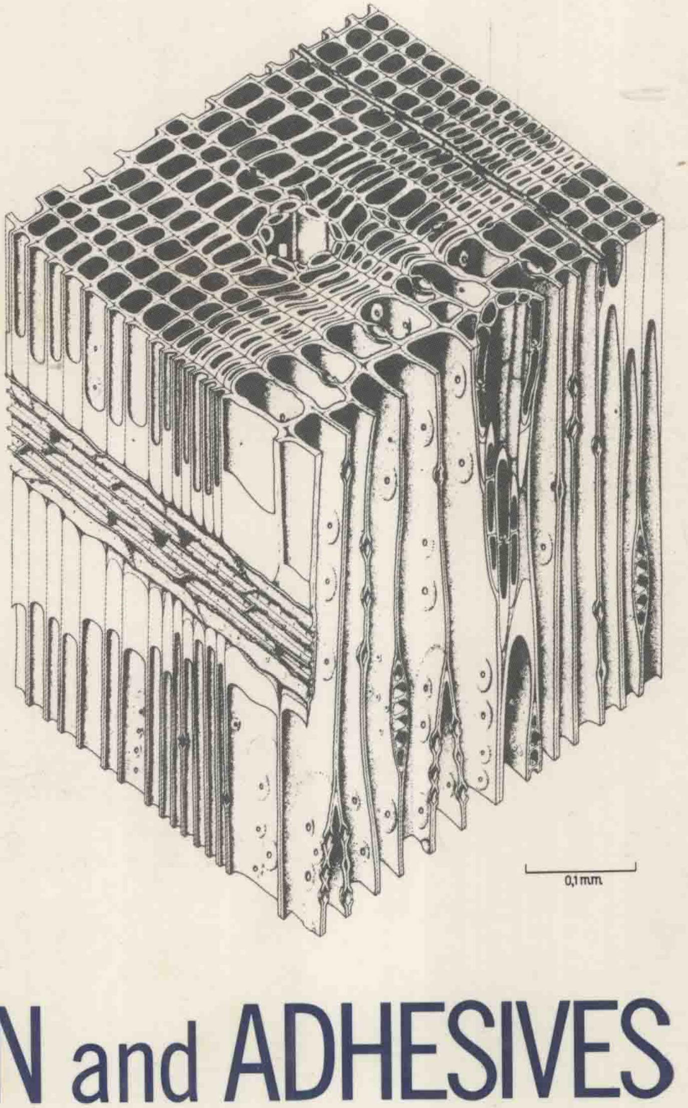
volume 7



Treatise on ADHESION and ADHESIVES

edited by

J. Dean Minford

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Consultant

Hilton Head Island, South Carolina

Marcel Dekker, Inc. New York • Basel • Hong Kong

ISBN 0-8247-8112-0

This book is printed on acid-free paper.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

Preface

As the new editor of the Treatise on Adhesion and Adhesives series from Marcel Dekker, Inc., I feel a considerable responsibility to maintain the high quality of subject matter that had been established by Dr. Robert L. Patrick, who originated the series back in 1967. As a contributor to Volumes 3 and 5, I had the opportunity to know Bob quite well and counted him among my very best of friends in the world of science. As a result of my work for many years at Alcoa studying the relative durability responses of adhesives with many adherends, Bob asked me to contribute one of the five lectures to be delivered at the first Annual Meeting of the Adhesion Society, which he helped organize. One of my fondest recollections about him will always be his obvious unbounded enthusiasm for his favorite field of adhesion science. Every encounter, whether for business or pleasure, always led to a fascinating discourse on some new phase of the subject that he had most recently adopted for study. While it was not always easy to be able to interject your own occasional inspirations into the discussion, with persistence, you could prevail and would receive a fair hearing.

When Bob came to the University of Pittsburgh to organize their Center for Adhesion Science, I had my best opportunities to visit with him more frequently because of my residence at the nearby Alcoa Research Laboratories just outside of metropolitan Pittsburgh. I then learned what a warm and friendly personality resided behind this buzzsaw of surface activity toward the study of adhesion science. It was at that time that the matter came up about the possibility of my helping him on his projects after my retirement from active laboratory pursuits at Alcoa. Bob's relatively sudden onset of illness ended our further discussion of this matter as he sought to fight what proved to be a terminal illness. Bob had already started to gather various technical contributions for Volume 6 of the series, but had only been able to complete selection of half the necessary authors before his illness prevented further progress.

The publisher asked me to complete the volume; however, when two of the authors Bob had chosen expressed a desire to complete the volume as a special memorial to him, I was most pleased to accede to their wishes. I would like to express my personal appreciation to Drs. G. P. Anderson and K. L. DeVries from Morton Thiokol and the University of Utah for their dedicated and successful effort in completing Volume 6 in Bob's honor. That volume can also be considered somewhat of a memorial for Garron Anderson, who was later the victim of a most unfortunate accident while hunting in his beloved Utah hills.

I would also like to extend my sincere appreciation to Dr. M. L. Williams of the University of Pittsburgh faculty, who composed a wonderful memorial of immense insight into the nature of his former associate. It is recommended that any reader of the past volumes read the memorial pages by Max in Volume 6. It is like listening to a recitation of fond recollections about Bob interspersed with episodic repartee of considerable humor. The stage is set for those of us who were fortunate to see and hear Bob speak similarly over the years about a multitude of subjects.

Volume 7 resulted from my idea that there might be an additional benefit to be gained from having a special theme for this volume, and that such a theme should lead to the selection of certain subjects and authors whose extensive survey work in these areas of adhesion science could be best described as state-of-the-art presentations. I also thought that a very wide range of individuals connected with scientific and commercial projects relating to bonding would be served by choosing the central theme of how to bond certain adherends and classes of adherends with particular commercial interest. The contributors to the volume were asked to conduct very extensive reviews of virtually all the significant investigations conducted over the years with respect to the joining of the adherend of their particular expertise.

It is apropos from a historical viewpoint to offer the bonding of wood as an adherend in Chapter 1. Undoubtedly, no other adherend material can match the length of time or number of investigations that have gone into studying the bonding of wood in all its multitudinous forms. Similarly, probably no single research institution has been more prolific over the last century in its studies of this subject than the U.S. Forest Products Laboratory in

Madison, Wisconsin. Accordingly, former Director of the Laboratory Bob Gillespie and Bryan River were most generous in accepting my challenge so that there would finally be a published comprehensive review of all that we know today about bonding wood and its derivative materials. They have been joined by Charles Vick who, by recent transfer from an affiliate laboratory, added a long-term expertise in complementary areas.

Although of much more recent origin than wood, there is another class of adherend materials that found its earliest interest in a natural product, i.e., natural rubber. Today, modern technology demands products that can be derived from the adhesive bonding of broad classes of materials that we generally refer to as elastomers and rubbers. After reading several of the recent reports by Ted Symes and David Oldfield about this general subject matter, I deduced they were the authorities that I wanted for this volume. Their comprehensive review in Chapter 2 explores all the current bonding theories, and shows how these concepts can be employed in the production of reliable commercial products with the bond integrity to last throughout the working life required. Virtually no known elastomer has been omitted.

The advancements in organic chemistry since Wohler first demonstrated that a natural product like urea could be synthesized in the laboratory have been almost beyond comprehension. Out of this advancement has come the development of a new industry devoted to the goal of theorizing and then producing hundreds of new materials that never existed in nature. All these new products have been generally categorized as being "plastics," and their joining by adhesive bonding is the subject of Chapter 3. At the Alcoa Laboratories, I often was confronted with the need to bond aluminum adherends to plastics, and the best source for general and specific recommendations was generally found at the laboratories of 3M's Adhesives, Coatings, and Sealers Division in St. Paul, Minnesota. It was most gratifying to have Dr. Al Pocius and his colleagues, Drs. Waid and Hartshorn, agree to develop Chapter 3, on adhesives in the joining of plastics. They have included an extensive literature search that complements their in-depth description of: (1) criteria for bonding, (2) surface science and pretreatments, and (3) the most often recommended practices for joining 22 of the most often used plastic adherends.

Finally, the last chapter changes the focus to another material present in nature, but requiring considerable processing and alloying with other metals: titanium. It was not too many years ago that titanium was considered a rather exotic and high-priced metal whose applications would be considered rare compared with those of steel and aluminum. This is certainly far from the situation in modern manufacturing, where potential uses abound for a metal with the unique properties of titanium. While its use in high-speed airplanes and space vehicles might be reason enough to need to know how to bond titanium effectively, numerous additional applications abound today in the chemical, petrochemical, process engineering, nuclear and power generation industries, defense systems, and medical fields. In the forefront of developing bonding technology for titanium has been the Martin Marietta Laboratories of Baltimore, Maryland, and I feel very fortunate to offer a comprehensive chapter on the subject by Kent Shaffer, Howard Clearfield, and John Ahearn of that laboratory. I believe the reader will be amazed by the depth and range of studies provided.

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Wood as an Adherend

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I. INTRODUCTION

Wood is a porous, permeable, hygroscopic, orthotropic, biological composite material of extreme chemical diversity and physical intricacy. Table 1.1 provides an overview of the may variables, including wood variables, that bear on the bonding and performance of wood in wood joints and wood-based materials. Of particular note is the fact that wood properties vary between species, between trees within a species, and even within a tree. Variability within a single species alone is enough to significantly challenge an adhesive to perform consistently and satisfactorily. In this chapter, we have attempted to describe wood and to explore how this complex biological material interacts with adhesives to affect the bonding process and the quality of the bonded joint or material. First, we will present a short review of the history connecting wood and adhesives.

The gluing of wood is ancient. No one knows where or when it began. We do know that early civilizations used mud, plant

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Table 1.1 Wood Bonding Variables

Resin	Wood	Process	Service
Type	Species	Adhesive spread	Strength
Viscosity	Species gravity	Adhesive distribution	Shear modulus
Tack	Moisture content	Relative humidity	Modulus of elasticity
Mole ratio of reactants	Plane of cut: radial, tangential, transverse, mix	Temperature	Creep
Filler	Heartwood versus sapwood	Open assembly time	Percentage of wood failure
Total solids	Juvenile versus mature wood	Closed assembly time	Failure type
Molecular weight distribution	Earlywood versus reaction wood	Pressure	Adhesive penetration
Solvent system	Grain angle	Gas-through	Dry versus wet
Age	Porosity	Press time	Temperature
pH	Surface roughness	Pretreatments	Finishing
Buffering	Drying damage	Posttreatments	Heat resistance
Cure rate	Machining damage	Adherend temperature	Hydrolysis resistance
Catalyst	Dirt		Swell—shrink resistance
Mixing	Contaminants		Ultraviolet resistance
	Chemical surface		Biological resistance: fungi, bacteria, insects, marine organisms
	Extractives		
	pH		
	Buffering capacity		

resins, beeswax, bitumen, and other naturally occurring substances for glue. Pottery and weapons bonded with resin have been discovered in grave sites almost 6000 years old (Stumbo 1965). Evidence has been found that lime-based plaster was used for bonding stone blades as long as 12,000 B.C. (Bower 1988). The use of fire for cooking undoubtedly led to the discovery that plant and animal proteins make sticky materials. Many of these naturally occurring materials were available to ancient peoples, including lime, egg white, and flour paste. With these primitive materials, wood bonding developed into a sophisticated art form. A love of luxury and a delight in beautiful surroundings evolved in the ruling families of ancient Egypt. They found wood to be an ideal material from which to fashion decorative furniture. But decorative woods were not abundant in that land of little rain. Ebony, teak, and rosewood were imported, no doubt at great expense, prompting craftsmen to learn to cut thin veneers to stretch supplies. Wall carvings in Thebes, dated about 1500 B.C., show thin wood veneers being glued to a plank of wood. A glue pot and brush, with the pot warming over a fire, suggest the glue was a hot animal glue (Knight and Wulpi 1927, referencing Wilkinson 1878). These veneers were glued to a core of ordinary material, which added strength and durability while conserving the supply of decorative but scarce and costly woods. Plywood, made by gluing together thin sheets or plies, was also well known. The people made table tops, chests, beds, and other furniture by gluing thin veneers to suitable core material. The decoration of furniture with inlays of precious stones, gold, and ivory, as well as the veneers of rare woods, was developed to a high artistic level in Egypt. We can appreciate the result of the Egyptians' gluing skill, for many beautifully veneered and inlaid wooden artifacts recovered from the tombs of the Pharaohs, and from other archeological excavations, survive to this day.

Undoubtedly the first articles of furniture were fashioned in one piece. Later, various parts were held together by leather thongs or wooden pegs. But the marriage of wooden parts with glued structural joints occurred at least as early as the eighth century B.C. An ornately decorated and intricately formed table recently discovered in a tomb, possibly that of the renowned King Midas, had been assembled with dowels and mortise and tenons joints (Simpson 1983). Although the table had failed under a heavy load of bronze pots, it demonstrates that artisans had discovered the structural advantages of adhesive-bonded joints for furniture (Darrow 1930).

After the Egyptian period, veneering continued as an art form in Greece and later in Rome. The ancient Greeks described a recipe for casein glue not unlike the recipes of the early twentieth century. The art suffered a setback with the fall of Rome and the loss of interest in decorative arts. Only traces of the veneering art from this period can be found today.

Interest in gluing rekindled during the Renaissance. From the fifteenth to the middle of the nineteenth century, the art of veneering and development of intricate glued structural joints led to the creation of magnificent furniture and architectural woodwork in Italy, France, England, Holland, and Flanders, and finally in the United States. Distinctive periods of styling were known by the names of ruling sovereigns or patrons of the arts—de Medici, Elizabethan, Victorian, Queen Anne, and Louis XIV, XV, and XVI. Great master cabinetmakers rose to prominence one after another, and styles were distinguished by their names—Adam, Hepplewhite, Chippendale, and Sheraton. All the great masters worked with animal glue and, to lesser extent, with fish and casein glues, to create the forms of their imaginations in wood. The lasting grace and beauty of their creations are, in no small measure, a tribute to the performance of these glues (Pollen).

Other glues from natural sources were neither highly developed nor widely used until after the beginning of the twentieth century. Then, F. G. Perkins developed a vegetable glue (actually tapioca starch) from the roots of the cassava plant (Perkins 1912). This glue became so successful for cold pressing furniture parts, plywood, veneering, and other wood applications that the Perkins Company sold 230×10^6 lb of it in 1930 (Darrow 1930). The use of animal blood as a glue goes back many centuries—Aztec Indians mixed blood with mortar for building construction. Two developments spurred its widespread use in modern times. One was the discovery in about 1910 that blood could be dried in a soluble form, making it easier to preserve and handle. The other was the urgent need for a water-resistant glue for plywood for aircraft construction during World War I (Lambuth 1977). The war also spurred the development of water-resistant casein glues for the manufacture of laminated wood aircraft propellers (Truax 1930). A water-resistant, soybean—protein glue was possibly the last major development in glues of natural origin (as compared to synthetic resin adhesives) (Johnson 1923, Laucks and Davidson 1928). It became the major glue for interior softwood plywood with production of 34×10^6 lb annually in the 1930s. Combinations of blood albumin and soybean protein took advantage of the best properties of each material (Lambuth 1977); these combinations were used extensively for plywood until displaced by synthetic resins in the 1950s.

Until about 1930, the term glue accurately described the materials used to bond wood because all materials were derived from naturally occurring substances such as casein and collagen. These materials, their processing and use, and their performance with different woods were carefully described by T. R. Truax (1929). At that time, furniture was the principal product manufactured by wood bonding. Softwood plywood was in its infancy, and it was suitable for only interior use because of the poor water-resistance of the vegetable-starch glues used in its manufacture.

With the development of synthetic resins, the term adhesive became a more appropriate word for the broad range of bonding agents that included synthetic resins as well as glues. The first important wood product made with the new synthetic resin adhesives was water-resistant plywood for airplane construction. But the impact of synthetic resin adhesives was not really felt until the early 1930s, when urea- and phenol-formaldehyde-bonded plywood began to be used in furniture and housing. World War II intensified the demand for water-resistant or waterproof bonded-wood products. During this time, adhesives based on the synthetic thermosetting resins—urea-formaldehyde, melamine-formaldehyde, phenol-formaldehyde, and resorcinol-formaldehyde—began to replace adhesives from natural resources. The emergence of commercial synthetic resin adhesives greatly expanded the variety of useful wood products that could be manufactured. In the early 1950s, adhesives based on thermoplastic vinyl acetate resin began to replace animal glue in furniture assembly. Two-polymer adhesives combining thermosetting and thermoplastic resins, such as polyvinyl-acetal/phenol-formaldehyde and nitrile rubber/phenol-formaldehyde resins, were developed that had the capability of bonding wood to metal. By the 1950s, the variety and number of synthetic resin adhesives and bonded-wood products mushroomed.

Practically all branches of the wood-using industry now use adhesives (White 1979). Adhesives and the industries they have spawned are responsible for new or improved products, dramatic improvements in the utilization of forest and mill residues, and conservation of timber supplies. New industries such as plywood, particleboard, flakeboard, and laminated-veneer lumber owe their very existence to synthetic resin adhesives. In the United States alone, these industries, which are entirely dependent on adhesives, annually produce:

21×10^9 ft^2 of structural panels (3/8-in.-thick basis).
10×10^9 ft^2 of nonstructural panels (3/8-in.-thick basis), excluding hardwood plywood.
104×10^6 ft^2 laminated-veneer lumber (1-1/2-in.-thick basis).

The United States also imports 3.1×10^9 ft^2 (surface measure) of hardwood and softwood plywood.

The development of these and other bonded-wood products and the growth of related industries over the years have resulted in