volume, or it can be scanned over a homogeneous region to lower the electron dose at any one point. Defocusing the beam or scanning it over an area

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[6] Johnson, G. G., Jr., and White, E. W., *X-Ray Emission Wavelengths and KeV Tables for Nondiffractive Analysis*, ASTM Data Series DS 46, ASTM, Philadelphia, 1970.

[7] Andersen, C. A., and Hasler, M. F., *X-Ray Optics and Microanalysis, 4th Intl. Cong. on X-Ray Optics and Microanalysis*, Hermann, Paris, 1966, p. 310.

of varying composition does not provide an average composition, because the correction factors applied to the intensity ratio are themselves a function of composition.

8.2.5 The current in the electron beam determines the flux of X rays that are generated. It does not affect spatial resolution for X-ray analysis in the same way it detracts from electron image resolution. Typically it is adjusted to keep the dead time in the EDS system below 40 %. Dead times of 20 to 30 % produce good spectra, whereas dead times above 40 % can lead to spectra containing artifacts, such as those discussed in 8.3.1. Maximum throughput, that is, the most X rays/real time, is achieved at about 40 % dead time. Higher count rates can be achieved by lowering the shaping time on the system amplifier from about 10 µs, but spectral resolution will be lost. For quantitative analysis, a shaping time of about 10 µs or greater is used. The beam current must remain stable throughout the analysis, because the counts collected are directly proportional to the beam current. Thus, a 1 % upward drift in beam current will produce a 1 % increase in all the reported mass fractions, resulting in a reported total >100 %. For quantitative analysis using standards, the beam current (not specimen current) must be the same for both the specimen and the standards or one must be normalized to the other.

8.2.6 The geometric configuration of the sample and detector, shown schematically in Fig. 1, also affects the analysis. The number of X-ray photons that reach the detector is a function of the solid angle and take-off angle, including the effect of specimen and detector tilt. The count rate incident on an X-ray detector is directly proportional to the size of the solid angle defined as follows for a detector normal to the line of sight to the specimen:

$$\Omega = A/r^2 \qquad (2)$$

where:

Ω = solid angle in steradians,

A = active area of the detector crystal; for example, 30 mm^2, and

r = sample-to-detector distance, mm.

The larger the active area of the detector, the more counts will be collected, but at the expense of spectral resolution.

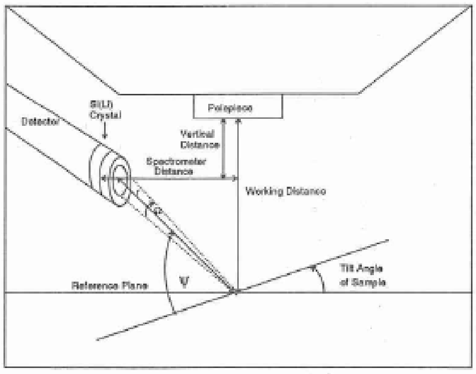

FIG. 1 Schematic Diagram of Electron Microscope System

Most detectors have a movable slide and can be brought closer to the sample if a higher count rate at a given beam current is needed. The take-off angle is defined as the angle between the surface of the sample and a line to the X-ray detector. If the sample is not tilted, the take-off angle is defined as follows:

$$\psi = \arctan(W - V)/S \qquad (3)$$

where:

ψ = take-off angle,

W = working distance,

V = vertical distance, and

S = spectrometer distance.

Working distance is measured in the microscope; its accuracy depends on the method used to measure it and the specimen position. Vertical distance is the distance from the bottom of the pole piece of the final lens to the centerline of the detector; it usually can be measured within the microscope with a ruler. Spectrometer distance is the horizontal distance from the spectrometer to the beam; it is measured using the scale provided by the manufacturer on the spectrometer slide. All distances must be in the same units. The take-off angle should be as high as possible to minimize absorption of X rays within the specimen and maximize the accuracy of quantitative analysis. If the specimen is tilted such that the beam is not perpendicular to the specimen surface, an effective take-off angle is used. There are several expressions in use by commercial manufacturers to calculate this, and all produce similar results if the tilt angle is not extreme. When analysis is performed on a tilted specimen, the azimuthal angle between the line from the analysis point to the EDS detector and the line perpendicular to the stage tilt axis must be known. If standards are used, they must be collected under the identical geometrical conditions as the unknowns.

8.3 *Spectral Artifacts:*

8.3.1 There are a number of artifacts possible with EDS, and these are discussed by Fiori, et al.[8] Most of them are related to detector electronics and are rarely seen in a properly functioning system. However, two artifacts that are commonly seen are pulse pileup peaks and silicon escape peaks. Pileup peaks occur when several X-ray photons reach the detector at the same time, and the pulse processing electronics erroneously record the sum of their energies rather than each one individually. Lowering the beam current to lower the count rate usually eliminates the problem. Alternatively, the amplifier shaping time can be decreased; this action will allow pulses to be processed faster, but at the expense of degraded spectral resolution.

8.3.2 A silicon escape peak occurs when an ionized atom of silicon in the detector generates an X ray. If that X ray escapes from the detector, its energy that would ordinarily have been measured is lost. The result is a peak at 1.74 keV (Si K_α) below the proper peak. This artifact is greatest at about 2 keV, near the P K_α or Zr L_α peaks. The artifact cannot occur at energies below the absorption edge of the Si

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[8] Fiori, C. E., Newbury, D. E., and Myklebust, R. L., "Artifacts Observed in Energy Dispersive X-ray Spectrometry in Electron Beam Instruments—A Cautionary Guide," *NIST Special Publication 604, Proceedings of the Workshop on Energy Dispersive Spectrometry*, National Institute of Standards and Technology, Gaithersburg, Maryland, 1981.

K line, and it becomes negligible at higher energies such as the Cu K_α line.

9. Quantification

9.1 *Background Subtraction and Peak Deconvolution:*

9.1.1 Before the proportionality between X-ray intensity and elemental concentration can be calculated, several steps are required to obtain the intensity ratio (k-ratio) between unknown and standard. Or, if the standardless technique is used, then a pure net intensity is required. A spectrum of X rays generated by electrons interacting with the specimen contains a background consisting of continuum X rays, often called Bremsstrahlung. Observing the high-energy cutoff of the continuum, as noted in 8.2.1, gives the most accurate determination of the beam voltage, and this is the value that should be used for quantitative analysis. If the voltage measured in this manner is much lower than the voltage setting, it may be an indication that the specimen is charging. The background in the spectrum is not linear and simple interpolation is inadequate. Two approaches to this problem commonly used in commercial systems are background modeling and digital filtering. The background models are based on known physics plus a suitable correction for the real world. This method lets the user pass judgment on the quality of the model by comparing the model with the actual spectrum. The digital filter method treats the background as a low frequency component of the spectrum and mathematically sets it to zero. This method is not based on any model and, therefore, is more general. It is also useful for the light element region of the spectrum where the models were never intended to be used; however, it does not take into account absorption edges. Some software also allows the operator to fit his own background.

9.1.2 The other step that must be accomplished before an intensity ratio can be measured is peak deconvolution. EDS detectors do not resolve all peaks. For example, the S K_α, Mo L_α, and Pb M_α lines are all within about 50 eV of each other and therefore are severely overlapped. Even though one cannot see the individual components of a peak envelope in a spectrum, there are computer methods of deconvolution. Two methods in common use are *1*) the method of overlap factors and *2*) the method of multiple least squares. Both methods work well, and they are usually combined with one of the background subtraction methods in the manufacturer's software. One should consult the manufacturer's instructions for their use.

9.1.3 Although in most cases these computer methods handle spectra well, the operator should be aware of conditions that are difficult. For example, trace element analysis is sensitive to background subtraction because the computer is looking for a small peak above the continuum. Accordingly the spectrum must be collected long enough to provide enough statistics to discern small peaks. In like manner, deconvolution routines work well in most cases, but not when the overlapped lines arise from elements present in widely different concentrations. For example, if one element constitutes 90 % of the specimen and the other element 10 %, precision will be greatly degraded. In this situation use of a different analytical line may be possible, or if not, a technique with higher spectral resolution such as wavelength dispersive spectrometry is indicated.

9.1.4 Once the background is subtracted and the peaks are stripped of interferences, one can calculate their ratio to those of similarly background-subtracted, deconvoluted standard spectra. The unknowns and standards must have been collected *1*) under the same geometrical configuration, *2*) at the same accelerating voltage, *3*) at the same count rate per current unit, and *4*) with the same processing algorithm.

9.1.5 Even standardless analysis requires background subtraction and peak deconvolution, but the intensity is calculated from pure intensity curves and the ratio of peak integrals in the unknown spectrum. Standardless analyses always total 100 %, or some other value specified by the analyst. In normalizing the total concentrations to 100 %, important information is lost. A true mass total, as in analysis against standards, provides information about the quality of the analysis. It calls attention to problems such as elements not specified for analysis or analysis of more than one phase under the beam. Analyses totaling exactly 100 % should always be viewed with skepticism, whether they be standardless or normalized standards analyses. Whichever method is used, all elements present must be specified even if some need not be analyzed. This is because a correction is necessary to account for the effect of other elements (the matrix) present in the specimen.

9.2 *Matrix Corrections:*

9.2.1 The k-ratio of an element is a starting estimate of that element's concentration. There are, however, effects of atomic number, absorption, and fluorescence between the unknowns and the standards. The atomic number or "Z" factor corrects for differences in the number of X rays generated. The absorption or "A" factor corrects for differences in the number of X rays that escape the sample to be detected. The fluorescence or "F" factor corrects for non-electron generated X rays, that is, those fluoresced by other X rays. If the unknown and standard were identical, each of these factors would equal one. There are many such "ZAF" computer programs available, each one using a set of fundamental parameters thought to give the best results. The differences in the results each produces are usually much less than the precision of the analysis.

9.2.2 There are also many computer programs using the "phi-rho-z" method. These approach the problem of matrix correction using more fundamental physics and sometimes combine the effects of Z and A into one, but they too require a set of fundamental parameters optimized to each program. Many phi-rho-z programs claim greater accuracy because they account for absorption better than the older ZAF programs. Consequently, one would expect the most improvement using a phi-rho-z method in light element analysis. However, in the absence of light elements, it is unlikely that the accuracy of most EDS analyses is limited by the matrix correction.

9.3 *Reporting Results:*

9.3.1 The analytical conditions are normally reported with the elemental concentrations determined by EDS. These conditions include the accelerating voltage, take-off angle and tilt, and the analytical line (KLM) used. The report should also specify whether standards or standardless methods were used, what matrix corrections were applied, and whether any elemental concentrations were calculated by difference or by stoichiometry. Additional items that may be reported include what standards were used, if any, the beam current, and the Z, A, and F factors. It would also be informative to mention the type of window on the EDS detector, if other than a conventional beryllium window. Concentrations are normally reported to a tenth of a percent; although many computer programs report more significant figures, they are rarely warranted.

10. Light Element Analysis

10.1 Light elements can be analyzed with an ultra-thin window detector that provides better efficiency for the soft X rays that light elements generate. Windowless detectors approach the theoretical highest efficiency of the detecting crystal, but in the open position contaminants in the sample chamber are free to condense on the cold crystal. Additionally, in the windowless mode any light, such as from cathodoluminescence, can be picked up by the crystal and will contribute to the overall noise of the system. Quantitative light element analysis is less precise than that of heavier elements, because the count rate of soft X rays is lower. The minimum detectability limit of light elements is also degraded because of the lower peak-to-background ratios found with soft X rays. If the stoichiometry of compounds containing light elements is known, then calculation by stoichiometry is the most accurate method. For example in silicates, analyzing silicon and multiplying by the gravimetric factor for SiO_2 (2.14) is more accurate than analyzing oxygen directly.

11. Standards

11.1 Suitable standards for EDS microanalysis must be *1)* homogeneous at the micrometre level, *2)* of known composition as analyzed by an independent method, and *3)* stable under the electron beam. For the highest accuracy, standards should be as similar as possible to the unknowns to minimize matrix effects. However, most matrix correction programs are sufficiently accurate to permit the use of pure element standards. Nevertheless, metals do not make good standards for nonmetals, and vice versa.

11.2 Standards may be obtained from microscopy suppliers, the National Institute for Standards and Technology, or from other microscopists. However, one of the best sources of standards similar to the materials analyzed is one's own facility, if they are checked for homogeneity.

11.3 Standards can also be used to check the performance of standardless programs. In many cases, the results are similar, and the standardless method may be used for convenience.

12. Precision and Bias

12.1 *Interlaboratory Test Program*—An interlaboratory study using two different metallurgical specimens was conducted to determine the precision of energy-dispersive spectroscopy (EDS). Both specimens were analyzed by various metal producers, EDS system manufacturers, and one university. A total of nine laboratories participated in the study. Each of the specimens was analyzed with a lithium-drifted silicon detector using a set of standardized operating parameters after an initial round-robin wherein parameters were selected by each participant. Both sets of data are reported, and the standardized operating parameters are listed in Table 1.

TABLE 1 Standardized Operating Parameters for Second Round-Robin Test Program

Accelerating voltage	20 kV
Acquisition time	200 s
Detector dead time	≈25 %
Take-off angle	≈40°

12.1.1 The specimens selected for the round-robin were Type 308 stainless steel and INCONEL[9] alloy MA 6000. To ensure homogeneity, the Type 308 stainless steel specimens were homogenized at 1975°F (1079°C) for one hour followed by a water quench. This produced a 100 % austenitic structure. This material was chosen as a routine analysis for iron, chromium, and nickel. Some manganese was also present, but because its Kα line overlaps the Cr K_β it was not required to be reported, although some participants did. The alloy MA 6000 specimen was selected because of its inherent homogeneity and because it presented several analytical problems. The alloy contained both high and low atomic number elements necessitating the use of K, L, and M lines. There was also a severe overlap between the M lines of tantalum and tungsten. The presence of eight elements also added to the difficulty in analyzing this material. The compositions of both alloys, as determined by wet chemical analysis, are given in Table 2.

12.1.2 Individual specimens of both materials were sent to each of the nine participants, all of whom reported the specimens to be homogeneous. Each participant was requested to analyze five random areas in each specimen using a standard beryllium window EDS detector and their own operating parameters. The nominal composition of each specimen was also included for reference. A second round-robin test program, which required the use of a standard accelerating voltage, detector dead time, take-off angle, and acquisition time, was also initiated. It was requested that analyses by both standards and standardless methods be reported.

12.2 *Precision:*

12.2.1 The results from the round-robin test program were analyzed in accordance with Practice E 691 to develop repeatability and reproducibility standard deviations (see Tables 3 and 4). The inherent precision of the EDS method is controlled by counting statistics. Clearly, for a given overall counting time, the relative precision associated with major elements is greater than for minor or trace elements, insofar as there are necessarily fewer counts in minor peaks. Practice E 691 is used to analyze the round-robin data for consistency and calculates intralaboratory repeatability and interlaboratory reproducibility statistics. The 95 % repeatability and reproducibility, r and R, are defined by E 691 as 2.8 times the standard deviations, Sr and SR, respectively. When these standard deviations are divided by the mean concentration for each element, the result is a measure of relative precision within and between laboratories.

12.2.2 In the case of the Type 308 stainless steel, the 95 % repeatability limit is 7 % of the mean value or better for each

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[9] INCONEL is a registered trademark of Inco Alloys International.

TABLE 2 Wet Chemical Analysis of Samples of Commercial Type 308 Stainless Steel and INCONEL Alloy MA 6000 Used in ASTM Round Robin

Sample	Chemical Composition—Wt %									
	Tantalum	Tungsten	Chromium	Titanium	Aluminum	Molybdenum	Nickel	Iron	Manganese	Y_2O_3
Commercial Type 308 Stainless Steel	—	—	19.62	—	—	—	9.50	69.0	1.30	—
INCONEL Alloy MA 6000	1.91	3.91	14.76	2.26	4.0	1.91	68.12	1.00	—	0.97

TABLE 3 Precision Statistics of an Interlaboratory Study for Quantitative Analysis by Energy Dispersive Spectroscopy

Quantitative EDS Analysis of Type 308 Stainless Steel with No Set Parameters

Elements	$\bar{x}$	Sr	SR	r	R
Nickel	9.04	0.21	0.35	0.58	0.98
Chromium	20.48	0.27	0.87	0.77	2.43
Iron	70.47	0.68	2.44	1.90	6.84

Quantitative EDS Analysis of Type 308 Stainless Steel with Set Parameters

Elements	$\bar{x}$	Sr	SR	r	R
Nickel	9.43	0.23	0.49	0.64	1.36
Chromium	20.31	0.23	0.47	0.65	1.32
Iron	69.41	0.38	1.05	1.06	2.95

Standardless Quantitative EDS Analysis of Type 308 Stainless Steel with Set Parameters

Elements	$\bar{x}$	Sr	SR	r	R
Nickel	9.23	0.22	0.29	0.60	0.82
Chromium	20.25	0.15	0.48	0.41	1.34
Iron	69.60	0.21	0.78	0.60	2.18

$\bar{x}$ = cell average
Sr = repeatability standard deviation
SR = reproducibility standard deviation
r = repeatability limit
R = reproducibility limit

TABLE 4 Precision Statistics of an Interlaboratory Study for Quantitative Analysis by Energy Dispersive Spectroscopy

Quantitative EDS Analysis of MA 6000 with No Set Parameters

Elements	$\bar{x}$	Sr	SR	r	R
Iron	0.96	0.09	0.12	0.24	0.32
Tantalum	1.89	0.26	0.37	0.72	1.04
Titanium	2.36	0.26	0.26	0.72	0.72
Molybdenum	2.43	0.16	0.86	0.45	2.41
Tungsten	3.67	0.30	0.67	0.84	1.87
Aluminum	4.49	0.22	1.31	0.63	3.67
Chromium	15.33	0.33	0.49	0.92	1.38
Nickel	67.78	1.66	2.43	4.64	6.81

Quantitative EDS Analysis of Type MA 6000 with Set Parameters

Elements	$\bar{x}$	Sr	SR	r	R
Iron	1.04	0.05	0.10	0.14	0.29
Tantalum	1.81	0.17	0.47	0.49	1.33
Molybdenum	2.02	0.07	0.12	0.20	0.34
Titanium	2.31	0.16	0.20	0.46	0.56
Tungsten	3.82	0.15	0.38	0.41	1.07
Aluminum	4.78	0.23	0.59	0.63	1.66
Chromium	15.07	0.33	0.46	0.91	1.30
Nickel	68.97	0.51	1.25	1.43	3.51

Standardless Quantitative EDS Analysis of MA 6000 with Set Parameters

Elements	$\bar{x}$	Sr	SR	r	R
Iron	0.99	0.08	0.12	0.22	0.32
Molybdenum	1.96	0.11	0.53	0.31	1.49
Tantalum	1.98	0.15	1.19	0.42	3.34
Titanium	2.30	0.15	0.18	0.43	0.51
Tungsten	3.48	0.17	1.39	0.48	3.90
Aluminum	4.56	0.22	2.33	0.63	6.53
Chromium	15.31	0.23	0.56	0.64	1.55
Nickel	64.29	0.43	3.06	1.21	8.56

$\bar{x}$ = cell average
Sr = repeatability standard deviation
SR = reproducibility standard deviation
r = repeatability limit
R = reproducibility limit

element ($\frac{r}{\bar{x}}$ = 0.64/9.43 = 0.068 for nickel), and about 2 % is possible for iron present at 70 wt %. The 95 % reproducibility limit ranges from about 14 % to 3 %. Requiring set parameters had little effect on the repeatability but improved the reproducibility for chromium and iron, but not for nickel. Standardless methods were about equivalent to those using standards for this specimen. The results obtained from this specimen represent a typical metallurgical microanalysis with no unusual problems. As such, the precision obtained should be representative of the technique. The interlaboratory reproducibility under standard conditions averaged 8.4 %, and the standardless method averaged 6.2 % relative to the mean.

12.2.3 In the case of alloy MA 6000, the 95 % repeatability values improve with increasing concentration with the exception of tantalum and tungsten. Those two elements are present at the level of a few percent and their lines are overlapped. The occurrence of these two conditions together resulted in considerably lower precision than for the other elements. The 95 % reproducibility limit varied greatly when the parameters were not specified, but improved with set parameters. It may be that differences in background subtraction, peak deconvolution method, matrix correction, and possibly geometric configuration caused this. It was not possible to specify all of these conditions because some are inherent to the system used.

12.2.4 The standardless method produced intralaboratory repeatability results similar to the standards methods but considerably less interlaboratory reproducibility, owing to the different standardless routines in use by different manufacturers. Although results of the standardless analyses were rather good on the Type 308 stainless steel, they may be considerably inferior on other types of specimens. On the MA6000 alloy, the reproducibility among laboratories was much less than that of the standards technique (R in Table 4). And even though the average errors compared with the reference composition (Table 5) are not great, they are probably the result of positive and negative errors among laboratories canceling each other. These errors arise from the different ways various systems generate the pure element intensities, rather than from differences in ZAF or phi-rho-z matrix corrections. Accordingly, before routinely using a standardless method for quantitative analysis, it is important to validate the method for a particular class of materials by comparing it against analysis with standards or against a completely different quantitative technique, such as X-ray fluorescence or wet chemical analysis if the specimen is homogeneous. If the results are comparable, the standardless method may be used for specimens of composition similar to

TABLE 5 Comparison Between EDS and Reference Wet Chemical Analysis

	Wet Chemistry	No Set Parameters (% error)	Set Parameters (% error)	Standardless (% error)
Type 308 Stainless Steel				
Nickel	9.50	9.04 (−4.84)	9.43 (−0.78)	9.23 (−2.84)
Chromium	19.62	20.48 (4.39)	20.31 (3.51)	20.25 (3.23)
Iron	69.00	70.48 (2.14)	69.41 (0.59)	69.60 (0.88)
Average error		0.56 %	1.11 %	0.42 %
Alloy MA 6000				
Iron	1.00	0.96 (−4.24)	1.04 (3.67)	0.99 (−1.43)
Tantalum	1.91	1.88 (−1.30)	1.81 (−5.08)	1.96 (2.62)
Titanium	2.26	2.36 (4.30)	2.02 (−10.55)	1.98 (−12.18)
Molybdenum	1.91	2.43 (27.31)	2.31 (20.82)	2.30 (20.19)
Tungsten	3.91	3.67 (−6.02)	3.82 (−2.27)	3.48 (−11.11)
Aluminum	4.00	4.49 (12.16)	4.78 (19.38)	4.56 (13.91)
Chromium	14.76	15.33 (3.87)	15.07 (2.09)	15.31 (3.71)
Nickel	68.12	67.78 (−0.49)	68.97 (1.24)	64.28 (−5.63)
Average error		4.45 %	3.66 %	1.26 %
Average Error for Type 308		0.70 %		
Average Error for MA 6000		3.12 %		
Overall Average Error		1.91 %		

those on which it was validated.

12.2.5 Precision can usually be improved by acquiring more counts in the spectrum if that is possible. Longer counting times and increased beam current produce more counts. There are practical limits, however, such as beam drift or carbon contamination increasing on the specimen and causing the total counts to be nonlinear with time. Decreasing the amplifier time constant also increases count rate, but at the expense of resolution. The 200s count specified for the round-robin was intended to represent typical operating conditions, not the best achievable precision.

12.3 *Bias:*

12.3.1 If the wet chemical analysis of each specimen (Table 2) is taken as an accepted reference value, the difference between it and the concentration measured by EDS can be determined. These values are given in Table 5. The EDS values are the average of five measurements in each of nine laboratories. To the extent that this number of replicate analyses averages out the effects of precision, the remaining error may be attributed to bias. For the Type 308 stainless steel, the average error was 0.7 % of the amount present—a value close enough to zero to be insignificant. For the alloy MA 6000, the average was 3.12 %. There are many potential sources of bias, but the effect of each is hard to predict. Some sources of bias that are under operator control are as follows.

12.3.1.1 *Geometric Configuration*—This must be known and reproducible among standards and unknown specimens.

12.3.1.2 *Standards*—The composition of these must be known accurately, and they must be homogeneous at the micrometre level.

12.3.1.3 *Electron Beam Current*—This must be stable throughout standard collection and unknown analysis or corrected for instability through continuous monitoring with an integrating picoammeter or beam current monitoring before and after analysis if the drift is linear.

12.3.1.4 *Conductive Coating*—This must be thick enough to prevent changing of the specimen, yet thin enough so as not to absorb X rays significantly. It should also be of similar composition and thickness between the standards and the unknowns.

12.3.2 Some sources of bias often not under operator control are as follows.

12.3.2.1 *Method of Background Subtraction and Peak Deconvolution*—These must use appropriate constants such as detector efficiency for the specific detector being used, background fitting regions, filter width, and others.

12.3.2.2 *Matrix Correction*—This program is dependent on the accuracy of many constants such as mass absorption coefficients, mean ionization potentials, fluorescent yields, and others.

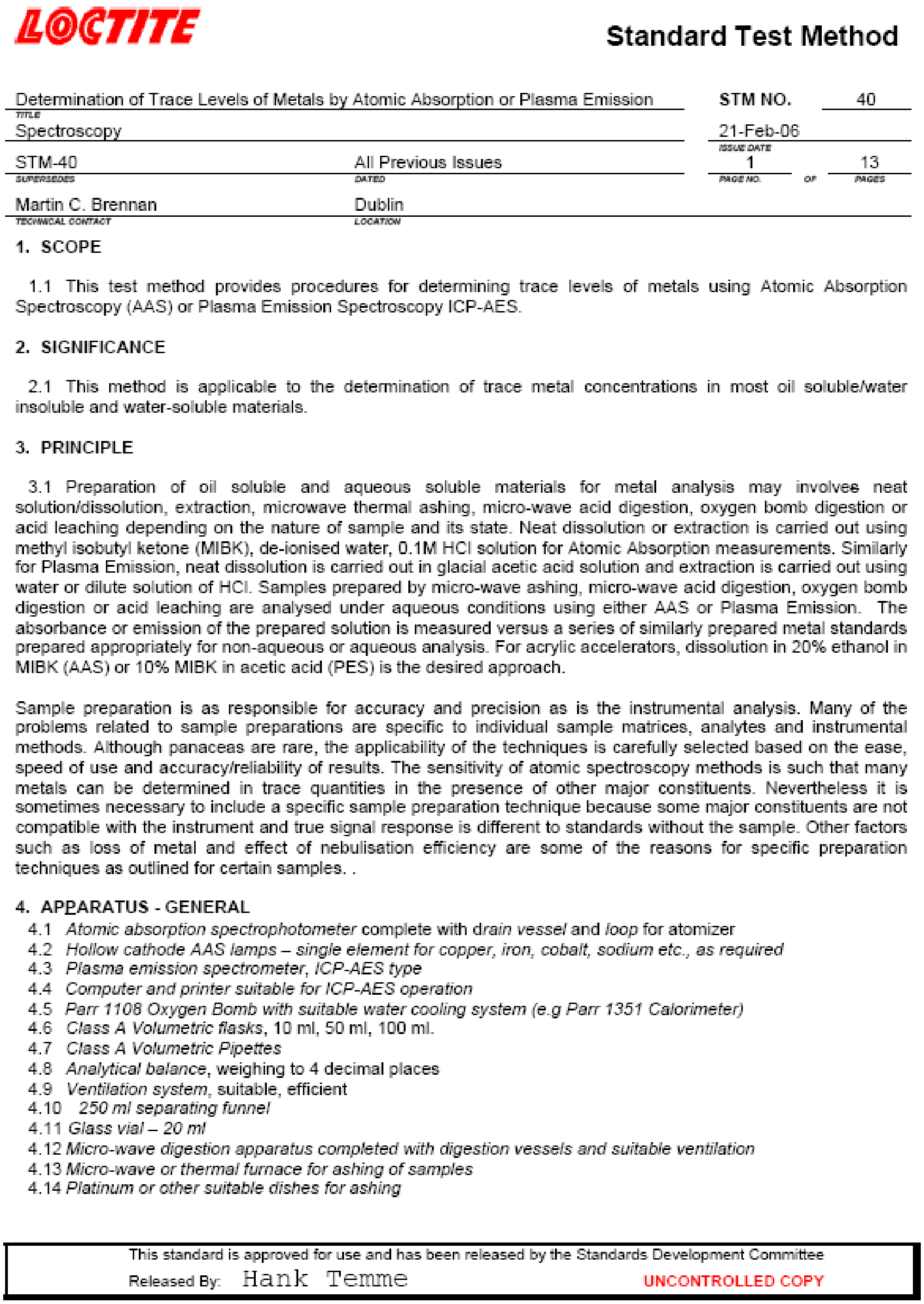
12.3.2.3 *Standardless Programs*—These are dependent on the accuracy of the intensity curves built into them as well as the sources of bias listed above.

12.4 Overall, when elements are present in major accounts, an intralaboratory repeatability of 6 % or better and an interlaboratory reproducibility of 14 % or better are possible. With trace elements, and especially with peak overlaps among trace elements, precision is significantly degraded and more X-ray counts must be collected. Most sources of bias are either insignificant or under operator control, and the overall accuracy of the technique is better than ±4 % relative to the reference composition.

13. Keywords

13.1 EDS; elemental analysis; energy-dispersive spectroscopy; light element; matrix correction; microanalysis; phi-rho-z; quantitative analysis; spectrum; standardless analysis; standards; X ray; X-ray microanalysis; ZAF

Appendix G: STM 40



LOCTITE

Standard Test Method

Determination of Trace Levels of Metals by Atomic Absorption or Plasma Emission Spectroscopy TITLE		STM NO.	40
		21-Feb-06 ISSUE DATE	
STM-40 SUPERSEDES	All Previous Issues DATED	1 PAGE NO. OF	13 PAGES
Martin C. Brennan TECHNICAL CONTACT	Dublin LOCATION		

1. SCOPE

1.1 This test method provides procedures for determining trace levels of metals using Atomic Absorption Spectroscopy (AAS) or Plasma Emission Spectroscopy ICP-AES.

2. SIGNIFICANCE

2.1 This method is applicable to the determination of trace metal concentrations in most oil soluble/water insoluble and water-soluble materials.

3. PRINCIPLE

3.1 Preparation of oil soluble and aqueous soluble materials for metal analysis may involvee neat solution/dissolution, extraction, microwave thermal ashing, micro-wave acid digestion, oxygen bomb digestion or acid leaching depending on the nature of sample and its state. Neat dissolution or extraction is carried out using methyl isobutyl ketone (MIBK), de-ionised water, 0.1M HCl solution for Atomic Absorption measurements. Similarly for Plasma Emission, neat dissolution is carried out in glacial acetic acid solution and extraction is carried out using water or dilute solution of HCl. Samples prepared by micro-wave ashing, micro-wave acid digestion, oxygen bomb digestion or acid leaching are analysed under aqueous conditions using either AAS or Plasma Emission. The absorbance or emission of the prepared solution is measured versus a series of similarly prepared metal standards prepared appropriately for non-aqueous or aqueous analysis. For acrylic accelerators, dissolution in 20% ethanol in MIBK (AAS) or 10% MIBK in acetic acid (PES) is the desired approach.

Sample preparation is as responsible for accuracy and precision as is the instrumental analysis. Many of the problems related to sample preparations are specific to individual sample matrices, analytes and instrumental methods. Although panaceas are rare, the applicability of the techniques is carefully selected based on the ease, speed of use and accuracy/reliability of results. The sensitivity of atomic spectroscopy methods is such that many metals can be determined in trace quantities in the presence of other major constituents. Nevertheless it is sometimes necessary to include a specific sample preparation technique because some major constituents are not compatible with the instrument and true signal response is different to standards without the sample. Other factors such as loss of metal and effect of nebulisation efficiency are some of the reasons for specific preparation techniques as outlined for certain samples. .

4. APPARATUS - GENERAL

4.1 *Atomic absorption spectrophotometer* complete with *drain vessel* and *loop* for atomizer
4.2 *Hollow cathode AAS lamps – single element for copper, iron, cobalt, sodium etc., as required*
4.3 *Plasma emission spectrometer, ICP-AES type*
4.4 *Computer and printer suitable for ICP-AES operation*
4.5 *Parr 1108 Oxygen Bomb with suitable water cooling system (e.g Parr 1351 Calorimeter)*
4.6 *Class A Volumetric flasks*, 10 ml, 50 ml, 100 ml.
4.7 *Class A Volumetric Pipettes*
4.8 *Analytical balance*, weighing to 4 decimal places
4.9 *Ventilation system*, suitable, efficient
4.10 *250 ml separating funnel*
4.11 *Glass vial – 20 ml*
4.12 *Micro-wave digestion apparatus completed with digestion vessels and suitable ventilation*
4.13 *Micro-wave or thermal furnace for ashing of samples*
4.14 *Platinum or other suitable dishes for ashing*

This standard is approved for use and has been released by the Standards Development Committee
Released By: Hank Temme UNCONTROLLED COPY

4.15 *250 µL variable micropipette*
4.16 *Variable dispensers suitable for attachment to Winchester bottles*
4.17 *Sample vapour extraction unit fitted directly over the sample tray*
4.18 *Hot-plate*
4.19 *Teflon Block at least 20 x 30 cm*

5. REAGENTS AND MATERIALS - GENERAL

5.1 *Certified Ferric nitrate standard solution* (1.0 ml = 1.00 mg Fe), EG BDH Cat. No. 14140.
5.2 *Certified Cupric nitrate standard solution* (1.0 ml = 1.00 mg Cu), EG BDH Cat. No. 14139.
5.3 *Certified* Cobaltous nitrate standard solution (1.0 mg Co), EG BDH Cat No. 14138.
5.4 *Certified Zinc nitrate standard solution (1.0 mg Zn).*
5.5 *Certified Aluminum standard solution (1.0 mg Al).*
5.6 *Other single certified aqueous metal standard~~s~~, solutions as required. (Na, K, Ca, Mg, etc.,)*
5.7 *Water*, distilled/deionized, or Analar.
5.8 *Chloroform*, Analar grade, or equivalent.
5.9 *Nitric acid*, 10% solution, for cleaning nebulizer.
5.10 *Hydrochloric acid*, 1.0M AVS EG BDH Cat. No. 19068.
5.11 *Conc. HCl*
5.12 *Conc. HNO3*
5.13 *Conc. HF*
5.14 *Conc. H2SO4*
5.15 *Glacial Acetic Acid (GAC)*
5.16 *MIBK* AnalaR grade
5.17 *0.05 M NaOH*
5.18 *5.0 M HCl*
5.19 *PTSA* (p-Toluene Sulphonic acid).
5.20 *Ammonium pyrrolidine dithiocarbamate (APDC)*
5.21 *Ethanol or industrial methylated spirits.*
5.22 *Pure grade acetylene or equivalent*, equipped with regulator and flashback safety device.
5.23 *Pure grade compressed air supply, at least 30 psi.*
5.24 *Zero grade argon supply, at least 60 psi.*

6. PROCEDURE FOR ATOMIC ABSORPTION AND INDUCTIVELY COUPLED PLASMA SPECTROSCOPY

6.1 Preparation of Metal Standards for Aqueous and Non-Aqueous Analysis

6.1.1 ***Preparation of Aqueous Acid Metal Standard Solutions.***

Note 1- These metal standards are suitable for samples to be measured for metals content on samples as received or soluble in aqueous solutions [at 10% solution] and containing trace levels of 0.01 ppm metal or greater. Unknown samples must be prepared at a concentration known not to alter the efficiency of nebulisation from that of the prepared standards.

6.1.1.1 Prepare calibration standard~~s~~ stock solution by adding 10 ml aliquots of the 1000 ppm of certified standard solutions of the desired metal into a 100 ml volumetric flask and diluting to volume with 1.0M HCl [Concentration is 100 ppm [100 µg/ml] for each metal]. This solution must be prepared weekly.

6.1.1.2 Dilute the resulting stock solution mixture as prepared in 6.1.1.1 with water or 1.0M HCl as appropriate to yield working calibration standards corresponding to 0.0, 0.1, 0.25, 0.5, 1.0, 2.0, 5.0 and 10.0 µg/ml of the metals. The working standards must prepared daily. Three of the working standards are only needed and are prepared to the appropriate level of metal in sample (e.g. samples after preparation suspected of containing ~0.05 ppm metal or less, the first three standards are prepared and those containing higher levels, the last three are prepared). Use the 0 µg/ml standard as blank. Samples containing greater than 10 ppm metal must be diluted accordingly to fit the calibration curve using the same aqueous solution as used to prepare standards.

6.1.2 *Preparation of Non-Aqueous Metal Standard Solutions*

6.1.2.1 Prepare a calibration standard stock solution by adding 10 ml aliquots of the 1000 ppm of certified standard solution of the desired metal into a 100 ml volumetric flask and dilute to volume with GAC. (Concentration is 100 ppm [100 µg/g] for each metal. This solution must be prepared weekly.

6.1.2.2 Dilute the resulting stock solutions prepared under 6.1.2.1 with MIBK or GAC solvent (used to prepare samples (by volume)) to yield working standard solutions corresponding to 0.0, 0.1, 0.25, 0.5, 1, 3, and 5 and 10 µg/ml of each metal in MIBK or GAC respectively. The working standards must be prepared fresh from stock solution every 24 hours. At least three working standards are required to span the range appropriate to the level of metal in the sample. Use the 0.0 ppm for the blank.

6.2 Instrument Operational Parameters and Metal Standards Calibration

6.2.1 Set up the appropriate instrument as per the manufacturer's instructions (including lamp selection, wavelength setting, slit adjustment, extraction hood switched on etc.). Allow the instrument to warm up for 15 minutes prior to use.

6.2.2 Generate standard calibration plots for each metal tested from standards prepared under 6.1.1 and 6.1.2 above as follows:

6.2.3 Read off absorbance or emission of each standard solution and construct calibration plots (µg/ml metal vs. absorbance/emission, etc.). Aspirate the blank solution between each standard for at least one minute to ensure that each reading commence from the same baseline. The calibration plot must be linear - if not, prepare a fresh set of standard calibration samples and/or check the performance of the instrument as detailed by the manufacturer.

6.3 Sample Preparation Techniques Employed in this Method:

(a) Neat
(b) Dilution method
(c) Chemical separation and preconcentration
(d) Micro-wave or Muffle furnace ashing
(e) Micro-wave acid digestion
(f) Oxygen bomb
(g) Standard addition approach
(h) Leachable metals.

6.3.1 (a) Neat

6.3.1.1 Neat analysis of sample can be carried out with ease providing sample behaves similarly to the standards (see note 3 above).

6.3.1.2 Read absorbance or emission and determine concentration from calibration curve prepared from the respective calibration standards prepared in water, MIBK or GAC where appropriate.

6.3.2 (b) **Simple Dilution Method** (Trace metals in raw materials and finished products containing 0.01 ppm or greater at 10% dilution). **See note 3 above.*

6.3.2.1 For water soluble solids or water miscible liquid samples, prepare an appropriate dilution [based on expected concentration of metal(s) of the material in water or 1.0 M hydrochloric acid (W/V).

6.3.2.2 Similarly for aqueous insoluble solids or liquid samples, prepare appropriate dilution [based on the expected concentration of metal(s)] of the material in MIBK for AAS or GAC for ICP-AES.

6.3.2.3 Obtain absorbance or emission of the sample solution and read the conc. from the respective standard calibration plot.

6.3.3 **Assay of Acrylic Accelerators (Special Case).**

> Note 2.- The level of copper, iron and cobalt used in Loctite accelerators are normally high i.e 20 - 40 ppm and 500 - 1000 ppm respectively and can be suitably diluted in a solvent without effecting the nebulisation efficiency providing the standards are prepared appropriately. (care must taken where high viscosity activators contain low levels of metals). New, unknown or competitors accelerators may require different weights/dilution in order to bring the concentration within the calibration range and such samples may need to be analysed under trial conditions before quantitative measurements can be used. See note 3 above.

6.3.3.1 **For Accelerators Containing 20-40 ppm Metal.**

6.3.3.1.1 Weigh between 2.0000 - 2.5000g of the accelerator into a 100 ml volumetric flask and dissolve in the 20% ethanol/MIBK mixture for AAS or GAC for ICP-AES measurement.

6.3.3.1.2 Obtain the absorbance or emission of the sample solution and read the concentration from the calibration plot.

6.3.3.2 **For Accelerators Containing 500-1000 ppm Metal.**

6.3.3.2.1 Weigh between 0.3000 - 0.4000g of the accelerator into a 100 ml volumetric flask and dissolve in the 20% ethanol/MIBK mixture for AAS or GAC for ICP-AES measurement.

6.3.3.2.2 Obtain the absorbance of the sample solution and read the concentration from the calibration plot.

6.3.4 (c). ***Chemical Separation and Preconcentration.***

> Note 3.- Aqueous samples containing less than 0.01 ppm metals cannot be accurately measured either directly or by dilution. The limit of quantification (10x S.D of background noise) is 0.01 ppm for copper and iron. Such samples need to be separated and preconcentrated by extraction into MIBK or Chloroform with a solubilising complexing agent (e.g. ammonium pyrrolidine thiocarbamate [APDC]) and measuring the concentrations of metals against standards prepared in the same solvent. The complexed metal(s) are only soluble in the MIBK or CHCl3. These solvents can be used on the AAS, however for ICP-AES it necessary to evaporate the solvent and redissolving the metal complex(s) in GAC. This technique is applicable to aqueous raw materials that are used in metal sensitive adhesive products
>
> Similarly aqueous insoluble liquid samples containing less than 0.01 ppm metals are dissolved in MIBK or CHCl3 and metals are extracted into a reduced volume of weak aqueous acid solution. The extracted metals are measured against aqueous acid standards prepared in the same acid.

6.3.4.1 **Procedure for Extraction of Aqueous Samples into APDC/MIBK or APDC/$CHCl_3$**

6.3.4.1.1 Dissolve 1.0 gram of purified APDC in de-ionised water and dilute to 100 ml.

6.3.4.1.2 To 25.0 ml of of liquid aqueous sample solution (or 10g of of solid dissolved in 50 ml of deionised water or AnalaR grade 1.0 M HCl) add 1.0 ml of APDC solution. Adjust the pH to ~5.0 with 1.0M NaOH. Transfer the solution to a 100 ml separating funnel, extract the metal complex(es) into 2 x 5.0 ml lots of MIBK /APDCor CHCl3/APDC (may need to centrifuge to break emulsion and assist separation). Combine the extracts and aspirate into AAS. Measure the absorbance of metals in samples against standards prepared in the same solvent used to extract the metal(s). For ICP-AES measurement, evaporate 10 ml to dryness and redissolve the APDC-Metal complexes in GAC.

6.3.5.1 Procedure for Extraction of Non-Aqueous Sample into an Aqueous Solution of 0.1M HCl.

6.3.5.1.1 Twenty five grams of liquid sample is diluted in 50 ml of $CHCl_3$. The solution is then extracted with 2 x 10 ml of 0.1M HCl and combined (may need to centrifuge to break the emulsion and aid separation). The metal(s) content are measured against aqueous standards prepared in 0.1M HCl.

6.3.6 (d) Total Metal Content of Fillers, Thixotropes and Pigments by Muffle Furnace Preparation.

Note 4. - The dry ashing methods are preferred where possible, as the residues can be taken up in the simplest possible acid solvent. Many organic matrices are completely oxidised at 550-600 °C. It also allows large sample sizes to be 'burned off' and the ash dissolved in the minimum volume of acid solvent concentrating the metals present in the sample. Some suspect volatile elements can be ashed in the presence of p-TSA (forms metal sulphates) will be retained. Platinum dishes are used because it minimises risk of contamination from previous sample and can be readily cleaned by boiling in 1.0 M HCl and finally washing with pure distilled water and drying prior to use. The ash/salts are readily soluble in 0.1M HCl. Multiple ashing may be required for very low levels of metals (i.e repeated ashing of same sample in the same crucible over two or three times).

6.3.6.1 Prior to use, contact the platinum crucibles and lids with boiling 1.0M HCL for 10 minutes.
6.3.6.2 Rinse the crucibles with de-ionised water and carefully dry.
6.3.6.3 Mix ~5.0g of sample (maximum sample size per crucible for muffle capacity) with 0.2g of P-TSA.
6.3.6.4 Ash to 550 °C using the ramping control as follows:
(i) 100 °C for 25 min, hold for 5 min.
(ii) 250 " " 25 min, " " 5 "
(iii) 450 " " 40 min, " " 5 "
(iv) 550 " " 40 min, " " 60 "
6.3.6.5 Prepare a blank by ashing 0.2g of p-TSA.
6.3.6.6 Dissolve the residue in 10 ml of 0.1M HCl. (DO NOT USE HNO3 WITH PLATINUM DISHES)
6.3.6.7 Read concentration against calibration curve prepared in 0.1M HCl.

6.3.7 (e) Sample Preparation Using Micro-Wave Acid Digestion.

Note 5. -This method of sample preparation is suitable for samples containing at least 0.2 ppm metal and is rapid, clean and reproducible. Maximium sample size for organics is approximately 0.5g which must be diluted to 10 ml (dilution = 5%) with a mixture of concentrated acids and water. The preferred method of quantification is carried out using standard addition approach prepared with the micro-wave digestor. Duplicate sample, standards and blank can prepared in a single operation. Refer to the manufacturer's handbook for details of ramping time, pressure and temperatures for samples to be prepared by this procedure. Since this is a relatively new technique routine protocols have not been developed for this approach. Reference to manufacturers handbook may give some guide to samples that are most appropriate to this technique.

6.3.8 (f) Sample Preparation Using Oxygen Bombing Digestion.

6.3.8.1 Contact a suitable 2.0 ml platinium dish with boiling 1.0M HCl for 10 minutes.
6.3.8.2 Wash with de-ionised water.
6.3.8.3 Charge the bomb with 0.5g of sample under test followed by 5.0 ml of 0.05M NaOH
6.3.8.4 Operate according to Method 205M detailed by manufacturers (Parr).
6.3.8.5 After firing allow to stand for 15 minutes after which it is opened slowly to allow the generated gases to escape slowly to avoid loss of sample and washed out with the minimum of deionised water to a maximum of 10 ml.
6.3.8.6 Read the concentration against aqueous standards prepared in 0.05M NaOH/water mixture.

6.3.9 (g) Measurement Using Standard Addition Approach.

Note 6. The principle of the method:
The sample is diluted in a solvent and aliquots of standards are added to overcome interference effects by matching standards with samples. The method corrects only for effects that modify the slope of the calibration curve, i.e. the elemental sensitivity, and not those interferences that affect the absorbance at zero concentration. This method can be applied to aqueous and non-aqueous samples.

The sample is divided into three aliquots and to each but one is added known increasing concentrations of the metal to be determined and the samples are then made up to the same volume/concentration. The curve generated is extrapolated and the concentration of metal is determined on the negative extension of the calibration line. Calibration standards containing the same concentrations but without the sample must be prepared and the curves must be parallel and passing through the origin. This method is applicable to the raw material, Matrimid 5292 A (Code 1-257).

6.3.9.1 Preparation of Aqueous and Non-Aqueous Samples for Analysis by Standard Addition Approach.

6.3.9.1.1 Three similar precise weight or volume of liquid sample or solid are transferred to volumetric flasks and known different volume of stock standard prepared under 6.3.1.1 are added to each except one. The solutions are then made up to mark with water, 1.0M HCl, MIBK or GAC where appropriate and signal response measured versus concentrations. A similar series of standards are prepared without the sample.
6.3.9.1.2 The standard addition graph is plotted and slope is extrapolated to determine the true concentration of metal in the sample.

6.3.9.1.3 A second series of standards of the same concentrations are prepared without the sample and the calibration curve must be parallel to slope and passing through the origin. If the slope is not parallel the interferences caused by the sample are too severe and recourse must be made to other forms of sample preparations eg. extraction, microwave acid digestion, ashing etc.,.

6.3.10 (h) Leachable Trace Metal Contents of Fillers, Thixotropes and Pigments (Insoluble Type)

6.3.10.1 To 50 ml 1N HCl, add 5-10 g (to 4 decimal places) of material.
6.3.10.2 Stir mixture on magnetic stirrer for 60 minutes.
6.3.10.3 Filter off solid and determine the concentration against standards prepared in 1.0M HCl using either AAS or ICP-AES.

7. PROCEDURES FOR SPECIAL SAMPLE HANDLING

7.1 Metal Content of Code 3-65

Note 7. - This procedure is based on acid extraction of metals from Code 3-65. The Code 3-65 is heated in 1N HCl to dissolve the compound and allowed to cool to room temperature. The reprecipitated 3-65 is filtered off after cooling and the filtrate is analyzed by AAS or ICP-AES in the usual way.

7.1.1 Weigh accurately (to 4 decimal places) 10 grams of Code 3-65 into a 250 ml beaker. Break up any agglomerate with a clean glass rod prior to dissolution.
7.1.2 Add 100 ml 1N HCl (Analar grade) to this and heat to boiling to dissolve the Code 3-65. Maintain this temperature for 15-20 minutes and observe volume change and top up.
7.1.3 Allow to cool to room temperature and finally to 4 °C in a fridge for two hours (80-90% should reprecipitate).
7.1.4 Decant and Filter approximately 15-20 ml through a fast flowing filter paper.
7.1.5 Determine the level of copper and iron against standards prepared in the same acid on the filtrate and on the acid blank.

Note 8. - It may be necessary to evaporate to a more concentrated volume if low, inaccurate readings are obtained (N.B. evaporate the blank acid in the same way). All changes in volume must be taken into consideration in the final calculations.

72. Determination of Total Metals Content of Plastic Bottles, Beads & Powders.

Note 9. - This procedure involves ashing the sample slowly as per 6.2.4 above in the presence of p-toluene sulphonic acid. The ash residue, which should be white, is dissolved in 1M HCl and read directly against a known standard calibration curve.

7.2.1 Weigh accurately between 5 - 6 grams of cut fragments of plastic bottles, beads & powder into a platinum dish (previously cleaned with 1M HCl) followed by 0.1g of p-toluene sulphonic acid.
7.2.2 Place the sample and dish with lid into a muffle furnace at room temperature and allow to burn gradually until a temperature of 550°C is attained.
7.2.3 Remove the dish from the furnace and allow to cool to room temperature.
7.2.4 Add 5 ml of 1M HCl and heat on a hot plate for 30 - 60 seconds to dissolve the ash.
7.2.5 Centrifuge after cooling and read against a zinc calibration curve prepared in 1M HCl.
7.2.6 Ash a blank of 0.1g of p-toluene sulphonic acid and read against the same calibration curve.
7.2.7 Calculate metal content as follows:

$$\text{ppm metal} = \frac{\text{Reading in µg/ml (Ex Calibration Plot)}}{\text{weight of sample}} \times 5\text{ml}$$

7.4 3 Determination of 'Surface' Zinc Content of Aluminum Tubes

7.4.3.1 Surface Zinc Content

7.4.3.1.1 Fill aluminum tube with 1.0M HCl and allow to stand for 20 minutes at room temperature.
7.4.3.1.2 Transfer acid solution to a clean glass vial and measure absorbance against standards prepared in 1.0M HCl using AAS or ICP-AES.
7.4.3.1.3 Calculate 'total' or 'surface' zinc content as follows:

$$\text{ppm Surface Zn} = \frac{\text{Reading in µg/ml (Ex Calibration Plot)}}{\text{weight of tube used}} \times \text{ml 1 N HCl}$$

7.4Total Metal Scan for Cyanacrylate Adhesive

Note14. Cyanoacrylate monomers as produced in Manufacturing Plant using stainless steel reaction vessels contain very low levels of metals. In order to measure them sample preparation involves multi-ashing of the same sample in the same platinum dish.

7.4.1 Procedure

7.4.1.1 Spread 2.0g of TAD reagent (0.1% N-t-butyl-2-benothiazole sulphanamide [3-147] in glycerol triacetate [4-105]) evenly over a flat Teflon block.
7.4.1.2 Spread 20g of CA evenly over the TAD reagent and mix with an applicator stick to aid polymerisation.
7.4.1.3 Collect the solid CA and break with Teflon spatula into reasonable small pieces
7.4.1.4 Weigh ~5.5g of solid CA into clean platinum dish and burn as per 6.3.6 above.
7.4.1.5 Repeat until all the sample is consumed using same dish.
7.4.1.6 Ash 2.0g of the TAD reagent as a blank.
7.4.1.7 Dissolve the residue in 1.0M HCl.
7.4.1.8 Scan for metals against a multi-element standards prepared 1.0M HCl

7.5 Metal Scan for Saccharin (3-2)

7.5.1 Three similar precise weights of saccharin (2.0g) were weight into clean 50.0 ml plastic volumetric flasks followed by ~25 ml of deionised water. Add 5.0 ml of Ammonia solution (+25% conc^n, *added in excess to maintain solubility during analysis*) to the flask and shake by hand for 2-3 minutes to dissolve the saccharin. To the first flask add 0.1 ppm/ml of Cu, Fe to the flask, to the second add 0.2 ppm/ml Cu, Fe and to the third flask add 0.0 ppm/ml. Dilute to mark with de-ionised water and measure signal response versus concentrations. A similar series of samples were prepared without the sample.

7.5.2 Continue as for 6.3.9 above.

7.6 Metal Content of Chipbonder Products.

Note 11. This product can be analysed using microwave acid digestion or microwave ashing method with equal reproducibility for ULTRA TRACE metals content. Extreme care in terms of accuracy, contamination and instrument calibration must be applied to ensure confidence in analysis. Extra care in handling strong acids, particularly HF must be applied. All sample preparations must be carried out in a suitable fumehood.

7.6.1 **Ashing Method Using Microwave Oven** (Standard addition comparison)

7.5.1.1 Prior to use, contact the platinum crucibles and lids with 1.0M HCl with heat for ~5-10 minutes. Rinse with de-ionised water and dry in an oven @150 $^{\circ}$C for 1.0 hour.
7.5.1.2 Prepare three samples for analysis in clean platinum dishes as follows:
7.5.1.2.1 Add approximately 1.0g of chipbonder sample weighed accurately with 0.1g of p-toluene sulphonic acid.
7.5.1.2.2 Add approximately 1.0g of chipbonder sample weighed accurately with 0.1g of p-toluene sulphonic acid and 0.5 ppm/g 'spike' of metals of interest from certified standard(s). *(where several elements are required 'spike' of 0.5 ppm/g of a suitable multi- element standard may be used)).*
7.5.1.2.3 Weigh 0.1g of p-toluene sulphonic acid to convert volatile elements to less volatile metal sulphates.

7.5.2 Ash slowly, using the ramping and temperature control of the microwave oven as follows:

(i) 100 °C for 40.0 minutes, hold for 5.0 minutes
(ii) 200 °C " "
(iii) 400 °C " "
(iv) 650 °C " "

7.5.2.1 After cooling, add to ash (*which is mostly SiO2*), 10.0 ml conc. HNO_3 + 2.0 ml conc. HCl. Transfer immediately to a teflon beaker with approximately 10.0 ml of deionised water washing traces of ash into the beaker. Heat gently on a hot plate to a maximum temperature of ~150 °C to reduce the volume to 25-30% of original volume. Cool add 5.0 ml conc HF and heat gently until the SiO_2 has dissolved. The volume may be further reduced to ~50%. Cool and transfer to a clean 25.0 ml plastic volumetric flask, wash and make up to mark with de-ionised water.

7.5.2.2 Analyse each sample against 0.0, 0.25, 0.5 and 1.0 ppm metal(s) standards prepared in 5.0 ml conc. HNO_3 + 5.0 ml conc. HCL + 5.0 ml conc. HF to 100.0 ml of de-ionised water in plastic volumetric flasks. A suitable internal standard (eg Sc, Y, Au etc.,) is used with an ultra sonic nebuliser.

7.5.2.3 The result of subtraction of the 'spiked' metal(s) from the total should be within 90—110% of the unspiked sample.

7.5.3 **Microwave Acid Digestion Method** (*Standard addition comparison*).

7.5.3.1 Clean teflon vessels with 1.0M HCl followed by de-ionised water dry in oven @120 °C.
7.5.3.2 Prepare three samples for analysis in clean teflon vessels as follows:
7.5.3.3 Weigh accurately approximately 0.5g of chipbonder sample into a vessel ensuring that it is placed at bottom. Add 10.0 ml of conc. HNO_3 + 2.0 ml conc. HCl.
7.5.3.4 Weigh accurately approximately 0.5g of chipbonder sample into a vessel ensuring it is at the bottom and add 0.5 ppm metal(s)/g from a certified standard(s). Add 10.0 ml of conc. HNO_3 + 2.0 ml conc. HCl.
7.5.3.5 Add 10.0 ml conc. HNO3 + 2.0 ml conc. HCl.
7.5.3.6 Allow samples to pre-digest for ~2.0 hours.

7.5.3.7 Assemble vessels suitable for microwave digestion according to manufacturer's instruction and digest as follows:

PART 1.

Stage	Watts	Power %	Ramp min.	Press. psi	Temp. °C	Hold min.
1	600	100	10.0	150	140	5.0
2	600	100	10.0	200	150	5.0
3	600	100	10.0	350	160	5.0
4	600	100	10.0	500	180	5.0
5	600	100	10.0	600	200	5.0

7.5.3.8 Allow the vessels to cool and open carefully in a fume hood. Add 5.0 ml of conc. HF and reassemble and digest as follows:

PART 2

Stage	Watts	Power %	Ramp min.	Press. psi	Temp. oC	Hold min.
1	600	100	30.0	150	200	15.0
2	600	100	30.0	400	210	15.0

7.5.3.9 After cooling, transfer the contents of each vessel to a 25.0 ml plastic volumetric flask and wash with deionised water up to mark.

7.5.3,10 Analyse each sample against 0.0, 0.25, 0.5, and 1.0 ppm metal(s) standards prepared in 5.0 ml conc. HNO_3 + 5.0 ml conc. HCl + 5.0 ml conc. HF in 100 ml plastic volumetric flasks. A suitable internal (Sc, Y, Au etc.,) is used with an ultra sonic nebuliser.

7.5.3.11 Similar to 7.5.2.3 above.

8. RECORDS

10.1 Record the following information:
10.1.1 Results (concentration of metals) in ppm to the nearest 0.1 ppm.
10.1.2 Any deviations from this method.

9. PRECISION

9.1 The precision of this test method is not known at this time because inter-laboratory data is not available.

ANNEX

Raw Matl.	Method	Raw Matl.	Method	Raw Matl.	Method
1-3	6.3.2.2	1-87	6.3.2.2	1-139	6.3.2.2
1-4	"	"	"	1-140	"
1-5	"	1-90	"	1-141	"
1-7	"	1-91	"	1-142	"
1-8	"	1-92	"	1-143	"
1-9	"	1-95	"	1-144	"
1-10	"	1-96	"	1-145	"
1-12	"	1-97	"	1-148	"
1-14	(50% in 0.1M HCl+ GAC)	1-98	"	1-151	"

1-15	(50% in 0.1M HCl+ GAC)	1-99	"	1-154	"
1-19	(C) 6.3.2.2	1-101	"	1-155	"
1-28	"	1-102	"	1-156	"
1-33	6.3.7	1-103	"	1-157	"
	6.3.2.2	1-107	"	1-158	"
1-40	"	1-111	"	1-162	"
1-41	"	1-112	"	1-163	"
1-42	6.3.7	1-116	"	1-164	"
1-43	6.3.2.2	1-117	"	1-169	"
1-44	"	1-118	"	1-170	"
1-47	"	1-119	6.3.7 (1-257)	1-172	"
1-60	"	1-120	6.3.2.2	1-173	"
1-61	"	1-121	"	1-175	"
1-63	"	1-123	"	1-176	"
1-64	"	1-125	"	1-180	"
1-65	"	1-126	"	1-181	"
1-66	"	1-129	"	1-182	"
1-69	"	1-132	"	1-183	"
1-77	"	1-134	"	1-186	"
1-79	"	1-135	"	1-205	"
			"	1-257	6.3.7
1-82	"	1-136	"	3-2	7.5
1-83	"	1-137	"	3-24	1.0N HCl See 6.3.2 (B) 10,000 fold dilution.
1-84	"	1-138	"	3-65	Aq. acid extract See 7.1

ANNEX (cont.)

Raw Matl.	Method	Raw Matl.	Method		
3-66	6.3.6	4-59	6.3.2.2		
3-76	6.3.6	4-60	6.3.7		
3-87	0.1g → 100 ml 1.0 ml → 100 ml 0.1M HCl	4-71	Ash " 6.3.7		
3-107	0.1g to 100ml MIBK 2 ml of this to 100ml with MIBK or GAC	4-75	6.3.2.2		
		4-89	6.3.7		
		4-92	6.3.2.2		
3-108	0.1g to 100ml MIBK 2 ml of this to 100ml with MIBK or GAC	4-96	6.3.7		
		4-109	6.3.7		
		4-117	Ash "		
3-131	Aq. acid extract See 7.1	4-127	See 6.3.4 (c) 6.3.2.2		
3-133	0.1g to 100ml MIBK 2 ml of this to 100ml with MIBK or GAC	4-160	Ash 6.3.7	4-55	6.3.10
		4-165	Ash "	9-75	See 6.3.9 (h) "
		4-199	6.3.2.2	9-78	"
3-135	0.1g to 100ml MIBK	5-24	6.3.10	9-80	0.2g in 5 ml Aqua regia

					0.5g → 100 water
	2 ml of this to 100ml with MIBK or GAC	5-35	"	9.81	6.3.10
		5-56	"	9-232	"
3-145	0.1g to 100ml MIBK 2 ml of this to 100ml with MIBK or GAC	5-62	"	11-5	6.3.2.2 "
		5-63	"	11-6	"
		5-67	"	11-7	"
3-146	0.1g → 100 ml 0.1M HCl 2.0 ml → 100 ml 0.1M HCl	5-69	"	11-17	"
4-1	6.3.2.2	5-70	Aq. acid extract "		
4-3	6.3.7	5-138	Aq. acid extract "		
4-4	"	7-31	6.3.7		
4-13	"	7-80	6.3.2.2		
4-14	"	9-1	0.1g → 100 ml 0.1M HCl 0.1 ml → 100 ml 0.1M HCl		
4-15	"	9-40	6.3.10		
4-20	6.3.2.2	9-51	"		
4-23	"	9-60	"		
4-24	"	9-62	"		
4-34	"	9-67	"		
4-44	6.3.7	9-70	"		

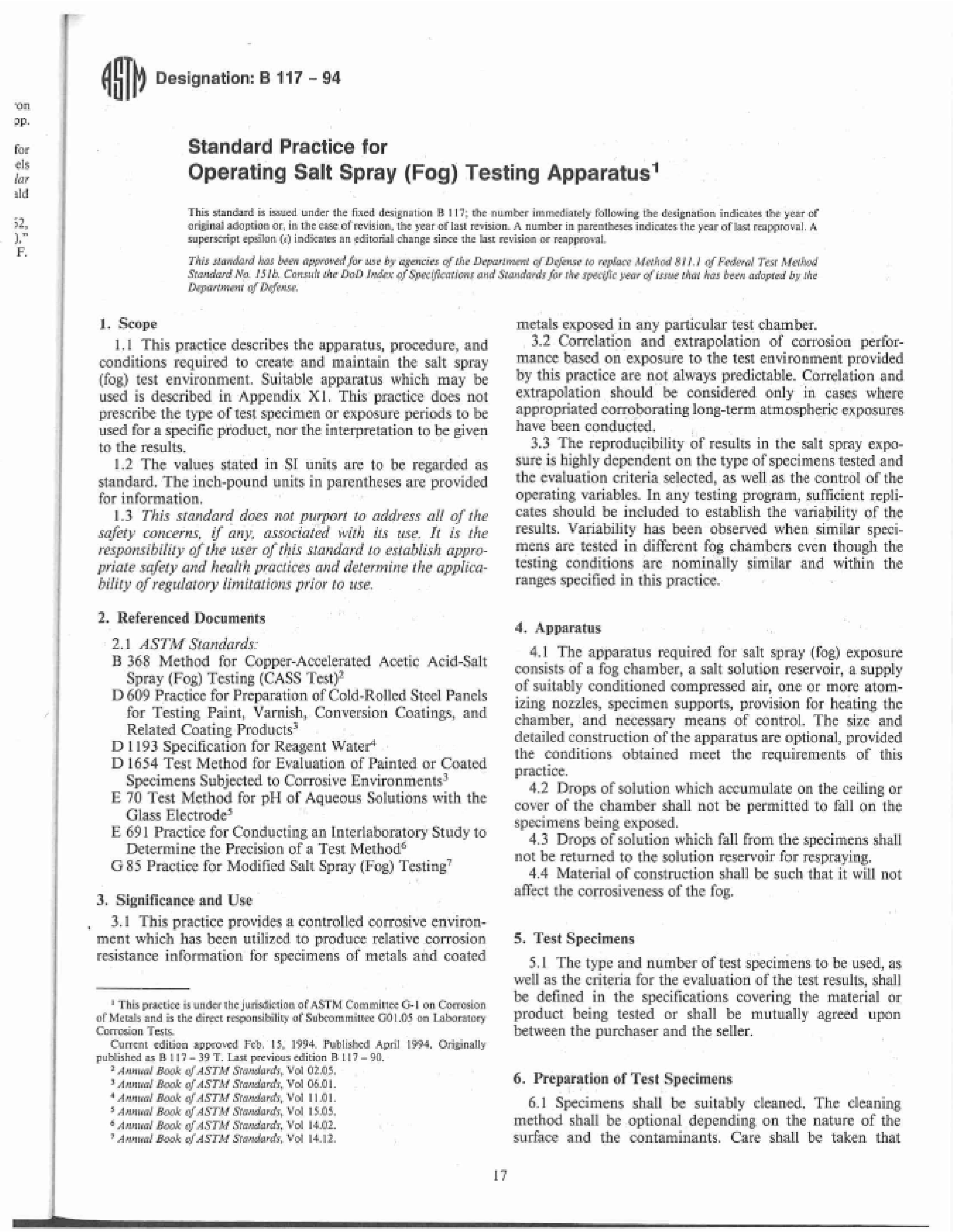
ANNEX (cont.)
Copper Analysis of Anaerobic Activators by AAS or ICP-OES

Product Number	Bulk Number	Conc. of Copper in Activator (ppm)	Dilution Factor (wt/vol)	Avg Results via AAS (ppm) as µg/ml)
LID 3074	178074	3200	2.0g →100ml MIBK 5 ml →100ml MIBK or GAC	3.20
LID 3075	178075	3200	2.0g →100ml MIBK 5 ml →100ml MIBK or GAC	3.20
7649	178276	850	0.5g →100ml MIBK or GAC	4.25
7639	178280	40000 (4.0%)	1.0g →100ml MIBK 1 ml →100ml MIBK or GAC	4.00
7641	178539	850	5.0g →100ml MIBK	4.25
734	170034	360	5.0g →100ml MIBK or GAC	3.60
7851	178006	7.5	5.0g →100ml MIBK or GAC	0.75
LID 3013	178013	360	5.0g →100ml MIBK or GAC	3.60
7342	178017	360	5.0g →100ml MIBK or GAC	3.60
7386	178278	30	5.0g →100ml MIBK or GAC	1.50
7407	178279	70	5.0g →100ml MIBK or GAC	3.50
7406	178314	72	5.0g →100ml MIBK or GAC	3.60
7388	178415	22.5	5.0g →100ml MIBK or GAC	1.50
LID 3195	178195	4000	5.0g →100ml MIBK	4.00

			5 ml →100ml MIBK or GAC	

NOTE: The above dilutions are designed to measure copper content against a calibration curve of linear range of 0.0 → 10.0 ppm copper. A second serial dilution by volume is required for the more concentrated activators. The average results listed in the table are at the lower end of the calibration curve to avoid over loading the sample in MIBK or GAC so that the sample/solvent effect will be minimum when compared with standards prepared in MIBK or GAC only. Consult the operator's manual to determine the recommended linear range of copper for the particular instrument and conditions used.

Appendix H: ASTM B117-94



Designation: B 117 – 94

Standard Practice for Operating Salt Spray (Fog) Testing Apparatus[1]

This standard is issued under the fixed designation B 117; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense to replace Method 811.1 of Federal Test Method Standard No. 151b. Consult the DoD Index of Specifications and Standards for the specific year of issue that has been adopted by the Department of Defense.

1. Scope

1.1 This practice describes the apparatus, procedure, and conditions required to create and maintain the salt spray (fog) test environment. Suitable apparatus which may be used is described in Appendix X1. This practice does not prescribe the type of test specimen or exposure periods to be used for a specific product, nor the interpretation to be given to the results.

1.2 The values stated in SI units are to be regarded as standard. The inch-pound units in parentheses are provided for information.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

B 368 Method for Copper-Accelerated Acetic Acid-Salt Spray (Fog) Testing (CASS Test)[2]

D 609 Practice for Preparation of Cold-Rolled Steel Panels for Testing Paint, Varnish, Conversion Coatings, and Related Coating Products[3]

D 1193 Specification for Reagent Water[4]

D 1654 Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments[3]

E 70 Test Method for pH of Aqueous Solutions with the Glass Electrode[5]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[6]

G 85 Practice for Modified Salt Spray (Fog) Testing[7]

3. Significance and Use

3.1 This practice provides a controlled corrosive environment which has been utilized to produce relative corrosion resistance information for specimens of metals and coated metals exposed in any particular test chamber.

3.2 Correlation and extrapolation of corrosion performance based on exposure to the test environment provided by this practice are not always predictable. Correlation and extrapolation should be considered only in cases where appropriated corroborating long-term atmospheric exposures have been conducted.

3.3 The reproducibility of results in the salt spray exposure is highly dependent on the type of specimens tested and the evaluation criteria selected, as well as the control of the operating variables. In any testing program, sufficient replicates should be included to establish the variability of the results. Variability has been observed when similar specimens are tested in different fog chambers even though the testing conditions are nominally similar and within the ranges specified in this practice.

4. Apparatus

4.1 The apparatus required for salt spray (fog) exposure consists of a fog chamber, a salt solution reservoir, a supply of suitably conditioned compressed air, one or more atomizing nozzles, specimen supports, provision for heating the chamber, and necessary means of control. The size and detailed construction of the apparatus are optional, provided the conditions obtained meet the requirements of this practice.

4.2 Drops of solution which accumulate on the ceiling or cover of the chamber shall not be permitted to fall on the specimens being exposed.

4.3 Drops of solution which fall from the specimens shall not be returned to the solution reservoir for respraying.

4.4 Material of construction shall be such that it will not affect the corrosiveness of the fog.

5. Test Specimens

5.1 The type and number of test specimens to be used, as well as the criteria for the evaluation of the test results, shall be defined in the specifications covering the material or product being tested or shall be mutually agreed upon between the purchaser and the seller.

6. Preparation of Test Specimens

6.1 Specimens shall be suitably cleaned. The cleaning method shall be optional depending on the nature of the surface and the contaminants. Care shall be taken that

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[1] This practice is under the jurisdiction of ASTM Committee G-1 on Corrosion of Metals and is the direct responsibility of Subcommittee G01.05 on Laboratory Corrosion Tests.

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[2] *Annual Book of ASTM Standards*, Vol 02.05.

[3] *Annual Book of ASTM Standards*, Vol 06.01.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] *Annual Book of ASTM Standards*, Vol 15.05.

[6] *Annual Book of ASTM Standards*, Vol 14.02.

[7] *Annual Book of ASTM Standards*, Vol 14.12.

specimens are not recontaminated after cleaning by excessive or careless handling.

6.2 Specimens for evaluation of paints and other organic coatings shall be prepared in accordance with applicable specification(s) for the material(s) being tested, or as agreed upon between the purchaser and the supplier. Otherwise, the test specimens shall consist of steel meeting the requirements of Practice D 609 and shall be cleaned and prepared for coating in accordance with the applicable procedure of Practice D 609.

6.3 Specimens coated with paints or nonmetallic coatings shall not be cleaned or handled excessively prior to test.

6.4 Whenever it is desired to determine the development of corrosion from an abraded area in the paint or organic coating, a scratch or scribed line shall be made through the coating with a sharp instrument so as to expose the underlying metal before testing. The conditions of making the scratch shall be as defined in Test Method D 1654, unless otherwise agreed upon between the purchaser and the seller.

6.5 Unless otherwise specified, the cut edges of plated, coated, or duplex materials and areas containing identification marks or in contact with the racks or supports shall be protected with a suitable coating stable under the conditions of the test, such as ceresin wax.

NOTE 1—Should it be desirable to cut test specimens from parts or from preplated, painted, or otherwise coated steel sheet, the cut edges shall be protected by coating them with paint, wax, tape, or other effective media so that the development of a galvanic effect between such edges and the adjacent plated or otherwise coated metal surfaces, is prevented.

7. Position of Specimens During Exposure

7.1 The position of the specimens in the salt spray chamber during the test shall be such that the following conditions are met:

7.1.1 Unless otherwise specified, the specimens shall be supported or suspended between 15 and 30° from the vertical and preferably parallel to the principal direction of flow of fog through the chamber, based upon the dominant surface being tested.

7.1.2 The specimens shall not contact each other or any metallic material or any material capable of acting as a wick.

7.1.3 Each specimen shall be so placed as to permit free settling of fog on all specimens.

7.1.4 Salt solution from one specimen shall not drip on any other specimen.

NOTE 2—Suitable materials for the construction or coating of racks and supports are glass, rubber, plastic, or suitably coated wood. Bare metal shall not be used. Specimens shall preferably be supported from the bottom or the side. Slotted wooden strips are suitable for the support of flat panels. Suspension from glass hooks or waxed string may be used as long as the specified position of the specimens is obtained, if necessary by means of secondary support at the bottom of the specimens.

8. Salt Solution

8.1 The salt solution shall be prepared by dissolving 5 ± 1 parts by mass of sodium chloride in 95 parts of water conforming to Type IV water in Specification D 1193 (except that for this practice limits for chlorides and sodium may be ignored). The salt used shall be sodium chloride substantially free of nickel and copper and containing on the dry basis not more than 0.1 % of sodium iodide and not more than 0.3 % of total impurities. Some salts contain additives that may act as corrosion inhibitors; careful attention should be given to the chemical content of the salt. Upon agreement between the purchaser and the seller, analysis may be required and limits established for elements or compounds not specified in the chemical composition given above.

8.2 The pH of the salt solution shall be such that when atomized at 35°C (95°F) the collected solution will be in the pH range from 6.5 to 7.2 (Note 3). Before the solution is atomized it shall be free of suspended solids (Note 4). The pH measurement shall be made at 25°C (77°F) using a suitable glass pH-sensing electrode, reference electrode, and pH meter system in accordance with Test Method E 70.

NOTE 3—Temperature affects the pH of a salt solution prepared from water saturated with carbon dioxide at room temperature and pH adjustment may be made by the following three methods:

(*1*) When the pH of a salt solution is adjusted at room temperature, and atomized at 35°C (95°F), the pH of the collected solution will be higher than the original solution due to the loss of carbon dioxide at the higher temperature. When the pH of the salt solution is adjusted at room temperature, it is therefore necessary to adjust it below 6.5 so the collected solution after atomizing at 35°C (95°F) will meet the pH limits of 6.5 to 7.2. Take about a 50-mL sample of the salt solution as prepared at room temperature, boil gently for 30 s, cool, and determine the pH. When the pH of the salt solution is adjusted to 6.5 to 7.2 by this procedure, the pH of the atomized and collected solution at 35°C (95°F) will come within this range.

(*2*) Heating the salt solution to boiling and cooling to 35°C (95°F) for maintaining it at 35°C (95°F) for approximately 48 h before adjusting the pH produces a solution the pH of which does not materially change when atomized at 35°C (95°F).

(*3*) Heating the water from which the salt solution is prepared to 35°C (95°F) or above, to expel carbon dioxide, and adjusting the pH of the salt solution within the limits of 6.5 to 7.2 produces a solution the pH of which does not materially change when atomized at 35°C (95°F).

NOTE 4—The freshly prepared salt solution may be filtered or decanted before it is placed in the reservoir, or the end of the tube leading from the solution to the atomizer may be covered with a double layer of cheesecloth to prevent plugging of the nozzle.

NOTE 5—The pH can be adjusted by additions of dilute cp hydrochloric acid or cp sodium hydroxide solutions.

9. Air Supply

9.1 The compressed air supply to the nozzle or nozzles for atomizing the salt solution shall be free of oil and dirt (Note 6) and maintained between 69 and 172 kN/m^2 (10 and 25 psi).

NOTE 6—The air supply may be freed from oil and dirt by passing it through a water scrubber or at least 610 mm (2 ft) of suitable cleaning material such as sheep's wool, excelsior, slag wool, or activated[7] alumina. Commercial cartridge filters which include an expiration indicator may also be used.

10. Conditions in the Salt Spray Chamber

10.1 *Temperature*—The exposure zone of the salt spray chamber shall be maintained at 35 + 1.1 − 1.7°C (95 + 2 − 3°F). The temperature within the exposure zone of the closed cabinet shall be recorded at least twice a day at least 7 h apart (except on Saturdays, Sundays, and holidays when the salt spray test is not interrupted for exposing, rearranging, or removing test specimens or to check and replenish the solution in the reservoir).

NOTE 7—A suitable method to record the temperature is by a continuous recording device or by a thermometer which can be read from outside the closed cabinet. The recorded temperature must be obtained with the salt spray chamber closed to avoid a false low reading because of wet-bulb effect when the chamber is open.

10.2 *Atomization and Quantity of Fog*—At least two clean fog collectors shall be so placed within the exposure zone that no drops of solution from the test specimens or any other source shall be collected. The collectors shall be placed in the proximity of the test specimens, one nearest to any nozzle and the other farthest from all nozzles. The fog shall be such that for each 80 cm^2 of horizontal collecting area there will be collected in each collector from 1.0 to 2.0 mL of solution per hour based on an average run of at least 16 h (Note 8). The sodium chloride concentration of the collected solution shall be 5 ± 1 mass % (Note 9). The pH of the collected solution shall be 6.5 to 7.2. The pH measurement shall be made as described in 8.2 (Note 3).

NOTE 8—Suitable collecting devices are glass or plastic funnels with the stems inserted through stoppers into graduated cylinders, or crystallizing dishes. Funnels and dishes with a diameter of 10 cm have an area of about 80 cm^2.

NOTE 9—A solution having a specific gravity of 1.0255 to 1.0400 at 25°C (77°F) will meet the concentration requirement. The sodium chloride concentration may also be determined using a suitable salinity meter (for example, utilizing a sodium ion-selective glass electrode) or colorimetrically as follows. Dilute 5 mL of the collected solution to 100 mL with distilled water and mix thoroughly; pipet a 10-mL aliquot into an evaporating dish or casserole; add 40 mL of distilled water and 1 mL of 1 % potassium chromate solution (chloride-free) and titrate with 0.1 *N* silver nitrate solution to the first appearance of a permanent red coloration. A solution that requires between 3.4 and 5.1 mL of 0.1 *N* silver nitrate solution will meet the concentration requirements.

10.3 The nozzle or nozzles shall be so directed or baffled that none of the spray can impinge directly on the test specimens.

11. Continuity of Exposure

11.1 Unless otherwise specified in the specifications covering the material or product being tested, the test shall be continuous for the duration of the entire test period. Continuous operation implies that the chamber be closed and the spray operating continuously except for the short daily interruptions necessary to inspect, rearrange, or remove test specimens, to check and replenish the solution in the reservoir, and to make necessary recordings as described in Section 9. Operations shall be so scheduled that these interruptions are held to a minimum.

12. Period of Exposure

12.1 The period of exposure shall be as designated by the specifications covering the material or product being tested or as mutually agreed upon between the purchaser and the seller.

NOTE 10—Recommended exposure periods are to be as agreed upon between the purchaser and the seller, but exposure periods of multiples of 24 h are suggested.

13. Cleaning of Tested Specimens

13.1 Unless otherwise specified in the specifications covering the material or product being tested, specimens shall be treated as follows at the end of the test:

13.1.1 The specimens shall be carefully removed.

13.2 Specimens may be gently washed or dipped in clean running water not warmer than 38°C (100°F) to remove salt deposits from their surface, and then immediately dried.

14. Evaluation of Results

14.1 A careful and immediate examination shall be made as required by the specifications covering the material or product being tested or by agreement between the purchaser and the seller.

15. Records and Reports

15.1 The following information shall be recorded, unless otherwise prescribed in the specifications covering the material or product being tested:

15.1.1 Type of salt and water used in preparing the salt solution,

15.1.2 All readings of temperature within the exposure zone of the chamber,

15.1.3 Daily records of data obtained from each fog-collecting device including the following:

15.1.3.1 Volume of salt solution collected in millilitres per hour per 80 cm^2,

15.1.3.2 Concentration or specific gravity at 35°C (95°F) of solution collected, and

15.1.3.3 pH of collected solution.

15.2 Type of specimen and its dimensions, or number or description of part,

15.3 Method of cleaning specimens before and after testing,

15.4 Method of supporting or suspending article in the salt spray chamber,

15.5 Description of protection used as required in 6.5,

15.6 Exposure period,

15.7 Interruptions in exposure, cause, and length of time, and

15.8 Results of all inspections.

NOTE 11—If any of the atomized salt solution which has not contacted the test specimens is returned to the reservoir, it is advisable to record the concentration or specific gravity of this solution also.

16. Keywords

16.1 controlled corrosive environment; corrosive conditions; determining mass loss; salt spray (fog) exposure

APPENDIXES

(Nonmandatory Information)

X1. CONSTRUCTION OF APPARATUS

X1.1 Cabinets

X1.1.1 Standard salt spray cabinets are available from several suppliers, but certain pertinent accessories are required before they will function according to this practice and provide consistent control for duplication of results.

X1.1.2 The salt spray cabinet consists of the basic chamber, an air-saturator tower, a salt solution reservoir, atomizing nozzles, specimen supports, provisions for heating the chamber, and suitable controls for maintaining the desired temperature.

X1.1.3 Accessories such as a suitable adjustable baffle or central fog tower, automatic level control for the salt reservoir, and automatic level control for the air-saturator tower are pertinent parts of the apparatus.

X1.1.4 The size and shape of the cabinet shall be such that the atomization and quantity of collected solution is within the limits of this practice.

X1.1.5 The chamber shall be made of suitably inert materials such as plastic, glass, or stone, or constructed of metal and lined with impervious plastics, rubber, or epoxy-type materials or equivalent.

X1.1.6 All piping that contacts the salt solution or spray should be of inert materials such as plastic. Vent piping should be of sufficient size so that a minimum of back pressure exists and should be installed so that no solution is trapped. The exposed end of the vent pipe should be shielded from extreme air currents that may cause fluctuation of pressure or vacuum in the cabinet.

X1.2 Temperature Control

X1.2.1 The maintenance of temperature within the salt chamber can be accomplished by several methods. It is generally desirable to control the temperature of the surroundings of the salt spray chamber and to maintain it as stable as possible. This may be accomplished by placing the apparatus in a constant-temperature room, but may also be achieved by surrounding the basic chamber of a jacket containing water or air at a controlled temperature.

TABLE X1.1 Operating Characteristics of Typical Spray Nozzle

Siphon Height, in.	Air Flow, L/min				Solution Consumption, mL/h			
	Air Pressure, psi				Air Pressure, psi			
	5	10	15	20	5	10	15	20
4	19	26.5	31.5	36	2100	3840	4584	5256
8	19	26.5	31.5	36	636	2760	3720	4320
12	19	26.5	31.5	36	0	1380	3000	3710
16	19	26.6	31.5	36	0	780	2124	2904

Siphon Height cm	Air Flow, dm³/min				Solution Consumption, cm³/h			
	Air Pressure, kPa				Air Pressure, kPa			
	34	69	103	138	34	69	103	138
10	19	26.5	31.5	36	2100	3840	4584	5256
20	19	26.5	31.5	36	636	2760	3720	4320
30	19	26.5	31.5	36	0	1380	3000	3710
40	19	26.6	31.5	36	0	780	2124	2904

X1.2.2 The use of immersion heaters in an internal salt solution reservoir or of heaters within the chamber is detrimental where heat losses are appreciable, because of solution evaporation and radiant heat on the specimens.

X1.3 Spray Nozzles

X1.3.1 Satisfactory nozzles may be made of hard rubber, plastic, or other inert materials. The most commonly used type is made of plastic. Nozzles calibrated for air consumption and solution-atomized are available. The operating characteristics of a typical nozzle are given in Table X1.1.

X1.3.2 It can readily be seen that air consumption is relatively stable at the pressures normally used, but a marked reduction in solution sprayed occurs if the level of the solution is allowed to drop appreciably during the test. Thus, the level of the solution in the salt reservoir must be maintained automatically to ensure uniform fog delivery during the test.[8]

X1.3.3 If the nozzle selected does not atomize the salt solution into uniform droplets, it will be necessary to direct the spray at a baffle or wall to pick up the larger drops and prevent them from impinging on the test specimens. Pending a complete understanding of air-pressure effects, etc., it is important that the nozzle selected shall produce the desired condition when operated at the air pressure selected. Nozzles are not necessarily located at one end, but may be placed in the center and can also be directed vertically up through a suitable tower.

X1.4 Air for Atomization

X1.4.1 The air used for atomization must be free of grease, oil, and dirt before use by passing through well-maintained filters. Room air may be compressed, heated, humidified, and washed in a water-sealed rotary pump, if the temperature of the water is suitably controlled. Otherwise cleaned air may be introduced into the bottom of a tower filled with water, through a porous stone or multiple nozzles. The level of the water must be maintained automatically to ensure adequate humidification. A chamber operated in accordance with this method and Appendix X1 will have a relative humidity between 95 and 98 %. Since salt solutions from 2 to 6 % will give the same results (though for uniformity the limits are set at 4 to 6 %), it is preferable to saturate the air at temperatures well above the chamber temperature as insurance of a wet fog. Table X1.2 shows the

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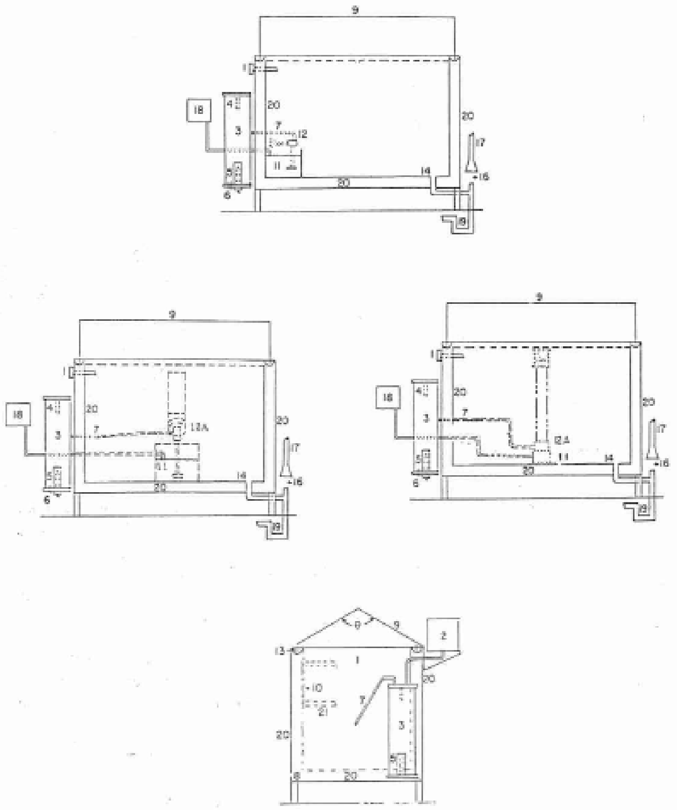
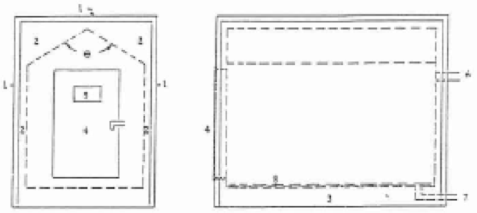
[8] A suitable device for maintaining the level of liquid in either the saturator tower or reservoir of test solution may be designed by a local engineering group, or may be purchased from manufacturers of test cabinets as an accessory.



NOTE 1—θ—Angle of lid, 90 to 125°
1—Thermometer and thermostat for controlling heater (Item No. 8) in base
2—Automatic water leveling device
3—Humidifying tower
4—Automatic temperature regulator for controlling heater (Item No. 5)
5—Immersion heater, nonrusting
6—Air inlet, multiple openings
7—Air tube to spray nozzle
8—Heater in base
9—Hinged top, hydraulically operated, or counterbalanced
10—Brackets for rods supporting specimens, or test table
11—Internal reservoir
12—Spray nozzle above reservoir, suitably designed, located, and baffled
12A—Spray nozzle housed in dispersion tower located preferably in center of cabinet (typical examples)
13—Water seal
14—Combination drain and exhaust. Exhaust at opposite side of test space from spray nozzle (Item 12), but preferably in combination with drain, waste trap, and forced draft waste pipe (Items 16, 17, and 19).
16—Complete separation between forced draft waste pipe (Item 17) and combination drain and exhaust (Items 14 and 19) to avoid undesirable suction or back pressure.
17—Forced draft waste pipe
18—Automatic leveling device for reservoir
19—Waste trap
20—Air space or water jacket
21—Test table or rack, well below roof area

NOTE 2—This figure shows the various components including alternate arrangements of the spray nozzles and solution reservoir.

FIG. X1.1 Typical Salt Spray Cabinet



NOTE—The controls are the same, in general as for the smaller laboratory type cabinet (Fig. X1.1), but are sized to care for the larger cube. The chamber has the following features:

θ—Angle of ceiling, 90 to 125°
1—Heavy insulated outer panels
2—Air space
3—Low-watt density heaters, or steam coils
4—Single- or double-, full-opening door (refrigeration type), with inward sloping door sill
5—Viewing window/s
6—Inner chamber vent
7—Inner chamber drain
8—Duct boards on floor

FIG. X1.2 Walk-in Chamber, 1.5 by 2.4 m (5 by 8 ft) and Upward in Overall Size

TABLE X1.2 Temperature and Pressure Requirements for Operation of Test at 95°F

	Air Pressure, psi			
	12	14	16	18
Temperature, °F	114	117	119	121
	Air Pressure, kPa			
	83	96	110	124
Temperature, °C	46	47	48	49

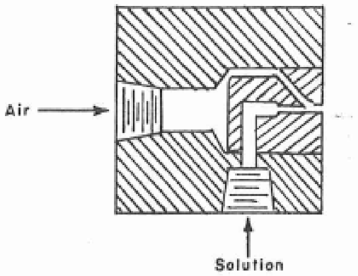


FIG. X1.3 Typical Spray Nozzle

temperatures, at different pressures, that are required to offset the cooling effect of expansion to atmospheric pressure.

X1.4.2 Experience has shown that most uniform spray chamber atmospheres are obtained by increasing the atomizing air temperature sufficiently to offset heat losses, except those that can be replaced otherwise at very low-temperature gradients.

X1.5 Types of Construction

X1.5.1 A modern laboratory cabinet is shown in Fig. X1.1. Walk-in chambers are usually constructed with a sloping ceiling. Suitably located and directed spray nozzles avoid ceiling accumulation and drip. Nozzles may be located at the ceiling, or 0.91 m (3 ft) from the floor directed upward at 30 to 60° over a passageway. The number of nozzles depends on type and capacity and is related to the area of the test space. An 11 to 19-dm^3 (3 to 5-gal) reservoir is required within the chamber, with the level controlled. The major features of a walk-in type cabinet, which differs significantly from the laboratory type, are illustrated in Fig. X1.2. Construction of a plastic nozzle, such as is furnished by several suppliers, is shown in Fig. X1.3.

X2. USE OF THE SALT SPRAY (FOG) TEST IN RESEARCH

X2.1 This practice is primarily used for process qualification and quality acceptance. Regarding any new applications it is essential to correlate the results of this practice with actual field exposure results.

X2.2 The salt spray has been used to a considerable extent for the purpose of comparing different materials or finishes. It should be noted there is usually not a direct relation between salt spray (fog) resistance and resistance to corrosion in other media, because the chemistry of the reactions, including the formation of films and their protective value, frequently varies greatly with the precise conditions encountered. Informed personnel are aware of the erratic composition of basic alloys, the possibility of wide variations in quality and thickness of plated items produced on the same racks at the same time, and the consequent need for a mathematical determination of the number of specimens required to constitute an adequate sample for test purposes. In this connection it is well to point out that Practice B 117 is not applicable to the study or testing of decorative chromium plate (nickel-chromium) on steel or on zinc-base die castings or of cadmium plate on steel. For this purpose Method B 368 and Practice G 85 are available, which are also considered by some to be superior for comparison of chemically treated aluminum (chromated, phosphated, or anodized), although final conclusions regarding the validity of test results related to service experience have not been reached. Practice B 117 and Practice G 85 are considered to be most useful in estimating the relative behavior of closely related materials in marine atmospheres, since it simulates the basic conditions with some acceleration due to either wetness or temperature, or both.

X3. EVALUATION OF CORROSIVE CONDITIONS

X3.1 *General*—This appendix covers test panels and procedures for evaluating the corrosive conditions within a salt spray cabinet. The procedure involves the exposure of steel test panels and the determination of their mass losses in a specified period of time. This may be done monthly or more frequently to ensure consistent operation over time. It is also useful for correlating the corrosive conditions among different cabinets.

X3.2 *Test Panels*—The required test panels, 76 by 127 by 0.8 mm, are made from SAE 1010 commercial-grade cold-rolled carbon steel (UNS G10080).

X3.3 *Preparation of Panels Before Testing*—Clean panels before testing by degreasing only, so that the surfaces are free of dirt, oil, or other foreign matter that could influence the test results. After cleaning, weigh each panel on an analytical balance to the nearest 1.0 mg and record the mass.

X3.4 *Positioning of Test Panels*—Place a minimum of two weighed panels in the cabinet, with the 127-mm length supported 30° from vertical. Place the panels in the proximity of the condensate collectors. (See Section 6.)

X3.5 *Duration of Test*—Expose panels to the salt fog for 48 to 168 h.

X3.6 *Cleaning of Test Panels After Exposure*—After removal of the panels from the cabinet, rinse each panel immediately with running tap water to remove salt, and rinse in reagent grade water (see Specification D 1193, Type IV). Chemically clean each panel for 10 min at 20 to 25°C in a fresh solution prepared as follows:

> Mix 1000 mL of hydrochloric acid (sp gr 1.19) with 1000 mL reagent grade water (D 1193, Type IV) and add 10 g of hexamethylene tetramine. After cleaning, rinse each panel with reagent grade water (Type IV) and dry (see 12.2).

X3.7 *Determining Mass Loss*—Immediately after drying, determine the mass loss by reweighing and subtracting panel mass after exposure from its original mass. The mass should not vary 20 % from test to test.

X3.7.1 Data generated in the interlaboratory study using this method are available from ASTM as a Research Report.[9]

X3.8 *Precision and Bias—Steel Panel Test:*

X3.8.1 An interlaboratory test program using three different sets of UNS G10090 steel panels, 76 by 127 by 0.8 mm has shown that the repeatability of the mass loss of the steel panels, that is, the consistency in mass loss results that may be expected when replicate panels are run simultaneously in a salt spray cabinet, is dependent upon exposure time and the panel lot or source. The interlaboratory program yielded repeatability standard deviations, S_r, from which 95 % repeatability limits, r, were calculated as follows (see Practice E 691):

$$r = 2.8\ S_r$$

The values of S_r and r are reported in Table X3.1. Note that the corrosion rate of steel in this environment is approximately constant over the exposure interval and that the ratio of the standard deviation to the average mass loss, the coefficient of variation, Cv, varies between 5 and 10 % with a weighted average of 7.4 % and an r of ±21 % of the average mass loss.

TABLE X3.1 Repeatability Statistics

NOTE—Based on two replicates in every test run. No. = number of different salt spray cabinets in test program; r = 95 % repeatability limits, g; $Cv = S_r$/avg, coefficient of variation, %; and S_r = repeatability standard deviations, g.

Materials	Test Duration, h	Average Mass Loss, g	S_r, g	Cv, %	r, g	No.
QP1	48	0.8170	0.0588	7.20	0.1646	12
QP1	96	1.5347	0.1048	7.28	0.2934	12
QP1	168	2.5996	0.2498	9.61	0.6994	12
AP	48	0.7787	0.0403	5.17	0.1128	10
AP	96	1.4094	0.0923	6.55	0.2584	10
AP	168	2.4309	0.1594	6.56	0.4463	10
QP2	48	0.8566	0.0686	8.01	0.1921	5
QP2	96	1.5720	0.0976	6.21	0.2733	5
QP2	168	2.7600	0.2588	9.38	0.7246	5

X3.8.2 This interlaboratory program also produced results on the reproducibility of results, that is, the consistency of mass loss results in tests in different laboratories or in different cabinets in the same facility. This program yielded reproducibility standard deviations S_R from which 95 % reproducibility limits, R were calculated as follows (See Practice E 691):

$$R = 2.8\ S_R$$

The values of S_R and R are reported in Table X3.2. Note that the ratio of standard deviation to the average mass loss, the coefficient of variation, Cv, varies between 8 to 14 % with a weighted average of 12.7 % and an R of ±36 % of the average mass loss.

X3.8.3 The mass loss of steel in this salt spray practice is dependent upon the area of steel exposed, the temperature, time of exposure, salt solution make up and purity, pH, spray conditions, and the metallurgy of the steel. The procedure in Appendix X3 for measuring the corrosivity of neutral salt spray cabinets with steel panels has no bias because the value of corrosivity of the salt spray is defined only in terms of this practice.

TABLE X3.2 Reproducibility Statistics

NOTE—No. = number of different salt spray cabinets in test program; R = 95 % reproducibility limits, g; $Cv = S_R$/avg, coefficient of variation, %; and S_R = reproducibility standard deviation, g.

Materials	Test Duration, h	Average Mass Loss, g	S_R, g	Cv, %	R, g	No.
QP1	48	0.8170	0.0947	11.58	0.2652	12
QP1	96	1.5347	0.2019	14.02	0.5653	12
QP1	168	2.5996	0.3255	12.52	0.9114	12
AP	48	0.7787	0.0805	10.33	0.2254	10
AP	96	1.4094	0.1626	11.54	0.4553	10
AP	168	2.4309	0.3402	14.00	0.9526	10
QP2	48	0.8566	0.1529	17.85	0.4281	5
QP2	96	1.5720	0.1319	8.39	0.3693	5
QP2	168	2.7600	0.3873	14.03	1.0844	5

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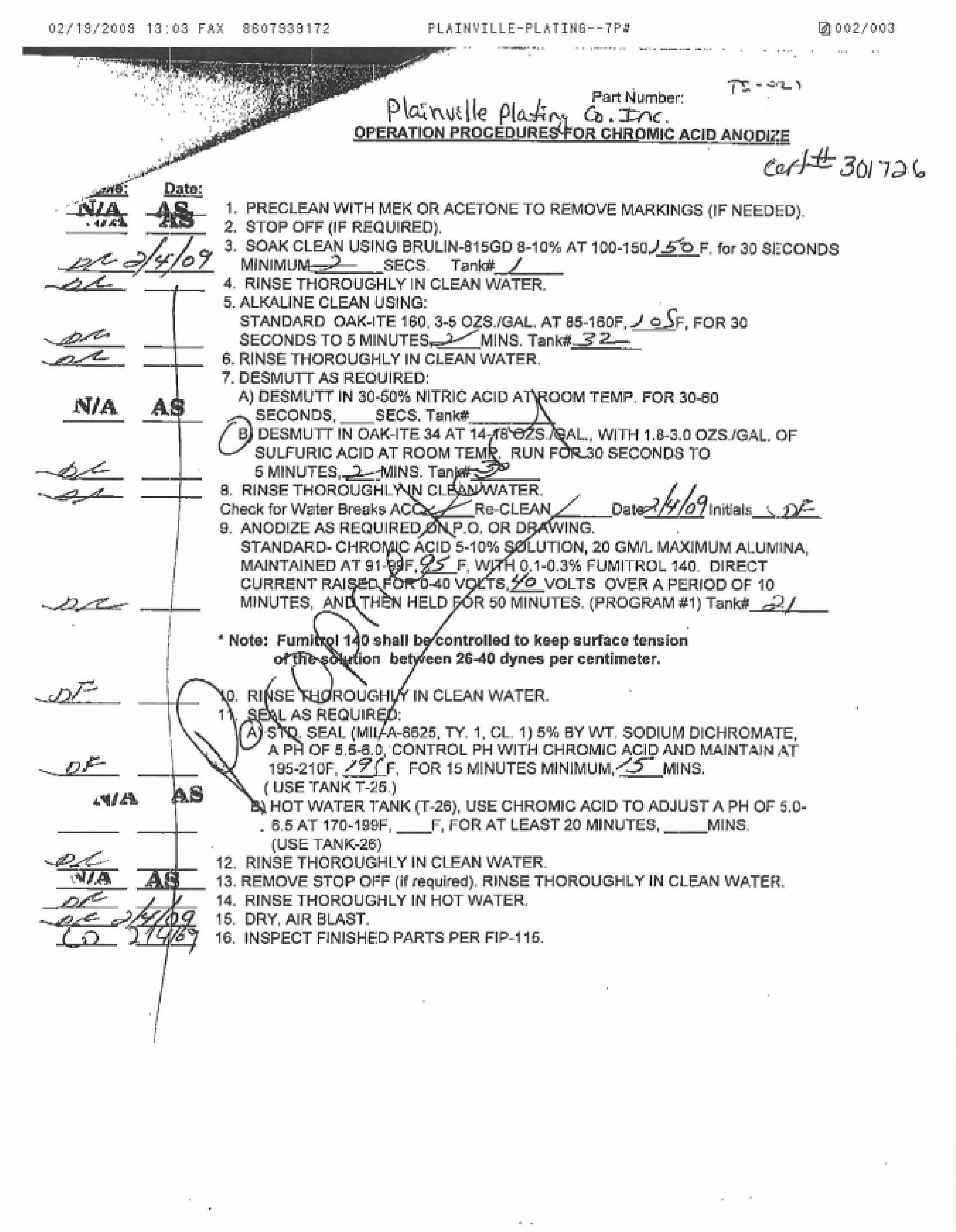
[9] Available from ASTM Headquarters. Request RR No. G1-1003.

Appendix I: Chromic Acid Anodizing Specifications



02/19/2009 13:03 FAX 8607939172 PLAINVILLE-PLATING--7P# 002/003

Part Number: TS-021

Plainville Plating Co. Inc.

OPERATION PROCEDURES FOR CHROMIC ACID ANODIZE

Cert # 301726

Initials:	Date:	
N/A	AS	1. PRECLEAN WITH MEK OR ACETONE TO REMOVE MARKINGS (IF NEEDED).
N/A	AS	2. STOP OFF (IF REQUIRED).
DF	2/4/09	3. SOAK CLEAN USING BRULIN-815GD 8-10% AT 100-150 150 F. for 30 SECONDS MINIMUM 2 SECS. Tank# 1
DF		4. RINSE THOROUGHLY IN CLEAN WATER.
DF		5. ALKALINE CLEAN USING: STANDARD OAK-ITE 160, 3-5 OZS./GAL. AT 85-160F, 105 F, FOR 30 SECONDS TO 5 MINUTES, 2 MINS. Tank# 32
DF		6. RINSE THOROUGHLY IN CLEAN WATER.
		7. DESMUTT AS REQUIRED:
N/A	AS	A) DESMUTT IN 30-50% NITRIC ACID AT ROOM TEMP. FOR 30-60 SECONDS, ____SECS. Tank#________
DF		B) DESMUTT IN OAK-ITE 34 AT 14-18 OZS./GAL., WITH 1.8-3.0 OZS./GAL. OF SULFURIC ACID AT ROOM TEMP. RUN FOR 30 SECONDS TO 5 MINUTES, 2 MINS. Tank# 30
DF		8. RINSE THOROUGHLY IN CLEAN WATER.

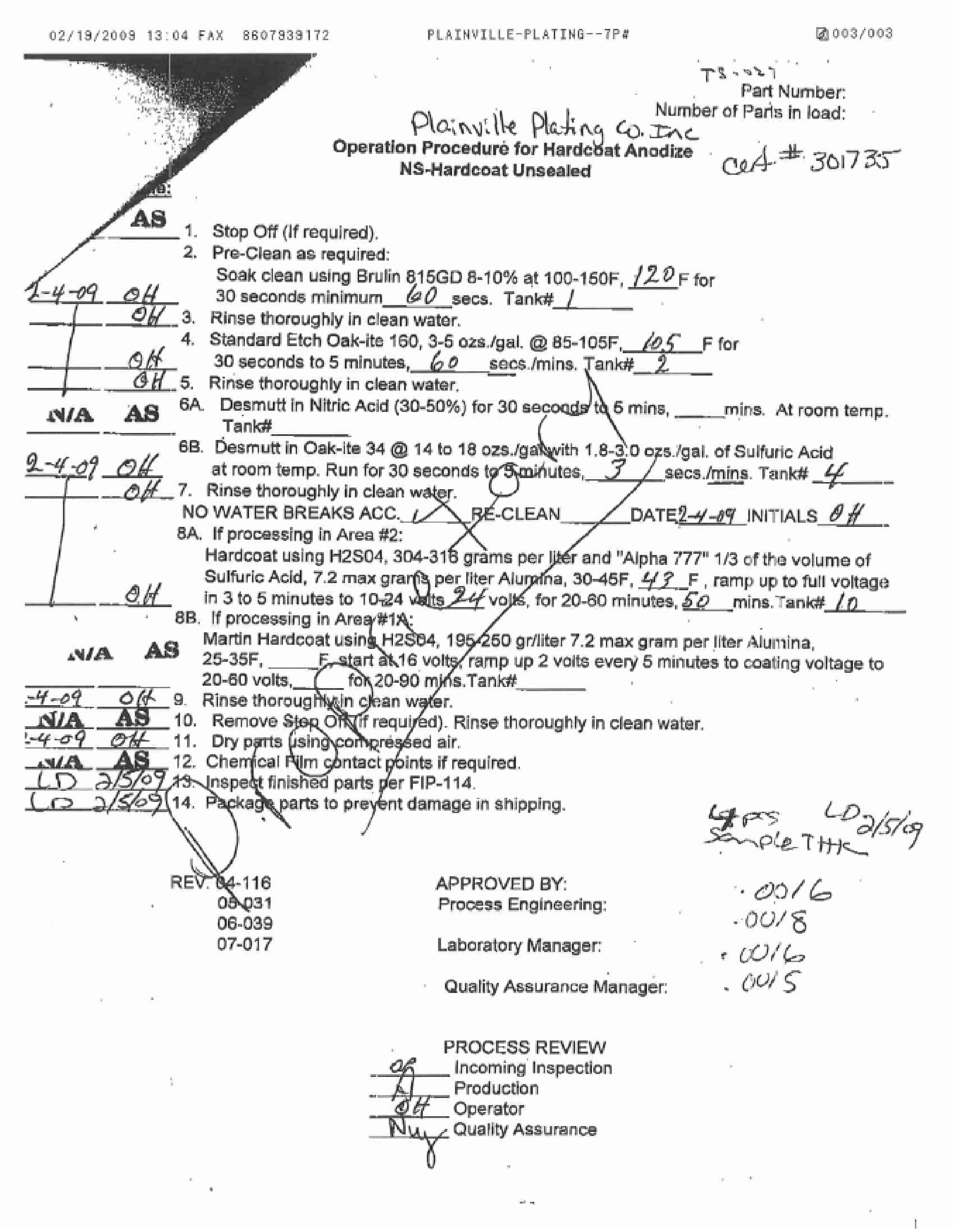
Check for Water Breaks ACC ✓ Re-CLEAN ____ Date 2/4/09 Initials DF

DF		9. ANODIZE AS REQUIRED ON P.O. OR DRAWING. STANDARD- CHROMIC ACID 5-10% SOLUTION, 20 GM/L MAXIMUM ALUMINA, MAINTAINED AT 91-99F, 95 F, WITH 0.1-0.3% FUMITROL 140. DIRECT CURRENT RAISED FOR 0-40 VOLTS, 40 VOLTS OVER A PERIOD OF 10 MINUTES, AND THEN HELD FOR 50 MINUTES. (PROGRAM #1) Tank# 21

*** Note: Fumitrol 140 shall be controlled to keep surface tension of the solution between 26-40 dynes per centimeter.**

DF		10. RINSE THOROUGHLY IN CLEAN WATER.
		11. SEAL AS REQUIRED:
DF		A) STD. SEAL (MIL-A-8625, TY. 1, CL. 1) 5% BY WT. SODIUM DICHROMATE, A PH OF 5.5-6.0, CONTROL PH WITH CHROMIC ACID AND MAINTAIN AT 195-210F, 195 F, FOR 15 MINUTES MINIMUM, 15 MINS. (USE TANK T-25.)
N/A	AS	B) HOT WATER TANK (T-26), USE CHROMIC ACID TO ADJUST A PH OF 5.0-6.5 AT 170-199F, ____F, FOR AT LEAST 20 MINUTES, _____MINS. (USE TANK-26)
DF		12. RINSE THOROUGHLY IN CLEAN WATER.
N/A	AS	13. REMOVE STOP OFF (if required). RINSE THOROUGHLY IN CLEAN WATER.
DF		14. RINSE THOROUGHLY IN HOT WATER.
DF	2/4/09	15. DRY, AIR BLAST.
CO	2/4/09	16. INSPECT FINISHED PARTS PER FIP-115.

Appendix J: Sulfuric “Hard” Anodizing Specifications



02/19/2009 13:04 FAX 8607939172 PLAINVILLE-PLATING--7P# 003/003

TS-027
Part Number:
Number of Parts in load:

Plainville Plating Co. Inc
Operation Procedure for Hardcoat Anodize
NS-Hardcoat Unsealed
Cert.# 301735

AS 1. Stop Off (If required).
2. Pre-Clean as required:
Soak clean using Brulin 815GD 8-10% at 100-160F, 120 F for
2-4-09 OH 30 seconds minimum 60 secs. Tank# 1
OH 3. Rinse thoroughly in clean water.
4. Standard Etch Oak-ite 160, 3-5 ozs./gal. @ 85-105F, 105 F for
OH 30 seconds to 5 minutes, 60 secs./mins. Tank# 2
OH 5. Rinse thoroughly in clean water.
N/A AS 6A. Desmutt in Nitric Acid (30-50%) for 30 seconds to 5 mins, _____mins. At room temp. Tank#________
6B. Desmutt in Oak-ite 34 @ 14 to 18 ozs./gal with 1.8-3.0 ozs./gal. of Sulfuric Acid
2-4-09 OH at room temp. Run for 30 seconds to 5 minutes, 3 secs./mins. Tank# 4
OH 7. Rinse thoroughly in clean water.
NO WATER BREAKS ACC. ✓ RE-CLEAN______ DATE 2-4-09 INITIALS OH
8A. If processing in Area #2:
Hardcoat using H2S04, 304-316 grams per liter and "Alpha 777" 1/3 of the volume of Sulfuric Acid, 7.2 max grams per liter Alumina, 30-45F, 43 F , ramp up to full voltage
OH in 3 to 5 minutes to 10-24 volts 24 volts, for 20-60 minutes, 50 mins. Tank# 10
8B. If processing in Area #1A:
N/A AS Martin Hardcoat using H2S04, 195-250 gr/liter 7.2 max gram per liter Alumina, 25-35F, _____F, start at 16 volts, ramp up 2 volts every 5 minutes to coating voltage to 20-60 volts,_____ for 20-90 mins.Tank#_______
-4-09 OH 9. Rinse thoroughly in clean water.
N/A AS 10. Remove Stop Off (if required). Rinse thoroughly in clean water.
-4-09 OH 11. Dry parts using compressed air.
N/A AS 12. Chemical Film contact points if required.
LD 2/5/09 13. Inspect finished parts per FIP-114.
LD 2/5/09 14. Package parts to prevent damage in shipping.

4 pcs LD 2/5/09
Sample THK

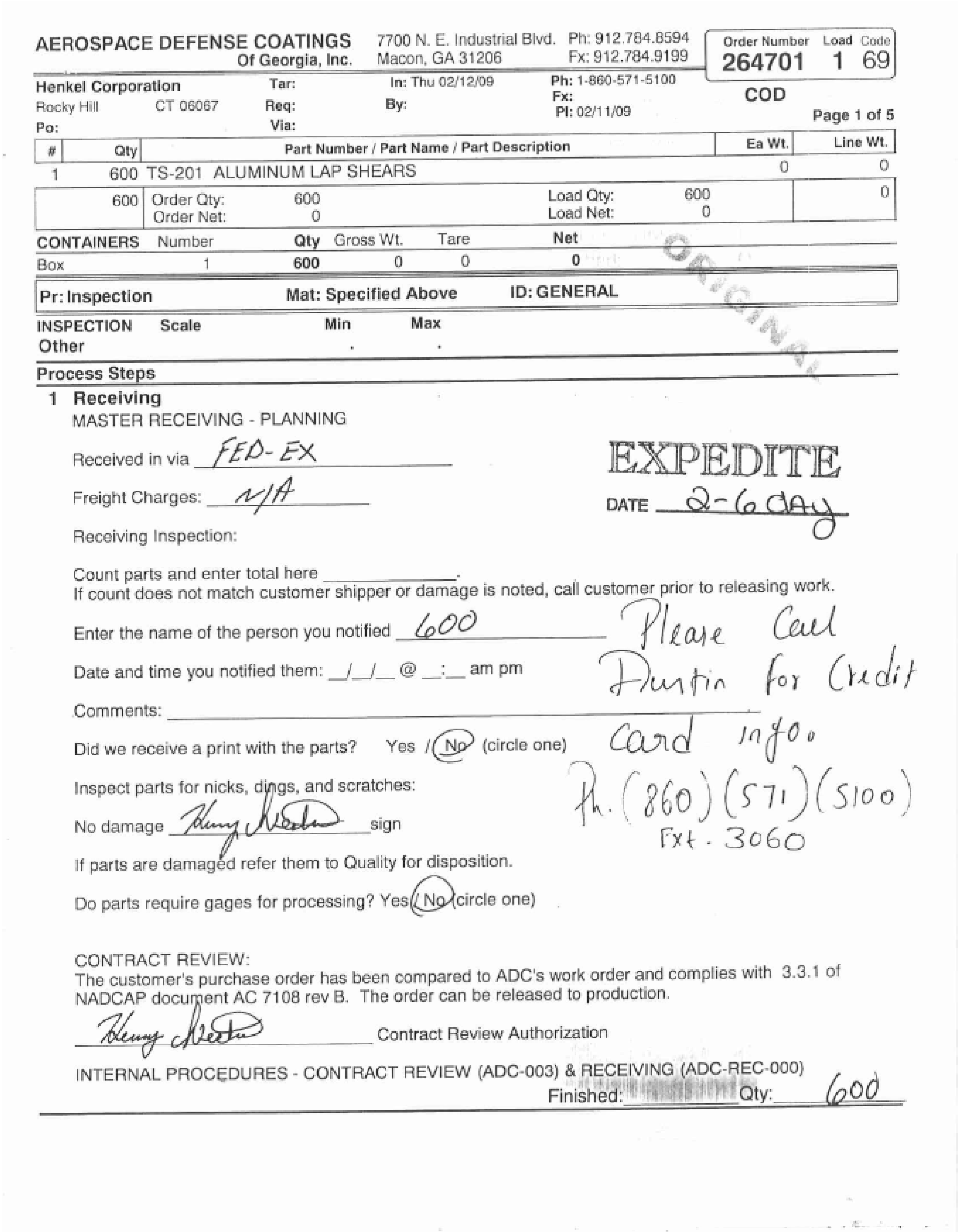
REV. 04-116
05-031
06-039
07-017

APPROVED BY:
Process Engineering:
Laboratory Manager:
Quality Assurance Manager:

.0016
.0018
.0016
.0015

PROCESS REVIEW
OG Incoming Inspection
AJ Production
OH Operator
Nuy Quality Assurance

Appendix K: Phosphoric Acid Anodizing Specifications



AEROSPACE DEFENSE COATINGS
Of Georgia, Inc.
7700 N. E. Industrial Blvd.
Macon, GA 31206
Ph: 912.784.8594
Fx: 912.784.9199

Order Number 264701 Load 1 Code 69

COD

Page 1 of 5

Henkel Corporation
Rocky Hill CT 06067
Po:

Tar:
Req:
Via:

In: Thu 02/12/09
By:

Ph: 1-860-571-5100
Fx:
Pl: 02/11/09

#	Qty	Part Number / Part Name / Part Description	Ea Wt.	Line Wt.
1	600	TS-201 ALUMINUM LAP SHEARS	0	0
	600	Order Qty: 600 Order Net: 0 Load Qty: 600 Load Net: 0		0

CONTAINERS	Number	Qty	Gross Wt.	Tare	Net
Box	1	600	0	0	0

ORIGINAL

Pr: Inspection **Mat: Specified Above** **ID: GENERAL**

INSPECTION	Scale	Min	Max
Other		.	.

Process Steps

1 **Receiving**
MASTER RECEIVING - PLANNING

Received in via FED-EX

Freight Charges: N/A

EXPEDITE
DATE 2-6 DAY

Receiving Inspection:

Count parts and enter total here ______.
If count does not match customer shipper or damage is noted, call customer prior to releasing work.

Enter the name of the person you notified 600

Date and time you notified them: _/_/_ @ _:_ am pm

Comments: ______

Please Call Dustin for Credit Card info.
Ph. (860) (571) (5100)
Ext. 3060

Did we receive a print with the parts? Yes / [✓ No] (circle one)

Inspect parts for nicks, dings, and scratches:

No damage ______ sign

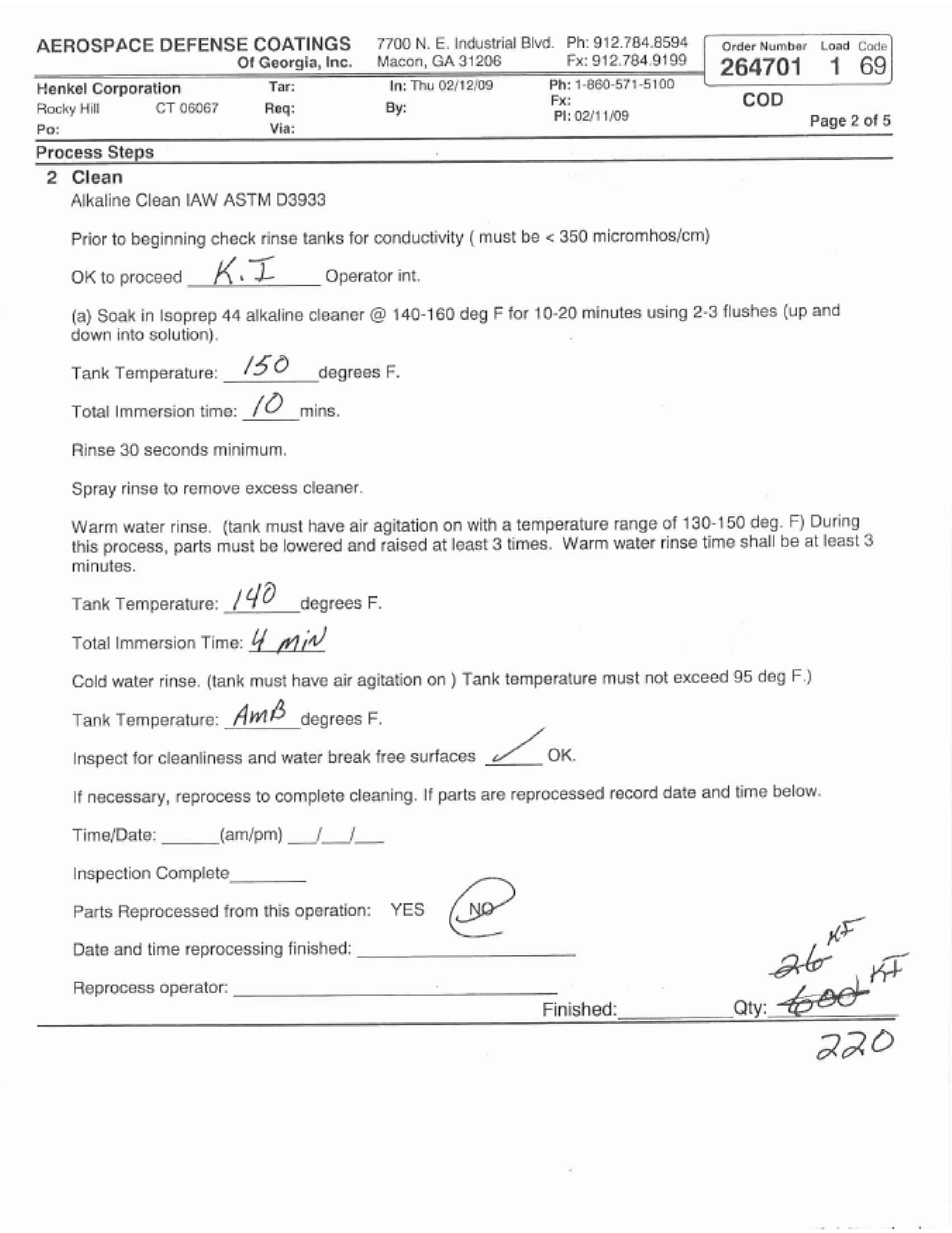
If parts are damaged refer them to Quality for disposition.

Do parts require gages for processing? Yes / [✓ No] (circle one)

CONTRACT REVIEW:
The customer's purchase order has been compared to ADC's work order and complies with 3.3.1 of NADCAP document AC 7108 rev B. The order can be released to production.

______ Contract Review Authorization

INTERNAL PROCEDURES - CONTRACT REVIEW (ADC-003) & RECEIVING (ADC-REC-000)
Finished: ______ Qty: 600



AEROSPACE DEFENSE COATINGS
Of Georgia, Inc.
7700 N. E. Industrial Blvd.
Macon, GA 31206
Ph: 912.784.8594
Fx: 912.784.9199

Order Number	Load	Code
264701	1	69

Henkel Corporation
Rocky Hill CT 06067
Po:

Tar:
Req:
Via:

In: Thu 02/12/09
By:

Ph: 1-860-571-5100
Fx:
Pl: 02/11/09

COD

Page 2 of 5

Process Steps

2 Clean

Alkaline Clean IAW ASTM D3933

Prior to beginning check rinse tanks for conductivity (must be < 350 micromhos/cm)

OK to proceed K.I Operator int.

(a) Soak in Isoprep 44 alkaline cleaner @ 140-160 deg F for 10-20 minutes using 2-3 flushes (up and down into solution).

Tank Temperature: 150 degrees F.

Total Immersion time: 10 mins.

Rinse 30 seconds minimum.

Spray rinse to remove excess cleaner.

Warm water rinse. (tank must have air agitation on with a temperature range of 130-150 deg. F) During this process, parts must be lowered and raised at least 3 times. Warm water rinse time shall be at least 3 minutes.

Tank Temperature: 140 degrees F.

Total Immersion Time: 4 min

Cold water rinse. (tank must have air agitation on) Tank temperature must not exceed 95 deg F.)

Tank Temperature: AmB degrees F.

Inspect for cleanliness and water break free surfaces ✓ OK.

If necessary, reprocess to complete cleaning. If parts are reprocessed record date and time below.

Time/Date: ______(am/pm) ___/___/___

Inspection Complete________

Parts Reprocessed from this operation: YES [✓ NO]

Date and time reprocessing finished: ____________________

Reprocess operator: ______________________________

~~26~~ KF

Finished:__________ Qty: ~~600~~ KF

220

AEROSPACE DEFENSE COATINGS
Of Georgia, Inc.
7700 N. E. Industrial Blvd.
Macon, GA 31206
Ph: 912.784.8594
Fx: 912.784.9199

Order Number	Load	Code
264701	1	69

Henkel Corporation
Rocky Hill CT 06067
Po:

Tar:
Req:
Via:

In: Thu 02/12/09
By:

Ph: 1-860-571-5100
Fx:
Pl: 02/11/09

COD

Page 3 of 5

Process Steps

3 Phosphoric

CAUTION: PROCESS MUST BE CONTINOUS. DO NOT ALLOW PARTS TO DRY BETWEEN PROCESSES.

Phosphoric Acid Deoxidation (PAD)
Immerse parts in the phosphoric acid solution for 8 to 12 minutes. Increase the potential of 7+-1 volts DC at a rate increase of 2 to 7 volts / minute.

Time in solution 10 minutes

DO NOT AGITATE SOLUTION WHILE PARTS ARE IMMERSED.

Rinse for 5 minutes minimum. DO NOT ALLOW MORE THAN 1.5 MINUTES BETWEEN ANODIZE AND RINSE.

Rinse until parts are water break free K.I OK (Tech Initials)

PHOSPHORIC ANODIZE:
Immerse parts in phosphoric acid solution IAW ASTM D3933.

Raise voltage to a potential of 15+- 1 volts DC for 20 to 25 minutes. Begin with 5 volts maximum and increase 4 volts per minute.

Remove parts from solution and rinse for 5 to 15 minutes.

Rinse water shall not exceed 110 degrees Maximum.

Parts shall be water break free K'I tech initials

Dry parts using air no hotter than 160 degrees F.

Finished:__________ Qty: 220

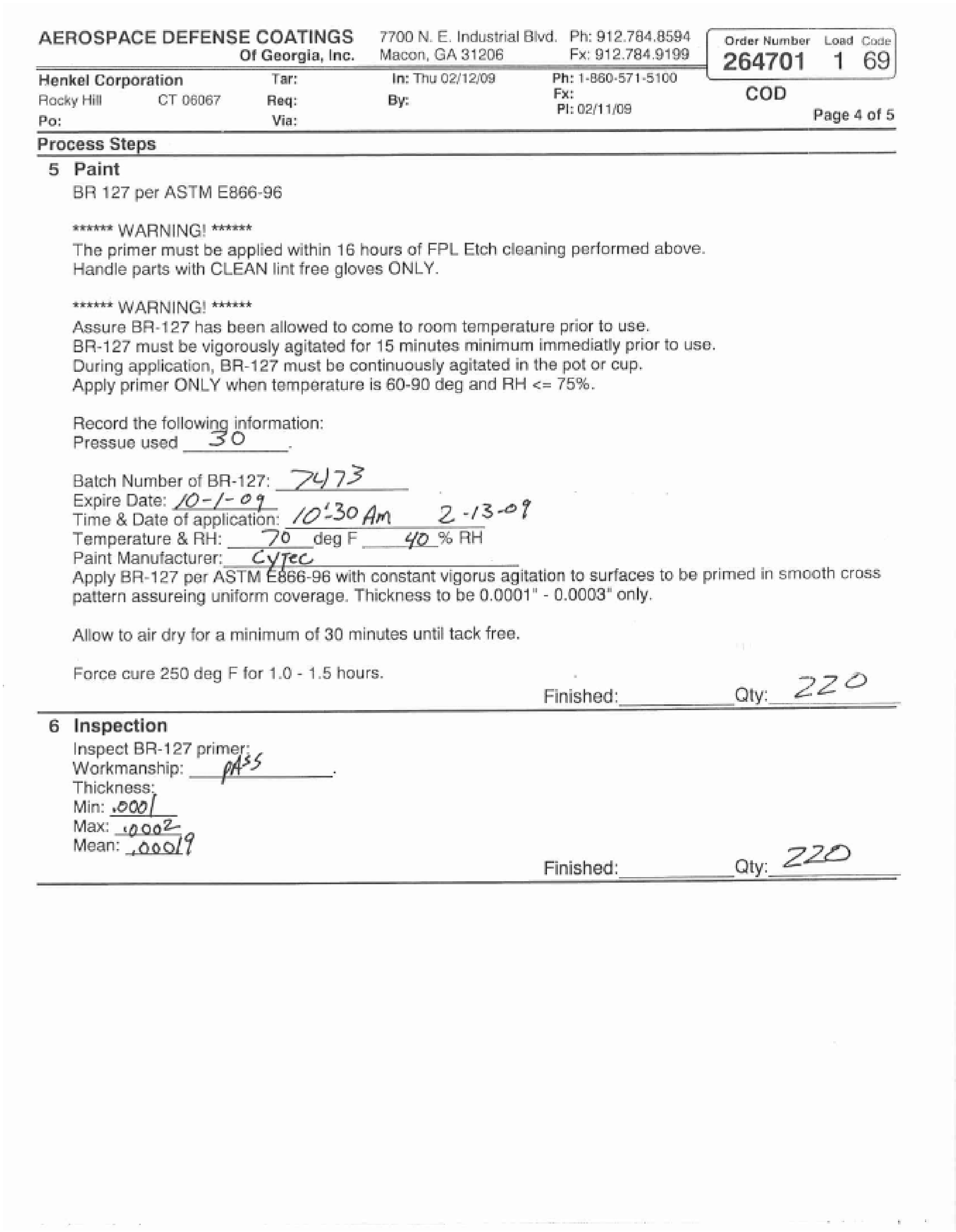
4 Inspection

Inspect Phosphoric Acid Anodize
The anodic coating should be continuous, smooth, uniform in appearance, and free from discontinuities such as abrasion, breaks, burned areas, and areas that are not anodized when examined visually within the following limitations:
(a) On clad material, minor burns and pits that do not penetrate through the cladding to the base metal are accepatable
(b) On bare material, pits that have round bottoms and are clear of foreign material are acceptable. Maximum depth is 0.003 inch
(c) Unanodized surfaces under electrical contacts are acceptable
There shall be no Smut on the detail parts after anodize.
There shall be not stains which were a result of improper processing
Abrupt differences in color of local areas are unacceptable

VISUAL INSPECTION: [✓ PASS] FAIL

VERIFICATION OF PRESENCE OF ANODIC COATING: [✓ PASS] FAIL

Finished:__________ Qty: 220



AEROSPACE DEFENSE COATINGS
Of Georgia, Inc.
7700 N. E. Industrial Blvd.
Macon, GA 31206
Ph: 912.784.8594
Fx: 912.784.9199

Order Number	Load	Code
264701	1	69

Henkel Corporation
Rocky Hill CT 06067
Po:

Tar:
Req:
Via:

In: Thu 02/12/09
By:

Ph: 1-860-571-5100
Fx:
Pl: 02/11/09

COD

Page 4 of 5

Process Steps

5 Paint

BR 127 per ASTM E866-96

****** WARNING! ******
The primer must be applied within 16 hours of FPL Etch cleaning performed above.
Handle parts with CLEAN lint free gloves ONLY.

****** WARNING! ******
Assure BR-127 has been allowed to come to room temperature prior to use.
BR-127 must be vigorously agitated for 15 minutes minimum immediatly prior to use.
During application, BR-127 must be continuously agitated in the pot or cup.
Apply primer ONLY when temperature is 60-90 deg and RH <= 75%.

Record the following information:
Pressue used 30.

Batch Number of BR-127: 7473
Expire Date: 10-1-09
Time & Date of application: 10:30 Am 2-13-09
Temperature & RH: 70 deg F 40 % RH
Paint Manufacturer: Cytec
Apply BR-127 per ASTM E866-96 with constant vigorus agitation to surfaces to be primed in smooth cross pattern assureing uniform coverage. Thickness to be 0.0001" - 0.0003" only.

Allow to air dry for a minimum of 30 minutes until tack free.

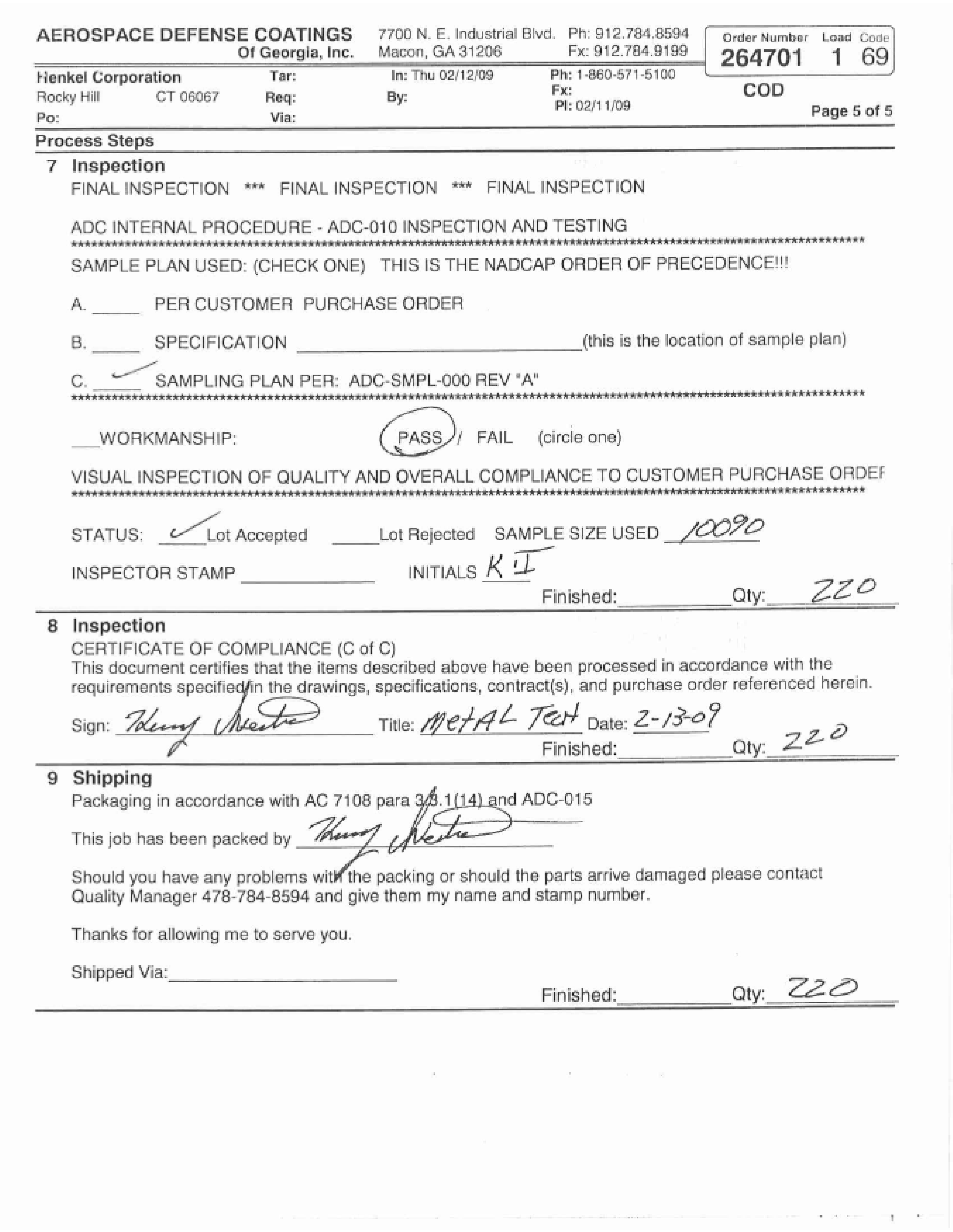
Force cure 250 deg F for 1.0 - 1.5 hours.

Finished:__________ Qty: 220

6 Inspection

Inspect BR-127 primer:
Workmanship: pASS.
Thickness:
Min: .0001
Max: .0002
Mean: .00019

Finished:__________ Qty: 220



AEROSPACE DEFENSE COATINGS
Of Georgia, Inc.
7700 N. E. Industrial Blvd.
Macon, GA 31206
Ph: 912.784.8594
Fx: 912.784.9199

Order Number 264701 Load 1 Code 69

COD

Henkel Corporation
Rocky Hill CT 06067
Po:

Tar:
Req:
Via:

In: Thu 02/12/09
By:

Ph: 1-860-571-5100
Fx:
Pl: 02/11/09

Page 5 of 5

Process Steps

7 Inspection

FINAL INSPECTION *** FINAL INSPECTION *** FINAL INSPECTION

ADC INTERNAL PROCEDURE - ADC-010 INSPECTION AND TESTING

****

SAMPLE PLAN USED: (CHECK ONE) THIS IS THE NADCAP ORDER OF PRECEDENCE!!!

A. _____ PER CUSTOMER PURCHASE ORDER

B. _____ SPECIFICATION ________________________(this is the location of sample plan)

C. ✓ SAMPLING PLAN PER: ADC-SMPL-000 REV "A"

****

___WORKMANSHIP: [✓ PASS] / FAIL (circle one)

VISUAL INSPECTION OF QUALITY AND OVERALL COMPLIANCE TO CUSTOMER PURCHASE ORDEF

****

STATUS: ✓ Lot Accepted _____Lot Rejected SAMPLE SIZE USED 10090

INSPECTOR STAMP _____________ INITIALS K I

Finished:__________ Qty: 220

8 Inspection

CERTIFICATE OF COMPLIANCE (C of C)
This document certifies that the items described above have been processed in accordance with the requirements specified in the drawings, specifications, contract(s), and purchase order referenced herein.

Sign: ________________ Title: MetAL Tech Date: 2-13-09

Finished:__________ Qty: 220

9 Shipping

Packaging in accordance with AC 7108 para 3.3.1(14) and ADC-015

This job has been packed by ________________

Should you have any problems with the packing or should the parts arrive damaged please contact Quality Manager 478-784-8594 and give them my name and stamp number.

Thanks for allowing me to serve you.

Shipped Via:____________________

Finished:__________ Qty: 220

Appendix L: Comparative Analysis Raw Data

Run	Strength	Failure Mode	Run	Strength	Failure Mode	Run	Strength	Failure Mode	Run	Strength	Failure Mode	Run	Strength	Failure Mode
1-1	3848	Cohesive	**2-1**	1872	Adh/Coh	**3-1**	1841	Adh/Coh	**4-1**	4043	Cohesive	**5-1**	1435	Adh/Coh
1-2	3303	Cohesive	**2-2**	2434	Adh/Coh	**3-2**	1520	Adh/Coh	**4-2**	4204	Cohesive	**5-2**	1387	Adh/Coh
1-3	3537	Cohesive	**2-3**	1014	Adh/Coh	**3-3**	1140	Adh/Coh	**4-3**	4457	Cohesive	**5-3**	685	Adh/Coh
1-4	3120	Cohesive	**2-4**	165	Adh/Coh	**3-4**	1519	Adh/Coh	**4-4**	4925	Cohesive	**5-4**	1149	Adh/Coh
1-5	2724	Adh/Coh	**2-5**	1803	Adh/Coh	**3-5**	2241	Adh/Coh	**4-5**	3660	Adh/Coh	**5-5**	1517	Adh/Coh
1-6	2343	Adh/Coh	**2-6**	748	Adh/Coh	**3-6**	1670	Adh/Coh	**4-6**	3672	Cohesive	**5-6**	1790	Adh/Coh
1-7	2473	Cohesive	**2-7**	1709	Adh/Coh	**3-7**	2528	Adh/Coh	**4-7**	4233	Cohesive	**5-7**	2452	Adh/Coh
1-8	2164	Cohesive	**2-8**	1486	Adh/Coh	**3-8**	2131	Cohesive	**4-8**	3043	Cohesive	**5-8**	3105	Adh/Coh
1-9	2518	Cohesive	**2-9**	1994	Adh/Coh	**3-9**	2360	Adh/Coh	**4-9**	3816	Cohesive	**5-9**	2882	Adh/Coh
1-10	2418	Cohesive	**2-10**	114	Adh/Coh	**3-10**	1724	Adh/Coh	**4-10**	3831	Cohesive	**5-10**	2168	Adh/Coh
6-1	2740	Cohesive	**7-1**	Broke	Cohesive	**8-1**	2188	Adh/Coh	**9-1**	1504	Adh/Coh	**10-1**	387	Adh/Coh
6-2	2401	Cohesive	**7-2**	Broke	Cohesive	**8-2**	1905	Adh/Coh	**9-2**	1298	Adh/Coh	**10-2**	182	Adh/Coh
6-3	2196	Cohesive	**7-3**	Broke	Cohesive	**8-3**	1527	Adh/Coh	**9-3**	1004	Adh/Coh	**10-3**	269	Adh/Coh
6-4	2611	Adh/Coh	**7-4**	Broke	Cohesive	**8-4**	1391	Adh/Coh	**9-4**	1249	Adh/Coh	**10-4**	289	Adh/Coh
6-5	2598	Cohesive	**7-5**	Broke	Cohesive	**8-5**	2251	Cohesive	**9-5**	1234	Adh/Coh	**10-5**	261	Adh/Coh
6-6	3039	Cohesive	**7-6**	Broke	Cohesive	**8-6**	2100	Adh/Coh	**9-6**	1417	Adh/Coh	**10-6**	249	Adh/Coh
6-7	2493	Cohesive	**7-7**	Broke	Cohesive	**8-7**	1958	Adh/Coh	**9-7**	1215	Adh/Coh	**10-7**	343	Adh/Coh
6-8	2292	Cohesive	**7-8**	Broke	Cohesive	**8-8**	571	Adh/Coh	**9-8**	1456	Adh/Coh	**10-8**	Broke	Adh/Coh
6-9	2457	Adh/Coh	**7-9**	Broke	Cohesive	**8-9**	1470	Adh/Coh	**9-9**	1325	Adh/Coh	**10-9**	188	Adh/Coh
6-10	2390	Cohesive	**7-10**	639	Cohesive	**8-10**	932	Adh/Coh	**9-10**	1299	Adh/Coh	**10-10**	354	Adh/Coh
11-1	2836	Adh/Coh	**12-1**	1637	Adh/Coh	**13-1**	1773	Adh/Coh	**14-1**	2564	Cohesive	**15-1**	2871	Adh/Coh
11-2	3192	Cohesive	**12-2**	1899	Adh/Coh	**13-2**	1977	Adh/Coh	**14-2**	2249	Cohesive	**15-2**	2886	Adh/Coh
11-3	3000	Cohesive	**12-3**	1399	Adh/Coh	**13-3**	2286	Adh/Coh	**14-3**	2552	Cohesive	**15-3**	2741	Adh/Coh
11-4	2917	Cohesive	**12-4**	1939	Adh/Coh	**13-4**	2061	Adh/Coh	**14-4**	2580	Cohesive	**15-4**	3365	Adh/Coh
11-5	3132	Cohesive	**12-5**	2502	Adh/Coh	**13-5**	1993	Adh/Coh	**14-5**	2892	Cohesive	**15-5**	3169	Adh/Coh
11-6	3138	Cohesive	**12-6**	Broke	Adh/Coh	**13-6**	2450	Adh/Coh	**14-6**	2445	Cohesive	**15-6**	3021	Adh/Coh
11-7	2580	Adh/Coh	**12-7**	1362	Adh/Coh	**13-7**	1958	Adh/Coh	**14-7**	2650	Cohesive	**15-7**	3209	Adh/Coh
11-8	2998	Adh/Coh	**12-8**	2026	Adh/Coh	**13-8**	963	Adh/Coh	**14-8**	2424	Cohesive	**15-8**	2919	Adh/Coh
11-9	3056	Cohesive	**12-9**	1122	Adh/Coh	**13-9**	2074	Adh/Coh	**14-9**	2028	Cohesive	**15-9**	2898	Adh/Coh
11-10	3134	Cohesive	**12-10**	1515	Adh/Coh	**13-10**	2098	Adh/Coh	**14-10**	2991	Cohesive	**15-10**	2841	Adh/Coh

16-1	2577	Cohesive	**17-1**	2859	Cohesive	**18-1**	1686	Cohesive	**19-1**	3587	Cohesive	**20-1**	1790	Cohesive
16-2	2816	Cohesive	**17-2**	2503	Cohesive	**18-2**	1492	Cohesive	**19-2**	3938	Cohesive	**20-2**	1734	Cohesive
16-3	2412	Cohesive	**17-3**	2365	Cohesive	**18-3**	1673	Cohesive	**19-3**	3754	Cohesive	**20-3**	2079	Cohesive
16-4	2457	Cohesive	**17-4**	2380	Cohesive	**18-4**	1690	Cohesive	**19-4**	2759	Cohesive	**20-4**	1858	Cohesive
16-5	2555	Cohesive	**17-5**	1706	Cohesive	**18-5**	1917	Cohesive	**19-5**	3319	Cohesive	**20-5**	1750	Cohesive
16-6	2478	Cohesive	**17-6**	2320	Cohesive	**18-6**	1594	Cohesive	**19-6**	3361	Cohesive	**20-6**	1746	Cohesive
16-7	2562	Cohesive	**17-7**	2299	Cohesive	**18-7**	1958	Cohesive	**19-7**	3061	Cohesive	**20-7**	1957	Cohesive
16-8	2495	Cohesive	**17-8**	2651	Cohesive	**18-8**	1689	Cohesive	**19-8**	2990	Cohesive	**20-8**	1753	Cohesive
16-9	2648	Cohesive	**17-9**	2127	Cohesive	**18-9**	1681	Cohesive	**19-9**	3492	Cohesive	**20-9**	1649	Cohesive
16-10	2630	Cohesive	**17-10**	2296	Cohesive	**18-10**	1936	Cohesive	**19-10**	2898	Cohesive	**20-10**	1814	Cohesive
21-1	2253	Cohesive	**22-1**	2533	Cohesive	**23-1**	1430	Cohesive	**24-1**	1656	Cohesive	**25-1**	132	Adh/Coh
21-2	2326	Cohesive	**22-2**	1842	Cohesive	**23-2**	1737	Cohesive	**24-2**	2145	Cohesive	**25-2**	340	Adh/Coh
21-3	2217	Cohesive	**22-3**	2485	Cohesive	**23-3**	1597	Adh/Coh	**24-3**	1918	Cohesive	**25-3**	314	Adh/Coh
21-4	2364	Cohesive	**22-4**	2011	Cohesive	**23-4**	1904	Cohesive	**24-4**	1642	Cohesive	**25-4**	396	Adh/Coh
21-5	2157	Cohesive	**22-5**	3001	Cohesive	**23-5**	1624	Cohesive	**24-5**	1827	Cohesive	**25-5**	255	Adh/Coh
21-6	2283	Cohesive	**22-6**	2172	Cohesive	**23-6**	1660	Cohesive	**24-6**	1776	Cohesive	**25-6**	333	Adh/Coh
21-7	2454	Cohesive	**22-7**	2596	Cohesive	**23-7**	1905	Cohesive	**24-7**	1968	Cohesive	**25-7**	362	Adh/Coh
21-8	1969	Adh/Coh	**22-8**	1920	Cohesive	**23-8**	1498	Cohesive	**24-8**	1812	Cohesive	**25-8**	Broke	Adh/Coh
21-9	2190	Cohesive	**22-9**	2225	Cohesive	**23-9**	1519	Cohesive	**24-9**	1780	Cohesive	**25-9**	125	Adh/Coh
21-10	2425	Cohesive	**22-10**	2179	Cohesive	**23-10**	1762	Cohesive	**24-10**	2088	Cohesive	**25-10**	381	Adh/Coh
26-1	2174	Cohesive	**27-1**	1561	Cohesive	**28-1**	2023	Cohesive	**29-1**	1892	Cohesive	**30-1**	2436	Cohesive
26-2	2069	Cohesive	**27-2**	1826	Cohesive	**28-2**	1866	Cohesive	**29-2**	2386	Cohesive	**30-2**	2337	Cohesive
26-3	2119	Cohesive	**27-3**	2179	Cohesive	**28-3**	1970	Cohesive	**29-3**	2077	Cohesive	**30-3**	2282	Cohesive
26-4	1982	Cohesive	**27-4**	1999	Cohesive	**28-4**	1846	Cohesive	**29-4**	2008	Cohesive	**30-4**	2275	Cohesive
26-5	2265	Cohesive	**27-5**	1938	Cohesive	**28-5**	1841	Cohesive	**29-5**	2108	Cohesive	**30-5**	2081	Cohesive
26-6	1997	Cohesive	**27-6**	1999	Cohesive	**28-6**	1666	Cohesive	**29-6**	2097	Cohesive	**30-6**	2268	Cohesive
26-7	2141	Cohesive	**27-7**	1920	Cohesive	**28-7**	2074	Cohesive	**29-7**	1848	Cohesive	**30-7**	2460	Cohesive
26-8	2143	Cohesive	**27-8**	1884	Cohesive	**28-8**	1773	Cohesive	**29-8**	1909	Cohesive	**30-8**	2459	Cohesive
26-9	2130	Cohesive	**27-9**	1837	Cohesive	**28-9**	1951	Cohesive	**29-9**	1995	Cohesive	**30-9**	2107	Cohesive
26-10	2271	Cohesive	**27-10**	2064	Cohesive	**28-10**	1978	Cohesive	**29-10**	2038	Cohesive	**30-10**	2233	Cohesive

31-1	2223	Cohesive	**32-1**	2558	Adh/Coh	**33-1**	2630	Adh/Coh	**34-1**	2361	Adh/Coh	**35-1**	1418	Adh/Coh
31-2	2663	Cohesive	**32-2**	2716	Cohesive	**33-2**	2567	Adh/Coh	**34-2**	2793	Adh/Coh	**35-2**	1807	Adh/Coh
31-3	2254	Cohesive	**32-3**	2813	Cohesive	**33-3**	2005	Adh/Coh	**34-3**	1974	Adh/Coh	**35-3**	1597	Adh/Coh
31-4	2884	Adh/Coh	**32-4**	2793	Cohesive	**33-4**	2181	Adh/Coh	**34-4**	2073	Adh/Coh	**35-4**	1555	Adh/Coh
31-5	2315	Cohesive	**32-5**	2793	Cohesive	**33-5**	2504	Cohesive	**34-5**	2398	Adh/Coh	**35-5**	1390	Adh/Coh
31-6	3018	Cohesive	**32-6**	2544	Cohesive	**33-6**	2427	Adh/Coh	**34-6**	2099	Adh/Coh	**35-6**	1698	Adh/Coh
31-7	2589	Cohesive	**32-7**	2215	Cohesive	**33-7**	2291	Cohesive	**34-7**	2519	Adh/Coh	**35-7**	1507	Adh/Coh
31-8	3133	Cohesive	**32-8**	2536	Cohesive	**33-8**	2396	Cohesive	**34-8**	2201	Adh/Coh	**35-8**	1523	Adh/Coh
31-9	3016	Cohesive	**32-9**	2557	Cohesive	**33-9**	2043	Cohesive	**34-9**	2440	Adh/Coh	**35-9**	1361	Adh/Coh
31-10	2990	Cohesive	**32-10**	2093	Cohesive	**33-10**	2425	Cohesive	**34-10**	2338	Adh/Coh	**35-10**	1529	Adh/Coh
36-1	1816	Adh/Coh	**37-1**	1369	Adh/Coh	**38-1**	1012	Adh/Coh	**39-1**	550	Cohesive	**40-1**	137	Cohesive
36-2	1699	Adh/Coh	**37-2**	1311	Adh/Coh	**38-2**	828	Adh/Coh	**39-2**	785	Cohesive	**40-2**	Broke	Cohesive
36-3	1195	Adh/Coh	**37-3**	1377	Adh/Coh	**38-3**	1022	Adh/Coh	**39-3**	724	Cohesive	**40-3**	Broke	Cohesive
36-4	1860	Adh/Coh	**37-4**	1269	Adh/Coh	**38-4**	952	Adh/Coh	**39-4**	859	Cohesive	**40-4**	2	Cohesive
36-5	1579	Adh/Coh	**37-5**	1323	Adh/Coh	**38-5**	1076	Adh/Coh	**39-5**	967	Cohesive	**40-5**	3	Cohesive
36-6	1888	Adh/Coh	**37-6**	1442	Adh/Coh	**38-6**	804	Adh/Coh	**39-6**	729	Cohesive	**40-6**	2	Cohesive
36-7	1642	Adh/Coh	**37-7**	1086	Adh/Coh	**38-7**	1103	Adh/Coh	**39-7**	725	Cohesive	**40-7**	18	Cohesive
36-8	1618	Adh/Coh	**37-8**	1329	Adh/Coh	**38-8**	725	Adh/Coh	**39-8**	928	Cohesive	**40-8**	141	Cohesive
36-9	1745	Adh/Coh	**37-9**	1027	Adh/Coh	**38-9**	1067	Adh/Coh	**39-9**	1097	Cohesive	**40-9**	2	Cohesive
36-10	1823	Adh/Coh	**37-10**	1248	Adh/Coh	**38-10**	909	Adh/Coh	**39-10**	769	Cohesive	**40-10**	108	Cohesive
41-1	2782	Cohesive	**42-1**	2572	Adh/Coh	**43-1**	2356	Adh/Coh	**44-1**	1679	Adh/Coh	**45-1**	1589	Adh/Coh
41-2	1971	Adh/Coh	**42-2**	2079	Cohesive	**43-2**	2372	Adh/Coh	**44-2**	1757	Adh/Coh	**45-2**	1710	Adh/Coh
41-3	2356	Cohesive	**42-3**	2597	Cohesive	**43-3**	2269	Adh/Coh	**44-3**	1722	Adh/Coh	**45-3**	1577	Adh/Coh
41-4	2598	Cohesive	**42-4**	2570	Adh/Coh	**43-4**	2272	Cohesive	**44-4**	2139	Adh/Coh	**45-4**	1802	Adh/Coh
41-5	2558	Cohesive	**42-5**	2429	Adh/Coh	**43-5**	2374	Adh/Coh	**44-5**	1419	Adh/Coh	**45-5**	1506	Adh/Coh
41-6	2444	Cohesive	**42-6**	2327	Adh/Coh	**43-6**	2472	Cohesive	**44-6**	1741	Adh/Coh	**45-6**	1679	Adh/Coh
41-7	2549	Cohesive	**42-7**	2374	Cohesive	**43-7**	2394	Cohesive	**44-7**	1686	Adh/Coh	**45-7**	1947	Adh/Coh
41-8	2646	Cohesive	**42-8**	2338	Adh/Coh	**43-8**	2384	Cohesive	**44-8**	1509	Adh/Coh	**45-8**	1765	Adh/Coh
41-9	2536	Cohesive	**42-9**	2622	Cohesive	**43-9**	2372	Cohesive	**44-9**	1813	Adh/Coh	**45-9**	1711	Adh/Coh
41-10	2666	Cohesive	**42-10**	2453	Cohesive	**43-10**	2108	Cohesive	**44-10**	1823	Adh/Coh	**45-10**	1425	Adh/Coh

46-1	2539	Adh/Coh	**47-1**	1979	Cohesive	**48-1**	1788	Adh/Coh	**49-1**	1718	Adh/Coh	**50-1**	811	Adh/Coh
46-2	2719	Adh/Coh	**47-2**	1766	Cohesive	**48-2**	2178	Adh/Coh	**49-2**	2243	Adh/Coh	**50-2**	626	Adh/Coh
46-3	2628	Adh/Coh	**47-3**	2006	Cohesive	**48-3**	1756	Adh/Coh	**49-3**	1662	Adh/Coh	**50-3**	754	Adh/Coh
46-4	3212	Adh/Coh	**47-4**	1820	Cohesive	**48-4**	1804	Adh/Coh	**49-4**	1734	Adh/Coh	**50-4**	766	Adh/Coh
46-5	2832	Adh/Coh	**47-5**	1950	Cohesive	**48-5**	1896	Adh/Coh	**49-5**	1360	Adh/Coh	**50-5**	771	Adh/Coh
46-6	2573	Adh/Coh	**47-6**	1897	Cohesive	**48-6**	2064	Adh/Coh	**49-6**	1979	Adh/Coh	**50-6**	1064	Adh/Coh
46-7	1767	Adh/Coh	**47-7**	2224	Cohesive	**48-7**	1815	Adh/Coh	**49-7**	1930	Adh/Coh	**50-7**	1001	Adh/Coh
46-8	2665	Adh/Coh	**47-8**	2033	Adh/Coh	**48-8**	1679	Adh/Coh	**49-8**	2187	Adh/Coh	**50-8**	578	Adh/Coh
46-9	2463	Adh/Coh	**47-9**	1642	Cohesive	**48-9**	1584	Adh/Coh	**49-9**	1919	Adh/Coh	**50-9**	910	Adh/Coh
46-10	2737	Adh/Coh	**47-10**	1686	Cohesive	**48-10**	1569	Adh/Coh	**49-10**	2341	Adh/Coh	**50-10**	765	Adh/Coh
51-1	2482	Adh/Coh	**52-1**	2096	Adh/Coh	**53-1**	1429	Cohesive	**54-1**	776	Cohesive	**55-1**	1	Cohesive
51-2	2271	Adh/Coh	**52-2**	2137	Adh/Coh	**53-2**	2036	Cohesive	**54-2**	1021	Cohesive	**55-2**	Broke	Cohesive
51-3	2660	Adh/Coh	**52-3**	2000	Adh/Coh	**53-3**	1749	Cohesive	**54-3**	1142	Cohesive	**55-3**	Broke	Cohesive
51-4	2332	Adh/Coh	**52-4**	2384	Adh/Coh	**53-4**	1755	Cohesive	**54-4**	991	Cohesive	**55-4**	2	Cohesive
51-5	2236	Adh/Coh	**52-5**	2373	Adh/Coh	**53-5**	1760	Cohesive	**54-5**	820	Cohesive	**55-5**	1	Cohesive
51-6	2215	Adh/Coh	**52-6**	2258	Adh/Coh	**53-6**	1639	Cohesive	**54-6**	932	Cohesive	**55-6**	1	Cohesive
51-7	2484	Adh/Coh	**52-7**	2157	Adh/Coh	**53-7**	1089	Cohesive	**54-7**	976	Cohesive	**55-7**	Broke	Cohesive
51-8	2452	Adh/Coh	**52-8**	2359	Adh/Coh	**53-8**	1385	Cohesive	**54-8**	1141	Cohesive	**55-8**	Broke	Cohesive
51-9	2361	Adh/Coh	**52-9**	2269	Adh/Coh	**53-9**	1206	Cohesive	**54-9**	990	Cohesive	**55-9**	Broke	Cohesive
51-10	2444	Adh/Coh	**52-10**	1997	Adh/Coh	**53-10**	Missing		**54-10**	891	Cohesive	**55-10**	5	Cohesive
56-1	636	Adhesive	**57-1**	418	Cohesive	**58-1**	986	Adh/Coh	**59-1**	641	Adh/Coh	**60-1**	1541	Adh/Sub
56-2	285	Adhesive	**57-2**	361	Adh/Coh	**58-2**	786	Adh/Coh	**59-2**	1484	Adh/Coh	**60-2**	499	Adh/Coh
56-3	436	Adhesive	**57-3**	1007	Adh/Coh	**58-3**	709	Adh/Coh	**59-3**	565	Adh/Coh	**60-3**	549	Adh/Coh
56-4	771	Adhesive	**57-4**	130	Cohesive	**58-4**	861	Adh/Coh	**59-4**	656	Adh/Coh	**60-4**	1264	Adh/Coh/Sub
56-5	1618	Adh/Coh	**57-5**	354	Adh/Coh	**58-5**	546	Adh/Coh	**59-5**	1121	Adh/Coh	**60-5**	1235	Adh/Coh/Sub
56-6	695	Adhesive	**57-6**	411	Adh/Coh	**58-6**	897	Adh/Coh	**59-6**	517	Adh/Coh	**60-6**	402	Cohesive
56-7	948	Adhesive	**57-7**	985	Adh/Coh	**58-7**	1364	Adh/Coh	**59-7**	399	Adh/Coh	**60-7**	920	Adh/Coh/Sub
56-8	1043	Adhesive	**57-8**	643	Adh/Coh	**58-8**	706	Adh/Coh	**59-8**	858	Adh/Coh	**60-8**	1169	Adh/Coh/Sub
56-9	591	Adhesive	**57-9**	546	Adh/Coh	**58-9**	1399	Adh/Coh	**59-9**	307	Adh/Coh	**60-9**	480	Adh/Coh
56-10	1315	Adhesive	**57-10**	636	Adh/Coh	**58-10**	1717	Adh/Coh	**59-10**	809	Adh/Coh	**60-10**	1397	Adh/Coh/Sub

61-1	3058	Cohesive	**62-1**	2758	Cohesive	**63-1**	2565	Cohesive	**64-1**	2851	Cohesive	**65-1**	1973	Cohesive
61-2	3056	Cohesive	**62-2**	3519	Cohesive	**63-2**	3250	Cohesive	**64-2**	3933	Cohesive	**65-2**	2086	Cohesive
61-3	2546	Cohesive	**62-3**	2560	Cohesive	**63-3**	2685	Cohesive	**64-3**	3183	Cohesive	**65-3**	2153	Cohesive
61-4	2964	Cohesive	**62-4**	3058	Cohesive	**63-4**	2355	Cohesive	**64-4**	3335	Cohesive	**65-4**	2073	Cohesive
61-5	2730	Cohesive	**62-5**	2472	Cohesive	**63-5**	2273	Cohesive	**64-5**	3955	Cohesive	**65-5**	1835	Cohesive
61-6	2839	Cohesive	**62-6**	2738	Cohesive	**63-6**	2398	Cohesive	**64-6**	3660	Cohesive	**65-6**	2111	Cohesive
61-7	2926	Cohesive	**62-7**	3964	Cohesive	**63-7**	3030	Cohesive	**64-7**	3638	Cohesive	**65-7**	1909	Cohesive
61-8	2701	Cohesive	**62-8**	3338	Cohesive	**63-8**	2817	Cohesive	**64-8**	3714	Cohesive	**65-8**	2195	Cohesive
61-9	3110	Cohesive	**62-9**	2493	Cohesive	**63-9**	3041	Cohesive	**64-9**	3860	Cohesive	**65-9**	1945	Cohesive
61-10	3170	Cohesive	**62-10**	3147	Cohesive	**63-10**	2684	Cohesive	**64-10**	2781	Cohesive	**65-10**	2208	Cohesive
66-1	3779	Cohesive	**67-1**	3937	Cohesive	**68-1**	4283	Cohesive	**69-1**	2731	Cohesive	**70-1**	Broke	Cohesive
66-2	3687	Cohesive	**67-2**	3696	Cohesive	**68-2**	4127	Cohesive	**69-2**	2378	Cohesive	**70-2**	1	Cohesive
66-3	3549	Cohesive	**67-3**	3738	Cohesive	**68-3**	3735	Cohesive	**69-3**	1892	Cohesive	**70-3**	1	Cohesive
66-4	3628	Cohesive	**67-4**	3649	Cohesive	**68-4**	3347	Cohesive	**69-4**	2076	Cohesive	**70-4**	Broke	Cohesive
66-5	3256	Cohesive	**67-5**	3037	Cohesive	**68-5**	4466	Cohesive	**69-5**	2549	Cohesive	**70-5**	Broke	Cohesive
66-6	3916	Cohesive	**67-6**	2899	Cohesive	**68-6**	3955	Cohesive	**69-6**	3106	Cohesive	**70-6**	Broke	Cohesive
66-7	3602	Cohesive	**67-7**	2750	Cohesive	**68-7**	3658	Cohesive	**69-7**	2158	Cohesive	**70-7**	1	Cohesive
66-8	3665	Cohesive	**67-8**	3997	Cohesive	**68-8**	3704	Cohesive	**69-8**	1953	Cohesive	**70-8**	Broke	Cohesive
66-9	3499	Cohesive	**67-9**	3306	Cohesive	**68-9**	4083	Cohesive	**69-9**	2480	Cohesive	**70-9**	Broke	Cohesive
66-10	3506	Cohesive	**67-10**	3674	Cohesive	**68-10**	3657	Cohesive	**69-10**	2490	Cohesive	**70-10**	Broke	Cohesive
71-1	2221	Adh/Coh	**72-1**	2040	Cohesive	**73-1**	2373	Cohesive	**74-1**	2159	Cohesive	**75-1**	2045	Cohesive
71-2	2187	Cohesive	**72-2**	2170	Cohesive	**73-2**	2083	Cohesive	**74-2**	2052	Cohesive	**75-2**	2240	Cohesive
71-3	2305	Cohesive	**72-3**	2035	Cohesive	**73-3**	2139	Cohesive	**74-3**	1998	Cohesive	**75-3**	2165	Cohesive
71-4	1988	Cohesive	**72-4**	2028	Cohesive	**73-4**	1910	Adh/Coh	**74-4**	2115	Cohesive	**75-4**	2193	Cohesive
71-5	2050	Cohesive	**72-5**	2216	Cohesive	**73-5**	2335	Cohesive	**74-5**	2025	Cohesive	**75-5**	2279	Cohesive
71-6	2388	Cohesive	**72-6**	2147	Cohesive	**73-6**	2298	Cohesive	**74-6**	1979	Cohesive	**75-6**	2223	Cohesive
71-7	2137	Cohesive	**72-7**	2076	Cohesive	**73-7**	2124	Cohesive	**74-7**	1988	Cohesive	**75-7**	2396	Cohesive
71-8	2305	Cohesive	**72-8**	1974	Cohesive	**73-8**	2237	Cohesive	**74-8**	2121	Cohesive	**75-8**	2389	Cohesive
71-9	2196	Cohesive	**72-9**	2144	Cohesive	**73-9**	2313	Cohesive	**74-9**	2135	Cohesive	**75-9**	2352	Cohesive
71-10	1959	Cohesive	**72-10**	2112	Cohesive	**73-10**	2314	Cohesive	**74-10**	2039	Cohesive	**75-10**	2128	Cohesive

76-1	3510	Cohesive	**77-1**	1981	Adh/Coh	**78-1**	1818	Cohesive	**79-1**	3363	Adh/Coh	**80-1**	1151	Adh/Coh
76-2	2654	Cohesive	**77-2**	2577	Adh/Coh	**78-2**	1157	Cohesive	**79-2**	3191	Adh/Coh	**80-2**	982	Adh/Coh
76-3	2802	Cohesive	**77-3**	2086	Adh/Coh	**78-3**	2002	Adh/Coh	**79-3**	3868	Adh/Coh	**80-3**	1202	Adh/Coh
76-4	2724	Cohesive	**77-4**	2234	Adh/Coh	**78-4**	2115	Adh/Coh	**79-4**	3694	Adh/Coh	**80-4**	1285	Adh/Coh
76-5	2918	Cohesive	**77-5**	1606	Adh/Coh	**78-5**	1454	Adh/Coh	**79-5**	4191	Adh/Coh	**80-5**	1697	Adh/Coh
76-6	2571	Cohesive	**77-6**	1192	Adh/Coh	**78-6**	2266	Adh/Coh	**79-6**	4140	Adh/Coh	**80-6**	1635	Adh/Coh
76-7	1278	Adh/Coh	**77-7**	2013	Adh/Coh	**78-7**	1091	Adh/Coh	**79-7**	4338	Cohesive	**80-7**	2213	Adh/Coh
76-8	682	Adh/Coh	**77-8**	2131	Adh/Coh	**78-8**	1909	Adh/Coh	**79-8**	4077	Cohesive	**80-8**	1804	Adh/Coh
76-9	1923	Cohesive	**77-9**	2307	Adh/Coh	**78-9**	1593	Adh/Coh	**79-9**	3468	Cohesive	**80-9**	1864	Adh/Coh
76-10	1110	Adh/Coh	**77-10**	2452	Adh/Coh	**78-10**	1432	Adh/Coh	**79-10**	3665	Cohesive	**80-10**	1807	Adh/Coh
81-1	2389	Adh/Coh	**82-1**	Broke	Adh/Coh	**83-1**	1360	Cohesive	**84-1**	1118	Adh/Coh	**85-1**	Broke	Adh/Coh
81-2	2014	Adh/Coh	**82-2**	Broke	Adh/Coh	**83-2**	1513	Cohesive	**84-2**	1058	Adh/Coh	**85-2**	Broke	Adh/Coh
81-3	2008	Adh/Coh	**82-3**	Broke	Adh/Coh	**83-3**	1593	Cohesive	**84-3**	854	Cohesive	**85-3**	3	Adh/Coh
81-4	2050	Adh/Coh	**82-4**	Broke	Adh/Coh	**83-4**	1807	Cohesive	**84-4**	1232	Cohesive	**85-4**	Broke	Adh/Coh
81-5	1998	Adh/Coh	**82-5**	Broke	Adh/Coh	**83-5**	1285	Cohesive	**84-5**	1084	Adh/Coh	**85-5**	2	Adh/Coh
81-6	2124	Adh/Coh	**82-6**	Broke	Adh/Coh	**83-6**	1551	Cohesive	**84-6**	1087	Cohesive	**85-6**	Broke	Cohesive
81-7	1870	Adh/Coh	**82-7**	Broke	Adh/Coh	**83-7**	1525	Cohesive	**84-7**	1243	Adh/Coh	**85-7**	Broke	Adh/Coh
81-8	2666	Cohesive	**82-8**	Broke	Adh/Coh	**83-8**	1395	Cohesive	**84-8**	1013	Cohesive	**85-8**	107	Adh/Coh
81-9	1898	Adh/Coh	**82-9**	Broke	Adh/Coh	**83-9**	1726	Cohesive	**84-9**	1022	Cohesive	**85-9**	Broke	Cohesive
81-10	2027	Adh/Coh	**82-10**	Broke	Adh/Coh	**83-10**	1551	Cohesive	**84-10**	1096	Cohesive	**85-10**	91	Cohesive
86-1	1812	Adh/Coh	**87-1**	951	Adh/Coh	**88-1**	774	Adh/Coh	**89-1**	1837	Cohesive	**90-1**	2343	Cohesive
86-2	1778	Adh/Coh	**87-2**	1181	Adh/Coh	**88-2**	1325	Adh/Coh	**89-2**	2066	Cohesive	**90-2**	2327	Cohesive
86-3	2008	Cohesive	**87-3**	1422	Adh/Coh	**88-3**	1068	Adh/Coh	**89-3**	2039	Cohesive	**90-3**	2239	Cohesive
86-4	1839	Adh/Coh	**87-4**	1183	Adh/Coh	**88-4**	1441	Adh/Coh	**89-4**	1955	Cohesive	**90-4**	2140	Cohesive
86-5	1967	Adh/Coh	**87-5**	1308	Adh/Coh	**88-5**	1297	Adh/Coh	**89-5**	1936	Cohesive	**90-5**	2364	Cohesive
86-6	1953	Adh/Coh	**87-6**	1656	Adh/Coh	**88-6**	1328	Adh/Coh	**89-6**	1988	Cohesive	**90-6**	2414	Cohesive
86-7	1962	Adh/Coh	**87-7**	1163	Adh/Coh	**88-7**	1653	Adh/Coh	**89-7**	2226	Cohesive	**90-7**	2472	Cohesive
86-8	1823	Adh/Coh	**87-8**	1215	Adh/Coh	**88-8**	1190	Adh/Coh	**89-8**	1838	Cohesive	**90-8**	2290	Cohesive
86-9	1695	Adh/Coh	**87-9**	936	Adh/Coh	**88-9**	1557	Adh/Coh	**89-9**	1935	Cohesive	**90-9**	2175	Cohesive
86-10	1871	Adh/Coh	**87-10**	1452	Adh/Coh	**88-10**	1395	Adh/Coh	**89-10**	1988	Cohesive	**90-10**	2381	Cohesive

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