



Surface Preparation Techniques for Adhesive Bonding

Second Edition



Raymond F. Wegman
James Van Twisk

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*Raymond F. Wegman and
James Van Twisk*



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Dedication

To all those engineers and scientists who have dedicated their careers to the advancement of the field of materials and processing for adhesive bonding; and to my wife, Rose, whose encouragement, indulgence, and sacrifice made this book possible.

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Preface

The purpose of this handbook is to provide information on processing adherends prior to adhesive bonding. Where sufficient data were available the processes are given in the form of process specifications. Further, where available, data are given to provide potential users with a basis for the selection of the process most suitable for their particular application and facility.

It is known that many of the chemicals used in these processes are hazardous due to their strong oxidizing properties, or may be toxic or hazardous to one's health. It is the user's responsibility to assure that proper safety, handling and disposal procedures are implemented and monitored when any of these methods is employed.

Raymond F. Wegman

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Raymond F. Wegman

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The book is intended for information only. It is known that many of the chemicals used in the processes described are hazardous, due to their strong oxidizing properties, or may be toxic or hazardous to one's health. It is the user's responsibility to assure that proper safety, handling and disposal procedures are implemented and monitored when any of these methods is employed. Expert advice should be obtained at all times when implementation is being considered.

1 Introduction

1.1 Adhesion

Adhesion is a surface phenomenon, i.e., adhesion is controlled by the condition of the surface of the adherend. The ASTM [1] defines adhesion as “the state in which two surfaces are held together by interfacial forces which consist of valence forces or interlocking actions or both.” Adhesion between surfaces which are held together by valence forces is called specific adhesion; this is the same type of force which gives rise to cohesion. Cohesion is defined as the state in which particles of a single substance are held together by primary or secondary forces. As used in the field, cohesion is defined as the state in which the particles of the adhesive (or the adherend) are held together.

Adhesion between surfaces in which the adhesive holds the parts together by interlocking action is known as mechanical adhesion.

Both specific adhesion and mechanical adhesion are important to the understanding of how adhesion is affected by surface preparation. Allen [2] in his discussion of the fundamentals of adhesion concluded by stating “. . . an adhesive bond achieves its strength from the combination of a variety of sources; (mechanisms). . . For these mechanisms, the relative importance and the proper way which they should be combined will vary from one example to another, but none should be excluded without very careful consideration and exploration.”

1.1.1 Specific Adhesion

According to the theory relating to specific adhesion, this type of adhesion involves the establishment of some kind of attraction between the atoms and the molecules which make up the adhesive and the adherends. These attractions may involve primary bonding forces, which tend to be quite strong; hydrogen bonding, which yields intermediate strength; and the weaker secondary (Van der Waals) forces.

Primary bonding may be covalent or ionic in nature. Covalent bonding involves the sharing of electron pairs between adjacent atoms. Ionic or electrostatic forces are the type of primary bonds that are found in ionic crystals. Another type of primary bond is the metallic bond which is similar to the covalent bond except that it involves the valence electrons in the metal. This type of bonding is discussed by Verink [3], Wegman and Levi [4] and Salomon [5].

Secondary bonding involves dipole-dipole interactions, induced dipole interactions and dispersion forces. Secondary bonding becomes important in adhesion when nonpolar or chemically inert surfaces are involved. Hydrogen bonding may be considered a special case of dipole interaction, since hydrogen bonds result from the sharing of a proton by two electron-negative atoms. However, hydrogen bond strengths are of the same order as a weak primary bond.

Another type of bond, discussed by DeLollis [6], is described as a chemisorbed bond. This type of bonding is proposed as the reason why adhesive promoters, such as primers and coupling agents, are successful in overcoming potentially weak boundary layers and result in good durable bonds.

In dealing with specific adhesion, good contact must be obtained between the adhesive and the surface of the adherend. To obtain this molecular contact with a solid adherend requires the wetting of the solid surface by the liquid adhesive. During the bonding process even the solid adhesive must go through a liquid phase. To understand the conditions of adequate wetting one must consider the role of surface energetics in adhesion. This, simply stated, requires that in order for a liquid to wet and spread on a solid surface the critical surface tension of the solid or solids must be greater than the surface tension of the liquid. In the case of polar solids such as metals and metal oxides this requirement is easily met, because the surface energies of the solid, provided that the surfaces are clean, are greater than 500 dyne/cm while the surface energies of the liquid adhesives are less than 500 dyne/cm [4]. However, even if good wetting and good contact between the adhesive and adherend are obtained, it may be difficult to obtain good durable bonds if there is a weak boundary layer on the adherend. Therefore, it is necessary to carefully select the proper surface preparation technique for the particular adherend, in order to make sure that such a weak boundary layer does not occur, which would make the bond practically useless. Surface energetics is further discussed by Kaelble [7].

1.1.2 Mechanical Adhesion

Mechanical adhesion results from an interlocking action between the surface structure of the adherend and the adhesive or primer.

Bickerman [8] proposed that adhesion was due to the inherent roughness of all surfaces. He accepted the fact that molecular forces of attraction caused an adhesive to wet and spread on the surface. Once this was achieved, however, Bickerman felt that mechanical coupling between the adhesive and the inherently rough adherend was more than enough to account for bond strength. Surface roughness can also account for a number of negative factors such as trapped gas bubbles, as described by DeBruyne [9], and imperfect molecular fit, as described by Eley [10]. Many arguments have been presented against Bickerman's theory and inherent surface roughness should be considered to be a contributing factor only, rather than a basic factor in the theory of adhesion.

In 1977, Chen et al. [11] proposed that the surface of Forest Products Laboratory (FPL) etched aluminum consisted of fine finger-like structures of

aluminum oxide which were determined to be about 50 Angstroms thick and approximately 400 Angstroms in height. Each of the fine fingers protruded from the tripoint of the oxide structure. This finding was made possible by advanced electron microscopy using such techniques as the scanning transmission microscope. Similar findings were made when the surface of phosphoric acid anodized aluminum was studied.

Further discussions and stereomicrographs of treated aluminum surfaces are presented in Chapter 2 of this book.

In 1980, Ditchek et al. [12] described the morphology and composition of titanium adherends prepared for adhesive bonding. In this work they discussed macro-rough and micro-rough surfaces. From their determination of the morphology of various surfaces they predicted the order of bondability of the surfaces and the reliability of the resultant bonds. Their predictions were confirmed by Brown [13] using the wedge test and by Wagman and Levi [14] using stress durability testing. This work is described in more detail in Chapter 3. Some excellent micrographs of these surfaces were presented by Venables [15] using extended resolution scanning electron microscopy.

This work shows that mechanical adhesion on a microscopic level does play a major role in adhesion and the durability of the resultant bonds. Therefore, as in the case of specific adhesion, it is equally important that proper surface preparation be used when one considers mechanical adhesion.

Whether one subscribes to the specific adhesion theory, the mechanical adhesion theory, or a combination of the two, surface preparation is a major item that must be considered.

At a National Research Council Workshop held in Washington DC [16] it was suggested that any study of the interface should begin with the realization that the traditional picture of the two-dimensional nature of the interface is outdated. It was further suggested that the interface is a three-dimensional "interphase." This interphase was described as "extending from some point in the adherend where the local properties begin to change from the bulk properties, through the interface, and into the adhesive to where the local properties approach the bulk properties." The interphase can extend from a few to a few hundred nanometers. On the adherend side it includes morphological alterations in the adherend near the surface, as well as oxides, whether deliberately constructed or native to the adherend surface. The oxide layer can vary in porosity and microstructure. Absorbed gases may be present on the oxide surface giving rise to conditions unfavorable to a good durable bond. A polymeric adhesive may be affected by the presence of the adherend surface. The polymeric network may be altered in the region close to the adherend surface, giving rise to a material which is different in composition and mechanical properties. This is caused by diffusion of certain adhesive components into the oxide surface leaving a layer of adhesive which contains a smaller amount of these components than does the bulk. Acceptance of the interphase as a working model of the actual joint interface leads to the conclusion that the logical beginning of a strong, durable adhesive bonded joint is the selection of the proper surface treatment.

1.2 Bonding

Adhesive bonding is widely accepted as the method for joining material, distributing stress, and producing structures that could not otherwise be made. The successful performance of these structures depends upon the ability to control all of the independent steps of the production line.

Wegman and Levi [17] describe the various considerations involved in setting up a satisfactory adhesive bonding shop. A summary of these steps includes:

1. Receiving materials. These materials include adherends, adhesives, and the chemicals and solvents required for cleaning.
2. Knowledge of the fabrication processes for the parts to be bonded. The process by which the individual parts were produced may affect the type of cleaning process which will be required. The use of cutting oils, release agents, or the type of binder used in the manufacture of a casting mold can have an effect upon the selection of a cleaning process and the success of subsequent bonding steps.
3. Mating of parts to be bonded. Some cleaning processes such as acid etching will remove material, while processes such as anodizing and other coating processes will add material. Therefore, in some designs it is important to know how much material was removed or added to allow for a satisfactory glue line. Machined parts should be mated prior to application of adhesive to insure there are no misfits which could cause voids, surface bulges or stress concentration points.
4. Surface preparation. This is often the most critical, complex, and frequently abused step in the bonding sequence.

It is important to remember these factors regarding surface preparation:

1. Know the adherend material, its surface condition and how it was prepared.
2. Use good safety and health practices when using cleaning agents.
3. For wiping parts, only clean white cotton cloths with no sizing or finish or paper towels with little or no organic binders should be used. Never use synthetic materials.
4. Hot solvent washing or vapor degreasing should not be used to clean composite materials or for secondary bonding preparations, unless these materials have been tested and proven to be safe.
5. Train, qualify and requalify personnel who operate the cleaning facility.
6. Check the cleaning line regularly.
7. Cleanliness, vigilance and attention to detail are of primary importance on the job.
8. Don't rely on faith. Know your process, materials, personnel and quality control tests and results at all times.

Another important but often neglected step in processing for adhesive bonding is quality control. Control of the temperature of the solution, control of the drying between immersions and control of the type and flow of rinse waters are all very important. One of the most critical steps requiring control is the rinsing of adherends. McNamara et al. [18] concluded that "the rinsing operation during FPL pre-treatment of aluminum surfaces for bonding is crucial to the success of the bonding operation." Immersion rinse solutions with a $\text{pH} < 3.0$, if allowed to dry on the adherend surface, can lead to catastrophic bond failure. This control of rinsing is required for other treatments as well. McNamara et al. [19] also pointed out that

aging studies on standard and optimized FPL solutions indicate that no significant change in oxide morphology occurs up to very high levels of dissolved aluminum (approximately 2 wt % Al). Long before this level is reached, reaction by-products precipitate from the solution as it cools to room temperature. This may cause rinsing problems. The authors suggest that a specific gravity measurement be used to monitor the useful life of the tank. Shearer [20] recommends the monitoring of wedge test [21] results as the best control of the etch tank. The floating roller peel test [22] can also be used as a quality assurance test to monitor the etch tank [20,23].

Shearer [19] also states that higher than normal etch bath temperature may affect the effectiveness of an etch solution. Other points that should be considered include the health hazards involved, the protection of materials that have been prepared for bonding, the inspection of bonded parts and the development of the process specification.

1.3 Plasma Surface Treatment of Material for Improved Adhesive Bonding

Surface preparation of many of the materials in the preceding chapters to improve adhesive bonding and bond durability has required the use of strong, dangerous, and often hazardous chemicals. A newer surface preparation technology for cleaning surfaces for bonding is atmospheric plasma technology, a technology similar to corona treatment.

“Corona treatment (sometimes referred to as air plasma) is a surface modification technique that uses a low temperature corona discharge plasma to impart changes to the properties of the surface. The corona plasma is generated by the application of a high voltage to sharp electrode tips which form plasma at the ends of the sharp tips” [24]. Corona treatments are limited largely to flat thin surfaces. While the treatment speed can be high, the surface activation is marginal (usually up to 60 dyne/cm). Corona does not remove organic contamination from the surface, exposes an electrical charge, and produces large amounts of ozone which are detrimental to human health and very corrosive to metals.

Another more effective treatment is achieved via atmospheric pressure (air) plasma (APP). “Like corona, atmospheric pressure plasma is the electrical ionization of a gas. The plasma (glow) discharge creates a smooth, undifferentiated cloud of ionized gas with no visible electrical filaments. Unlike corona, plasma is created at a much lower voltage” [25]. APP treatment is one of the most efficient surface treatment processes for cleaning, activating, or coating materials like plastic, metal (such as aluminum and titanium), or glass. APP improves low surface energy levels (22–32 dyne/cm) to as high as achieving complete wettability (72 dyne/cm). High dyne levels generally associated with better adhesion for various adhesives, paints, inks, and coatings. APP activates surfaces by creating functional groups such as carbonyl and hydroxyl groups (with polymer substrates). Atmospheric plasma is

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