ADHESIVES FOR METALS: Theory and Technology

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INDUSTRIAL PRESS INC.

200 Madison Avenue, New York, N.Y. 10016

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Library of Congress Catalog Card Number: 74-107875

ISBN 0-8311-1001-5

Preface

Adhesion theories and practices are continually changing as new resin materials are developed and old materials are improved. With these new developments and improvements, we hope, comes greater understanding.

I have worked with synthetic resins and adhesives for about twenty-five years, and in that time I have been involved in some of the controversy associated with adhesives theory and practice. As my ideas gelled, I finally succumbed to the urge to put them down on the printed page. Since I am not mathematically inclined, I have purposely avoided symbolism in favor of reasoned discussion, hoping that my ideas will be helpful to engineers actually working with adhesives application.

I owe considerable thanks to the Sandia Corporation for allowing me to use data accumulated while working on Sandia developments. Furthermore, this book could not have been written without the cooperation of Sandia typing, editing, and drafting personnel. Many thanks are due, in particular to Jo, Marge, Kathy, and Della, who learned frustration tolerance in the process of deciphering my hieroglyphics; to Edward Dlouhy who did many of the drawings; and to Lee Class who put the final polish on what I hope will be a gem. Finally, many thanks to my friends at Sandia, who, with their diversified scientific skills, helped through our discussions, to keep my thoughts well defined and uncluttered by biased ideas and wishful conclusions.

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Introduction

THE ORIGINS AND HISTORY OF ADHESIVES [1,2]

Man has used adhesives for many centuries. At first he simply learned to use materials found in nature. Mongol bowmen, for example, used adhesives probably made from the hide, hooves, bones, and even the blood of horses in making their laminated-wood bows. But man has always had the urge to imitate, influence, and duplicate nature. Among the first to follow this urge were imaginative, enterprising people known as alchemists, witches, wizards, and magicians. Many did little but inspire some wonderful stories—but some undoubtedly were individuals with genuinely inquiring minds who were not satisfied to let Mother Nature remain unchallenged and were constantly trying to outdo her.

Over the centuries, the old materials were refined and developed to the peak of their utility, but major changes were slow to occur. Some violin makers and cabinet makers of today are still using adhesives that were used in ancient Egypt. To a certain extent, the understanding of the old materials and processes became proprietary knowledge handed down from father to son, with the result that newcomers, finding it difficult to duplicate the ancient arts, were forced to turn to new materials.

The emergence of adhesives technology as a factor in industry took place in Europe in the eighteenth century and in the United States in the nineteenth century. At that time, adhesives were obtained almost entirely from animal and vegetable materials such as hide, hoof, bone, and blood proteins and from tree gums, casein, or starches.

The synthetic resins of today are made up chiefly of atoms of carbon, hydrogen, oxygen, and nitrogen, which are present in the air and in organic matter in virtually unlimited quantities. Silicon and sulfur, both common elements, are used in the silicone resins and the polysulfides, respectively. Other well-known elements such as copper, tin, lead, and titanium are used as catalytic ingredients.

SYNTHETIC RESINS

Synthetics saw the light of day early in the twentieth century with Dr. Baekeland's development of phenolic resins. The phenolic resins—not only the earliest but also the most prolific in terms of offspring developments—proved almost indispensable as ingredients in metal adhesives and in high temperature adhesives and resins for use in aerospace structures.

By itself, phenol formaldehyde is not suitable for use with metals. Not only is it too hard and brittle, but the water that is a by-product of the polymerization reaction interferes with resin adhesion to impermeable adherends such as metals. Phenol formaldehyde was first successfully applied to wood. Wood is a satisfactory adherend in this application; having a low modulus, at least in one direction, it can adapt itself to the hard, brittle resin, and its porous structure facilitates dissipation of the water by-product.

In spite of their original limitations, the phenolic resins proved versatile when they were co-polymerized with various rubbers, acetals, and epoxies, and the age of structural metal adhesives was well under way.

SEALANTS

Materials of another class play an important role in metal fabrication; these are sealants, whose development parallels that of the structural adhesives. The sealants are not normally considered as adhesives, yet in order to function properly they must adhere as well as or better than the structural adhesives, because they must withstand many types of conditions ranging from continuous immersion in all sorts of liquids to exposure to aerospace conditions and heat of atmospheric reentry. Under such conditions the sealants may be used either by themselves or as a protection for the structural adhesive (for example, edge sealants for bonded aircraft panels).

At one time, sealants were not required to exhibit great strength, but this is no longer true. Recent developments in polyurethane castable rubbers and silicone sealants have resulted in materials with tensile, peel, and tear strengths which equal and sometimes exceed those of the so-called structural adhesives. Thus under the proper conditions these materials can also be used in structural applications, especially where vibration damping and stress relief are required.

The polysulfide rubber sealants were the first to achieve wide use. Because of their resistance to petroleum fuels, they were first used as fuel tank sealants in aircraft, but have since found wider application in the automobile and building industries. During a search for information concerning the long-term aging properties of polysulfides, I learned from the Douglas Aircraft Company that the history of polysulfide sealants parallels that of the DC-3 aeroplane, in that polysulfide sealants were used in its fuel tanks. First built in 1936, the DC-3 is still in use all over the world.

SERVICE LIFE

The history of the polysulfide sealants points out a universal problem in the field of synthetic resins: The basic polymers and subsequent commercial formulations are continuously in the process of being changed with a view to improvement. Thus the polysulfide formulation which was used in the first DC-3 is no longer in existence. As new and better formulations and specifications are developed, the old are discarded. The result is that a manufacturer may want to make a reliable, long-lasting product, resistant to many environmental conditions, but finds himself handicapped by a lack of long-term aging data on present formulations, which are supposedly superior to older ones. To a certain extent the manufacturer must proceed on faith, and hope that time will resolve the dilemma in his favor.

Unfortunately, the task of preparing a program to determine the effects of aging on a given material—where one must minimize the number of variables in order to maintain a workable plan and at the same time retain enough significant variables so that the results are worthwhile—becomes so involved that many a plan dies from the inertia which increases in proportion to the plan's magnitude.

ADHESIVE/ADHEREND COMPLEX

The property of adhesives and sealants that makes them unique is that they have no identity by themselves. They are adhesives and sealants only to the extent that they bond to or seal some other material or materials.

The usual materials specialist is concerned with the bulk properties of a specific material; that is, modulus, temperature coefficients, density, and so on. His concern with surface properties is usually limited to those which affect the bulk properties, for example, *crazing, corrosion initiation,* stress cracking fracture, permeability. Thus his field of interest is essentially an isolated entity.

Materials Engineer

The adhesive materials engineer, however, faces a much more complex situation. He may be dealing with a material which is available in the uncured state as a liquid or without solvent; a solid which must be heated to a liquid before being used; or a solid film which requires heat and pressure to achieve the fluid state necessary for successful application. In each case, he must know and correctly specify the time, temperature, pressure, and viscosity relationship and must evaluate the ability of any one of these materials to wet and properly attach itself to a wide variety of adherends. Also, he must determine the proper surface treatment of the adherend necessary for achieving wettability and subsequent acceptable level of bond strength. The bulk properties of the adherends must be known, since if these are not similar they must be analyzed together with the properties of the adhesive material, to insure that the resulting stresses do not far exceed any possible bond strength or adherend strength. When all of these problems have been resolved, the adhesive materials engineer still has to be concerned with the physical and chemical stability of the bonded assembly with relation to its intended environment.

Materials (such as Teflon®) which were until recently considered unbondable, eventually yielded to the persistent efforts of the laboratory worker and today are easily bonded. Adhesives which at one time were limited to use in protected internal environments with limited temperature fluctuations have now been improved to the extent that they can successfully withstand temperature extremes ranging from −240C (−400F) to 260C (500F) operationally and to 816C (1500F) *for limited periods of time.* Resistance to aqueous and organic solvents has been similarly improved.

Advanced Development

A measure of the success with which synthetic adhesives and sealants have kept up with the times is that when the United States agreed to go ahead with the construction of the supersonic transport with its 260C (500F) skin temperatures, structural adhesives based on polyimide and polybenzimidazole resins were already available with thousands of hours of evaluation at 260C (500F). Fluorinated silicone materials had already been developed as fuel-resistant high-temperature sealants, and room temperature curing (RTV) silicone sealants and adhesives were ready for use at temperatures up to 316C (600F).

The future of these materials is particularly bright when one considers that the synthetic resin industry is only about thirty years old and seems to be accelerating its output rather than leveling out at a plateau. Recent developments such as polysulfones, polyphenylene oxides, borosilanes, polyquinoxylenes, and others emphasize the fact that the possible combinations and permutations of molecular structures are practically unlimited. Future possibilities are further enhanced by a synthetic resins industry which has the imagination to anticipate future requirements and the faith to invest in the work necessary to achieve them.

ADVANTAGES AND DISADVANTAGES OF ADHESIVE BONDS

Advantages:

The chief advantages of an adhesive bonded structure may be summarized as follows:

1. Possibly, the principal advantage of an adhesive bond is that the adhesive fastens to the entire bonded surface, thereby distributing the load more or less evenly (depending on the modulus of the adhesive) and thus avoiding highly localized stress. A nail driven into wood may crack the wood; a rivet in thin-gauge metal may initiate fatigue cracking. Use of adhesives overcomes these problems.
2. In the manufacture of aircraft and automobiles, adhesive bonding may be used to advantage instead of riveting and welding, since (a) riveted structures add weight and drag, (b) rivets and welds are unsightly and difficult to conceal, and (c) holes and welds may facilitate the start of corrosion. Adhesives in film form are particularly desirable for this type of application, since they facilitate close control of weight distribution and total weight of adhesive used.
3. In the presence of vibration, a bonded structure usually has a longer life than a riveted assembly. In addition, because adhesives of different moduli are available, damaging resonant frequencies can be modified or even eliminated by proper analysis and selection of the adhesive.

4. A bonded joint is a sealed joint. Aircraft wing-tanks and aluminum, honeycomb panels are sealed in this manner. This saves considerable weight and simplifies construction.
5. Adhesives are usually electrical insulating materials. When different metals are bonded together, this minimizes the possibility of electrolytic corrosion. When positive separation in the form of glass fiber cloth is incorporated in the bond, an electrically insulating layer becomes a part of the bonded assembly. Conversely, silver-filled adhesives make possible electrically conductive bonds between adherends.
6. Adherends with different coefficients of expansion can be bonded with low modulus or rubbery adhesives. Glass-to-metal and ceramic-to-metal joints can be made without stressing the glass or the ceramic. This makes it possible to bond ablative shields to missile structural shells. Otherwise it would be necessary to devise elaborate mechanical fasteners which would allow the shield to expand independently of the case and which would not conduct external heat to the structural case.
7. Adhesive sealants can be cured at comparatively low temperatures and do not melt on subsequent reheating. They are often used in preference to soldering, brazing, or welding since the high temperatures associated with the latter processes sometimes warp structures, crack glass-to-metal seals, or damage heat sensitive components.

Disadvantages:

1. The main disadvantage is that an adhesive bond, unlike a riveted joint, does not permit visual examination of the bond area. The continuity or lack of continuity in the bond cannot be seen, and evaluation must be destructive. Nondestructive test methods such as the various ultrasonic techniques can indicate only a complete lack of bonding, not the degree of bonding. It is sometimes possible to test bonded items to a certain percentage of ultimate strength if the size and shape are convenient.
2. Surface cleanliness and good process control are important in any bonding process. This requires considerable equipment, depending on the critical nature of the application.
3. Holding fixtures, presses, ovens and autoclaves, not usually

needed for other fastening methods, are necessities for adhesive bonding.

4. At present, adhesives cannot be used where extended life above 316C (600F) is a requirement.

TEMPERATURE DESIGNATION FOR ADHESIVE BONDING

The trend toward the centigrade–metric system is gaining headway in the United States. The American Society for Testing and Materials (ASTM) has issued recommendations for conversion to the metric system and for manner of presentation. These recommendations are contained in the manual, *Recommendation on Form of ASTM Standards*, January 1964, and in the pamphlet, *Recommended Procedures for Metric Conversion in ASTM Standards*, March 1966.

As international travel, communication, and trade increase and the precarious goal of worldwide unity comes nearer to reality, metric unification becomes inevitable and should be encouraged. Accordingly, in this book temperatures will be expressed in centigrade or Celsius units with Fahrenheit degrees in parentheses. However, since it would not be useful to give the exact Fahrenheit equivalent to the nearest decimal, the Fahrenheit temperatures will be rounded off to the nearest whole degree. Temperature ranges will be similarly treated.

NOMENCLATURE

Like other industries, the adhesives industry has developed its own nomenclature. ASTM defines about two hundred terms in the 1967 *Book of Standards.*

A few of the more commonly used terms are listed here:

Adherend—A body which is held to another body by an adhesive.

Adhesion—The holding together of two surfaces by interfacial forces which may consist of valence forces or interlocking action, or both.

Adhesive—A substance capable of holding materials together by surface attachment.

Assembly—A group of materials or parts, including adhesive, which has been placed together for bonding or which has been bonded together.

Binder—A component of an adhesive composition which is primarily responsible for the adhesive forces holding two bodies together.

Bond strength—The unit load applied in tension, compression, flexure, peel, impact, cleavage, or shear required to break an adhesive assembly with failure occurring in or near the plane of the bond.

Catalyst—A substance which markedly speeds up the cure of an adhesive when added in minor quantity as compared to the amounts of the primary reactants.

Consistency—That property of a liquid adhesive by virtue of which it tends to resist deformation.

Creep—The dimensional change with time of a material under load, following the initial instantaneous elastic or rapid deformation. Creep at room temperature is something called *cold flow.*

Diluent—An ingredient usually added to an adhesive to reduce the concentration of bonding materials.

Elastomer—A material which at room temperature can be stretched repeatedly to at least twice its original length and, upon immediate release of the stress, will return with force to its approximate original length.

Flow—Movement of an adhesive during the bonding process, before the adhesive is set.

Failure, adhesive—Rupture of an adhesive bond, such that the plane of separation appears to be at the adhesive-adherend interface.

Failure, cohesive—Rupture of an adhesive bond, such that the separation appears to be within the adhesive.

Film, adhesive-supported—An adhesive supplied in sheet or film form with an incorporated carrier that remains in the bond when the adhesive is applied and used.

Film, adhesive-unsupported—An adhesive supplied in sheet or film form without an incorporated carrier.

Hardener—(1) A substance or mixture of substances added to an adhesive to promote or control the curing reaction by taking part in it. (2) A substance added to control the degree of hardness of the cured film.

Inhibitor—A substance which slows down chemical reaction, sometimes used in certain types of adhesives to prolong storage or working life.

Joint—The location at which two adherends are held together with a layer of adhesive.

Joint, starved—A joint which has an insufficient amount of adhesive to produce a satisfactory bond.

Modifier—Any chemically inert ingredient added to an adhesive formulation that changes its properties.

Permanence—The resistance of an adhesive bond to deteriorating influences.

Plasticizer—A material incorporated in an adhesive to increase its flexibility, workability, or distensibility. The addition of the plasticizer may cause a reduction in melt viscosity, lower the temperature of the second-order transition, or lower the elastic modulus of the solidified adhesive.

Primer—A coating applied to a surface, prior to the application of an adhesive, to improve the performance of the bond.

Shelf life—The period of time during which a packaged adhesive can be stored under specified temperature conditions and remain suitable for use.

Storage life—Same as shelf life.

Temperature, curing—The temperature to which an adhesive or an assembly is subjected to cure the adhesive.

Temperature, drying—The temperature to which an adhesive on an adherend or in an assembly, or the assembly itself, is subjected to dry the adhesive.

Thermoplastic—A material which will repeatedly soften when heated and harden when cooled.

Thermosetting—Having the property of undergoing a chemical reaction by the action of heat, catalysts, ultraviolet light, etc., leading to a relatively infusible state.

Viscosity—The ratio of the shear-stress existing between laminae of moving fluid and the rate-of-shear between these laminae.

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