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ENVIRONMENTALLY COMPLIANT
ADHESIVE JOINING TECHNOLOGY

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ADHESIVE JOINING TECHNOLOGY

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Abstract- Adhesive joining offers one method of assembling products. The advantages of adhesive joining and assembly are many and include the distribution of applied forces, lighter weight, and appealing appearance, just to name a few. Selecting environmentally safe adhesive materials and accompanying processes is paramount in today’s business climate if a company wants to be environmentally conscious and stay in business. Four areas of adhesive joining — (1) adhesive formulation and selection, (2) surface preparation, (3) the adhesive bonding process, and (4) waste and pollution generation, clean-up, and management — all need to be carefully evaluated before adhesive joining is selected for commercial as well as military products. Designing for six sigma quality must also be addressed in today’s global economy. This requires material suppliers and product manufacturers to work even closer together.

INTRODUCTION

With few exceptions, everything that is designed must be attached in some way to something else. Adhesives offer one method of joining materials and assembling products. The advantages of adhesive joining include the distribution of any stresses, appealing appearance, and lighter weight compared to mechanical joining. Adhesive joining has been used in the wood products industry for some time, and the aerospace and commercial airplane industry have used it extensively. Adhesives are also used extensively in the electronics industry. Now the automotive and transportation industries are using adhesives to assemble their vehicle bodies and components.

Adhesive joining can roughly be divided into two segments: assembly joining and structural joining. Assembly joining uses an adhesive to hold two parts (materials) together. There is little or no load applied to the joint area other than the weight of the two materials or forces created by differences in thermal expansion. The joint may be temporary, have little or no durability requirement, or later be encapsulated. Structural joining is the formation of a load-carrying joint, usually between two high strength members. Elaborate surface preparation is performed on each adherent to obtain optimum strength and performance (environmental durability, fatigue resistance, and/or chemical resistance).

Adhesives, primarily organic in chemistry, and their associated processes have certain worker health, safety, and environmental issues associated with them. These issues must be addressed during the design phase of product conception along with pollution and waste generation from the manufacturing process. “Design is the mother of all factors.” “Decisions made at the design stage determine the composition of the ‘waste stream’ and determine environmental costs including any disposal costs.” (1)

This paper will discuss the adhesive joining process and many of the decisions the designer must address in selecting environmentally compliant adhesive joining.

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THE FOUR M's OF ADHESIVE JOINING TECHNOLOGY

All manufactured goods are produced with the 4 M's of manufacturing (materials, methods, machinery, and manpower). Figure 1 is a fishbone of the 4 M's which also applies to adhesive joining technology. Manufacturers not only have to select the correct adhesive (material) and its accompanying members (methods, machinery, and manpower) to do the job, but also must evaluate the overall impact on the environment (waste generation, amount and where it goes, employee health, and employee safety). Product design will have an impact on the adhesive assembly materials and process selection.

Figure 1
Manufacturing Fishbone

Design for
Manufacturability & Environment

Materials

Methods

Six Sigma
Quality

Products

Manpower

Machinery

ADHESIVE SELECTION

Today, manufacturers are fortunate to have a filled arsenal of adhesives to tackle some very interesting and challenging joining requirements. Not only are there many different types and forms of adhesives, but most can be used in ways that minimize waste, reduce pollution, and meet performance. In addition to favorable chemistry, adhesive manufacturers have identified the importance of packaging and dispensing as participants to environmentally conscious manufacturing. Table 1 is a listing of traditional versus replacement adhesives.

Table 1
Traditional versus Replacement Adhesives

<table>
<thead>
<tr>
<th>TRADITIONAL ADHESIVES</th>
<th>REPLACEMENT ADHESIVES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent Based (one and two part)</td>
<td>Water-based</td>
</tr>
<tr>
<td></td>
<td>100 % Solids</td>
</tr>
<tr>
<td></td>
<td>Hot Melts</td>
</tr>
<tr>
<td></td>
<td>Reactive Hot Melts</td>
</tr>
<tr>
<td></td>
<td>Pressure Sensitive Adhesives (PSA)</td>
</tr>
<tr>
<td>Brittle Epoxies</td>
<td>Flexibilized Epoxies</td>
</tr>
<tr>
<td></td>
<td>Acrylics</td>
</tr>
<tr>
<td></td>
<td>Urethanes</td>
</tr>
<tr>
<td>Solvent Cements, Cellulose and Gums</td>
<td>Cyanoacrylates</td>
</tr>
<tr>
<td></td>
<td>UV Cured (urethanes, epoxies, acrylates)</td>
</tr>
</tbody>
</table>

CLEANING AND SOIL (CONTAMINANT) REMOVAL

For years companies have relied upon chlorinated solvents such as trichloroethylene (TCE) and trichloroethane (TCA) to do any soil or contaminant removal from metals, plastics, and rubber parts. These solvents were used in hand-wiping operations (usually for assembly joining) as well as vapor degreasing operations (most often used for structural joining). These solvents removed a broad spectrum of organic soils and were rapid drying, non-flammable, widely available, and reasonably priced. An extra benefit was that although many plastic and rubber materials absorbed them and swelled, they readily gave up the solvent and returned to their original dimensions and shape without affecting the material and its
subsequent performance. These solvents were broad ranged cleaners and removed a wide spectrum of contaminants. Unfortunately, the availability and use of TCE and TCA are now long gone.

Today, a more methodical approach to cleaning must be taken. The author’s experience working with numerous companies through the Department of Energy’s Technology Transfer Program has been that many companies don’t know what soils and contaminants they have on their substrates or parts. Therefore, the first two steps in establishing a cleaning process are identifying what the contaminants are and asking the question, How clean is clean? Once the contaminants have been identified and/or categorized, finding a replacement cleaning agent is much easier. The following equation is used as a general rule for cleaning.

\[(\text{Cleaning Agent Concentration}) \times (\text{Temperature}) \times (\text{Time}) \times (\text{Mechanics}) \times (\text{Fixturing}) = \text{Clean}\]

CLEANING—HAND WIPING

Hand wiping consists of using a solvent-laden cloth to wipe the surfaces of substrates to be adhesive joined. Usually after several passes the worker looks at the cloth to see if there is any discoloration on it. If it is “clean,” then he/she stops wiping. For metals (high surface energy materials), a contact angle measurement can be used to test the cleanliness of the surface. A low contact angle indicates good wetting, which is absolutely necessary for adhesive joining. A water-break-free test can also be used. Individual beads of water on the surface are an indication of soils or contaminants.

Evaluating cleanliness on plastics and rubber surfaces is more difficult because they are low surface energy materials. They are sometimes difficult to wet, even when clean. Many rubber and plastic materials must be abraded, coated with a primer, or treated by corona or plasma to obtain sufficient wetting and ultimate adhesive bonding. Because there are so many different plastic and rubber formulations, it is difficult to make one general statement to cover all of them. Each material must be evaluated separately. A good place to start is the Processing Handbook on Surface Preparations for Adhesive Bonding (2).

Numerous alternative wiping solvents are available. Some are a blend of several different solvents to create a range of solvency and cleaning efficacy. A company must decide what it is comfortable using in its facility — a high vapor pressure (HVP) cleaning agent versus a low vapor pressure (LVP) cleaning agent. HVP cleaners are high volatile organic chemicals (HVOCs) and are characterized as having low flash points and rapid evaporation. LVP cleaners are low volatile organic chemicals (LVOCs) and are characterized as having high flash points and slower evaporation. Each company must address the issue of what hand-wipe cleaning agent they should use, both from a standpoint of cleaning efficacy as well as worker health, safety, and environmental concerns.

CLEANING—STRUCTURAL JOINING APPLICATIONS

With the reduction in use of TCE and TCA in vapor degreasers, alternate cleaning agents and methods had to be found. Fortunately, the metal plating and conversion coating industry has extensive experience with detergent cleaners and water. Many of these cleaners are alkaline, and much of the knowledge is being transferred to industries doing structural bonding. However, some precautions are necessary. Steel and magnesium are very resistant to alkaline cleaners. Aluminum is easily attacked by alkaline cleaners, and silicates must be added to the cleaning bath to protect the aluminum from excessive etching. More thorough rinsing is also necessary to remove the silicates. Ultrasonic cleaning equipment is an excellent mechanical means of assisting the detergent and water cleaner. Some ultrasonic cleaners have heaters that raise the cleaning agent temperature and thus improve cleaning efficacy.
CHEMICAL ETCHING FOR ALUMINUM BONDING

For years the standard for aluminum alloy structural bonding was the Forest Products Laboratory (FPL) sulfuric acid/sodium dichromate etch formulation. However, the formulation is not acceptable by today's environmental standards because of sodium dichromate. The Boeing Company developed the phosphoric acid anodizing (PAA) process which is much better because it produces a deeper and more stable aluminum oxide skeleton for adhesive attachment. This improved etching results in improved structural joint durability. It is used extensively in the aircraft industry. However, for many other aluminum applications it is not necessary, and therefore the additional expense is not justified. Such an example of reduced need for the PAA etch process is in the Department of Energy (DOE) weapons program, which for years used the FPL etch process. An alternate to the FPL etch process was needed for environmental reasons. Most DOE weapons program needs are for adhesive joining of small aluminum parts and assemblies that do not require high durability performance.

An alternate aluminum etching formulation was developed at Picatinny Arsenal, NJ (3). It has been identified as the P-2 etch and contains sulfuric acid and ferric sulfate. Aluminum parts are processed (etched) in a similar manner as they would be processed with FPL etch. The P-2 etch is more environmentally acceptable because it does not contain chrome. For adhesive producers who must test their products with aluminum alloys or manufacturers who do routine aluminum bonding, P-2 etch has been found to be an acceptable replacement (4). Today, FPL and P-2 etch formulations can be found in ASTM-D-2651, Preparation of Metal Surfaces for Adhesive Bonding. The FPL and P-2 formulations are listed in Table 2.

<table>
<thead>
<tr>
<th>COMPONENTS</th>
<th>FPL COMPOSITION</th>
<th>P-2 COMPOSITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric Acid</td>
<td>333 grams</td>
<td>370 grams</td>
</tr>
<tr>
<td>Sodium Dichromate</td>
<td>33 grams</td>
<td>----</td>
</tr>
<tr>
<td>Ferric Sulfate</td>
<td>----</td>
<td>150 grams</td>
</tr>
<tr>
<td>DI water to make</td>
<td>1 liter</td>
<td>1 liter</td>
</tr>
</tbody>
</table>

EVALUATION OF P-2 ETCHANT

Eight different adhesives (seven epoxies and one urethane) were evaluated with the P-2 etchant to see how they would perform. Many of the production joining operations used at Federal Manufacturing & Technologies (FM&T) involve materials other than aluminum. However, the facility does use 2024-T3 Alclad aluminum for all of its receiving inspection testing. Table 3 is a listing of the important information about the adhesives used in the evaluation. All test specimens were prepared and tested to meet the requirements of ASTM-D-1002, Strength Properties of Adhesives in Shear by Tension Loading.

Other materials and processing parameters comparing included (1) cleaning efficacy of trichloroethane (TCA) vapor degreasing versus alkaline cleaning in an ultrasonic cleaner versus acetone wipe followed by an isopropyl alcohol (IPA) wipe, (2) etch time, and (3) time between etching and bonding. Table 4 is a summary of the results.
Table 3
Candidate Adhesives

<table>
<thead>
<tr>
<th>ADHESIVE</th>
<th>DESCRIPTION</th>
<th>CURE SCHEDULE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epon 828 &amp;</td>
<td>Two part flexible epoxy (50/50)</td>
<td>24 hr @ RT + 2 hr @ 160°F</td>
</tr>
<tr>
<td>Versamid 140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC 2216 B/A</td>
<td>Two part flexible epoxy</td>
<td>16 hr @ RT + 16 hr @ 160°F</td>
</tr>
<tr>
<td>Epibond 104 A/B</td>
<td>Two part, highly filled, high</td>
<td>3 hr @ 160°F</td>
</tr>
<tr>
<td></td>
<td>modulus epoxy</td>
<td></td>
</tr>
<tr>
<td>EA 934 NA</td>
<td>Two part, high temp. resistant</td>
<td>2 hr @ 200°F</td>
</tr>
<tr>
<td></td>
<td>epoxy</td>
<td></td>
</tr>
<tr>
<td>FM-123-5</td>
<td>Nitrile-epoxy film</td>
<td>2 hr @ 250°F with 25-30 psi</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pressure</td>
</tr>
<tr>
<td>Ablefilm 501</td>
<td>General purpose epoxy film</td>
<td>2 hr @ 200°F</td>
</tr>
<tr>
<td>Halthane 88/61002</td>
<td>Two part urethane adhesive</td>
<td>4 hr @ RT + 2 hr @ 150°F+2 hr @</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200°F</td>
</tr>
<tr>
<td>Hysol 608</td>
<td>Two part fast cure epoxy</td>
<td>2 hr @ 140°F</td>
</tr>
</tbody>
</table>

Table 4
Materials and Processes Comparison

<table>
<thead>
<tr>
<th>PROCESS PARAMETER</th>
<th>OPTIMUM RESULTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>General soil removal</td>
<td>No difference between TCA vapor degreasing vs. alkaline cleaning in an ultrasonic</td>
</tr>
<tr>
<td></td>
<td>cleaner. Both are better than hand wiping with acetone and IPA.</td>
</tr>
<tr>
<td>Etch time</td>
<td>Ten minutes appears optimum for both etch systems. All specimens resulted in</td>
</tr>
<tr>
<td></td>
<td>cohesive bond failure.</td>
</tr>
<tr>
<td>Time between etching and adhesive bonding</td>
<td>Bond strength and cohesive failure mode appear to degrade after several days</td>
</tr>
<tr>
<td></td>
<td>for both etch materials.</td>
</tr>
</tbody>
</table>

In conclusion, it was determined that using an alkaline cleaner and water in an ultrasonic bath followed with the P-2 etch process for 10 minutes was an acceptable alternative to using trichloroethane in a vapor degreaser followed by FPL etch for 10 minutes. Both processes produced test results having cohesive failure. Cohesive failure is defined as a failure in the adhesive material as compared to adhesive failure, which is a failure in the adhesive/substrate interface. Cohesive failure is more desirable.

GUIDELINES FOR GOOD ADHESIVE JOINING

There are some good adhesive joining assembly guidelines that this author has established which are carried to any new product design and assembly meeting. The author feels these rules establish the foundation for using adhesive joining as a method of assembling materials and parts. These rules are listed in Table 5.

CHALLENGE THE ADHESIVE SUPPLIER

There are challenges that the designer must place upon adhesive suppliers who supply the materials used to join materials together. Some simple points to keep in mind when talking to an adhesive supplier are listed in Table 6.
### Table 5
Guidelines for Good Adhesive Joining

- Design sufficient joint area to handle the expected loads.
- Use surface preparation techniques to optimize the joint strength.
- The adhesive must wet both surfaces to be joined.
- Use a sufficient amount of adhesive.
- Have a match between the modulus of elasticity of the adhesive and substrates.
- Anticipate thermal expansion.
- Parts must fit well together.
- Read the cleaning, surface preparation, and adhesive material safety data sheets and understand any chemical dangers.

### Table 6
Selecting an Adhesive Joining System

Select an adhesive joining system for your application that is
- Easy to use
- Uses environmentally safe adhesives
- Requires minimal surface preparation
- Uses on-demand joining whenever possible
- Produces no or minimal waste
- Meets environmental regulations

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**DESIGNING FOR SIX SIGMA QUALITY**

Whether building boats, airplanes, automobiles, or furniture, there are certain steps one should take in order to produce quality products. These items should be addressed early in the design phase and are true for adhesive joining assembly or any other assembly methods. First, design is the weapon of choice in producing quality products. Design determines the limits of product quality and determines the type and size of a manufacturing waste stream. Any changes and/or modifications must be made during the design phase. Changes or modifications made once the product has gone into production will most likely maintain product quality, not improve product quality. Therefore, sufficient time must be spent in the design phase of a new product. Table 7 lists several other suggestions for attaining six sigma quality using adhesive joining technology.

### Table 7
Attaining Six Sigma Quality Using Adhesive Joining Technology

- Reduce the number of manufacturing steps.
- Specify manufacturing processes which do not require numerous secondary operations.
- Avoid variable processes:
  - skill intensive
  - difficult to monitor
  - use highly variable materials
- Use prepackaged materials.
- Automate as much of the assembly process as possible.
- Know the workers’ capabilities.
- Don’t try to implement several new processes simultaneously.
CONCLUSION

P-2 etchant has been found to be an acceptable replacement for FPL etchant for verifying the strength of adhesives purchased from numerous adhesive suppliers. In addition, it is an acceptable aluminum surface preparation treatment for applications that do not require joint durability. Each company must decide what cleaning material(s) they can accept and use in their manufacturing facility. In order to help make this determination, they must first identify what are the contaminants that must be removed. Second, they must answer the question, How clean is clean? In many cases, trade-offs must be made to select cleaning materials that will do the job and meet today’s environmental regulations.

In conclusion, using adhesive joining in today’s manufacturing climate is a challenge. Companies must not only consider Design for Manufacturing but also Design for the Environment. In the past, waste generation and pollution at the end of the manufacturing pipeline was a concern. Today, using the Environmental Protection Agency’s definition of pollution prevention, the manufacturer must consider waste and pollution streams as part of the product design process. In order to achieve high quality products using adhesive joining to assemble products, companies must minimize the number of manufacturing steps, especially those requiring secondary operations, and avoid variable processes that require judgments and/or decisions by their workers. Elimination of on-the-line decisions can be made by using prepackaged adhesives and automated application and assembly operations.
References

(1) Brown, Jr., George, E., Member of U. S. House of Representatives, Science, Space and Technology Committee.

