

Adhesives from Renewable Resources

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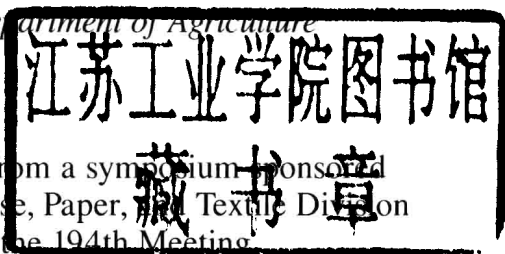
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Foreword

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

Preface

THE OBJECTIVE OF THIS SYMPOSIUM was to include research on a broad range of natural products directed to a wide variety of bonding applications. The speakers described research on adhesive polymers derived from lignins, tannins, carbohydrates, terpenes, and proteins for applications as diverse as tire-cord bonding and eye surgery.

Byproducts of the forest products industry are potentially primary sources of natural resource-based adhesives. Because this industry is both a producer of huge tonnages of residues and a major consumer of adhesives, this book focuses on adhesives from renewable resources derived from trees. Composites made from wood will remain the primary materials used for the construction of homes and their furnishings for the foreseeable future.

The date of the symposium on which this book is based marked the 15th anniversary of the severe petroleum shortage of 1973–1974. Much of the research presented in this volume was begun in the early 1970s in response to shortages of petroleum-based adhesives for the forest products industry when the nation was in the midst of a record-setting demand for housing materials. Left with this indelible memory, the forest products industry has supported the development of adhesives from renewable resources.

The chapters presented in this book show that new alternatives based on renewable resources will be available should supplies of resins derived from petrochemicals become inadequate again. Outstanding opportunities for the development of high-value specialty polymers are highlighted by work presented here on polymers derived from mollusks.

This book is the product of the efforts of chemists from around the world. Our thanks go first to the authors who so kindly contributed papers and patiently responded to our requests. We thank the American Chemical Society for providing a venue for the symposium that made this book possible. We also thank the clerical support staff of the U.S. Department of Agriculture, Forest Service at both the Southern Forest Experiment Station and the Forest Products Laboratory, who tirelessly worked to make this a meaningful enterprise.

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Chapter 1

Adhesives from Renewable Resources

Historical Perspective and Wood Industry Needs

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The wood products industry has a long and successful history of utilizing adhesives based on renewable resources. Their performance was adequate to see us through World War II and beyond. But the tremendous postwar expansion in the petrochemical industry provided compounds for synthetic resin adhesives so inexpensively, they steadily displaced natural adhesives. When embargo threatened key petrochemicals in 1973, their availability dropped and prices increased abruptly. Industry reacted with an immediate partial return to natural adhesives. As oil's availability improved and prices became more competitive, synthetic resin adhesives again became the industry standard. With over 70% of all wood products now bonded, industry is concerned about future sources of adhesives in the event that oil supplies are again disrupted by world events. There is strong support for research into adhesives based on renewable resources with emphasis on: 1) Phenol, methanol, urea, and resorcinol-acting compounds; 2) copolymeric adhesives involving synthetic resins and natural polymers; 3) new adhesive mechanisms and substrate treatments; 4) greater exterior durability for animal and vegetable protein adhesives.

From the days of early Egyptian artisans until the relatively recent past, the woodworking industry was entirely dependent on natural adhesives for all forms of bonded joinery. These applications were then largely preempted by low-cost, durable synthetic adhesive polymers developed from petrochemicals. Since the volume and utility of bonded wood products have greatly expanded and the continuing availability of synthetic adhesives is now somewhat uncertain, more

thorough research into natural adhesive performance and resources is clearly indicated. This overview chapter attempts to project wood industry needs and suggests appropriate areas for investigation.

History

There is a 58-year-old reference that gives a fairly clear picture of the wood-working industry's adhesive choices from, say, the Industrial Revolution in the mid-1700's until about 1930. The 1929 U.S. Department of Agriculture Bulletin by T. R. Truax entitled "The Gluing of Wood" lists the five classes of adhesives used most in woodworking during that long timespan. These included animal glues, liquid glues, casein and vegetable protein glues, starch glues, and blood albumin glues. Liquid glues were described as a lower strength variety of fish or animal glue that had been stabilized with acid for long-term storage in ready-to-use form. Passing reference was also made to a number of other "adhesive substances" such as sodium silicate, mucilage, pastes, rubber cements, phenol-aldehyde compounds, asphalts, gums, and shellacs that were used occasionally for wood bonding at the time.

Since there were really no other options, the chemistry and application of these naturally derived polymers evolved to a fine art that was summarized occasionally in such publications as the one mentioned. Fully exterior durable adhesives simply did not exist at that time. However, certain natural glues such as alkaline-dispersed casein and blood adhesives did develop a significant degree of water resistance. With adequate surface protection, they could be made to serve exterior purposes on an intermittent basis. This was the state of adhesive technology going into World War I. It was at that point that an urgent need arose for durable wood glues to bond wood laminations into aircraft propeller stock and other wooden elements into the panels and frames of the planes themselves. In the absence of better alternatives, both blood and casein glues were further improved in durability by the alteration of their proteins with various chemical denaturants and by the application of heat during cure. In this form, protein glues served the Allied war effort extremely well, while laying the groundwork for the advanced blood and casein glue technology of later years.

The Second World War saw the extensive use of alkaline-dispersed soybean and blood glues in plywood for all kinds of construction, packaging, and transportation uses. Thus, both vegetable and animal protein glues contributed heavily to wartime logistic successes. During this crisis, with petroleum in critically short supply, a truly exterior blood-based adhesive was developed involving the reaction of alkaline-dispersed soluble blood with cresylic acids. Plywood bonded with this adhesive was still performing well in unprotected outside locations a generation after it was made.

From about 1930 to the present, casein glues have been used successfully for bonding high-strength softwood lumber into glued laminated beams and arches for interior or covered exterior service. Even earlier, until perhaps 1900, casein

glues were used to laminate simpler structural members. Because of their very tolerant assembly properties and strong, gap-filling gluelines, these glues were particularly well suited to this heavy structural application and also to the end grain joinery of millwork.

Animal and starch glues, especially because of their low color and ease of application on complex joint surfaces, were the adhesives of choice in the furniture and cabinet industries from colonial days until the advent of synthetic emulsion adhesives after World War II. Service conditions were limited to dry interior applications, of course. Leaving a chair out in the rain meant dismantling and regluing.

These are just a few of the examples that can be cited with respect to the historical and comparatively recent uses of natural adhesives by the woodworking industry, hence, their familiarity.

Advent of Synthetics

As a result of successfully meeting the challenge of World War II, large oil-refining and petrochemical industries were in place, each with substantial idle capacity, just after the war. The economic pressure to develop new outlets for this productive capacity was tremendous. The synthetic resin and plastics industries as we know them today appear to have been actually created at that time by this pressure. True, resorcinol-formaldehyde resins for bonding white oak into minesweeper frames and birch veneer into helicopter blades were developed during the war to meet national emergencies, but on the basis that cost was no object. It's also true that phenol-formaldehyde resins, initially as dried films on paper and later as liquid resin syrups for adhesive formulating, had been known since the early 1930's. However, the cost of the chemical raw materials to make these synthetic resins was sufficiently high during that period to effectively limit their uses to specialty or military applications.

This situation changed abruptly with the postwar availability of relatively low-cost, high-volume petrochemicals. It was already known that phenolic resin adhesives set a standard of performance for exterior durability that could not be reasonably matched with natural adhesives of any existing type. This fact represented a strong stimulus for commercial research to optimize the performance and extend the applications of phenolic resins. It only remained for the prices of phenol, resorcinol, and formaldehyde to become low enough for phenolic and phenol-resorcinol resins to take over large segments of the bonded wood market. This occurred between 1945 and about 1950. The accompanying Table I of resin production volumes from 1942 through 1959, adapted from the 1962 edition of Irving Skeist's "Handbook of Adhesives," illustrates this rapid growth clearly. By 1978, the annual consumption of phenolic, urea, and vinyl adhesives for all purposes had each passed the billion-pound level.

Initially, only the exterior-bonded product markets fell to the synthetics. Glued products of interior or intermediate durability continued to be largely

the domain of natural adhesives (mainly soybean, casein, and blood) on the basis of their very fast hot-press times or cold-press capability until the early 1960's. At that point, the prices of commodity petrochemicals became so low under worldwide competitive pressures that a compelling case could be made for using exterior synthetic resin adhesives to bond essentially all structural wood products, both exterior and interior. For example, it became cheaper and simpler to purchase additional hot presses in order to reach the plywood production capacity offered until then only by the faster curing protein glues. With this change, the conversion to synthetic resin adhesives was nearly complete.

Table I. Principal Synthetic Resins Produced for Adhesives,
1942-1959¹
(millions of pounds)

Year	Phenolics	Vinyls	Urea and Melamine Types	Total
1942	2.6	1.5	—	4.1
1943	12.7	10.0	—	22.7
1944	26.3	15.0	27.1	68.4
1945	22.0	13.0	30.4	65.4
1946	22.3	16.9	37.5	76.7
1947	31.9	10.0	45.6	87.5
1948	22.3	10.0	50.0	82.3
1949	28.6	11.9	40.8	81.3
1950	31.5	15.5	85.6	132.6
1951	41.9	22.8	78.7	143.4
1952	42.4	17.8	79.8	140.0
1953	106.6	26.9	63.5	197.0
1954	109.6	29.0	86.2	224.8
1955	166.7	37.7	106.7	311.1
1956	169.1	43.9	115.2	328.2
1957	183.4	46.7	107.8	337.9
1958	162.0	52.1	113.2	327.0
1959 (Prelim.)	209.6	59.5	134.1	403.2

¹Excludes laminating. Source: U.S. Tariff Commission statistics.

A similar story of technical development, raw material cost reduction, and adhesive optimization can also be told for the amino resins, the urea and melamine polymers. Especially because of their versatile hot- and cold-curing capabilities, this development also led to the widespread replacement of natural adhesives. The rapid postwar growth of amino resins, along with phenolics

and vinyls, shows plainly in the Tariff Commission figures for annual resin production. Since the initial use of urea adhesives for plywood in 1937, entire new industries have arisen. The commodity manufacture of particleboard and medium density fiberboard is a familiar example.

Thus, the picture emerges of a multifaceted wood products industry founded largely on natural adhesives but successfully weaned onto synthetic resins by a combination of low material costs and formerly unattainable performance properties. As a result of this improved performance, the development of other useful bonded wood products was heavily stimulated.

Threat to Supply

The woodworking industry, now converted almost wholly to synthetics, grew and prospered for a decade between 1963 to 1973. Then, the worldwide crude oil crisis abruptly forced petrochemical suppliers to place their products on allocation. Whether the shortage was real or contrived, this interruption of access to low-cost, seemingly endless raw material supplies for synthetic resin adhesives deeply shocked the woodworking industry. This was especially significant because by 1973 about 70% of all wood products required gluing in one form or another. Thus, the threat to existing markets was very real and very large. Wood product manufacturers reacted to this crisis by seeking immediate alternatives wherever possible. In many cases, the older natural adhesives were still available, were still approved by certifying agencies, and were again pressed into service. In other cases, such as the structural flakeboard, waferboard, and strandboard industries, no workable prior alternatives existed. For them, it was phenolic, isocyanate, or possibly amino resins, or nothing. The choices were to operate as efficiently as possible on a reduced basis or simply shut down, as a number of commodity woodworking plants did at that time.

The oil crisis of 1973 is long gone, of course, but the memory of it is indelibly stamped on the woodworking industry. What if there were another oil embargo or a sudden regional war? (Current events in the Middle East make this a distinct possibility.) Or simply, what is going to happen as world oil reserves become increasingly limited in the not-too-distant future, and the transportation/energy industries preempt the remaining supply? There are reassurances, to be sure, such as this recent statement from the April 1987 issue of *Business Month*:

Forget OPEC's \$18-a-barrel goal. European analysts say the price of oil will remain far below that for at least the next five years because of sluggish demand in the industrialized economies and the discovery of vast new reserves in South America, Western Europe and the Far East. "I'm talking about \$15 oil in the first half of the 1990's," says Rotterdam Analyst Walter Ten Brinck. Economists at the Paris-based International Energy Agency agree. Says one, "I can't see oil

above \$15 for a sustained period unless there's a major international crisis. And if that happens, we'll all have more to worry about than the price of oil."

Such indications of continuing oil supply and price allow us to believe that we can look forward to business as usual in the near-term future. However, both from the standpoint of interruptability and also eventual price and supply, the woodworking industry strongly favors current research into renewable raw materials and practical adhesive systems based upon them. This can be seen in the annual review of the USDA Forest Service's research budgets and projects by the National Forest Products Association's Committee on Research Evaluation. For the last 9 years this industry group has strongly and consistently recommended research into alternative wood-bonding systems based on renewable resources. Likewise, groups of woodworking companies have helped support academic research into new adhesive concepts and renewable raw material sources.

Suggested Research

The research emphasized by industry falls roughly into four categories. First, the recovery or production of today's synthetic resin raw materials directly from renewable resources or as byproducts in waste streams from industries that utilize renewable resources themselves, such as pulp and paper. Examples would be:

1. The recovery of phenol, cresols, and guaiacol by extraction from kraft pulping process black liquor.
2. The steam pyrolysis of kraft black liquor to yield specific phenolic compounds by thermal decomposition.
3. The extraction and possible chemical modification of resorcinol-acting compounds from a variety of tree barks, nut shells, and other natural residues which are high in appropriate tannins.
4. The production of methanol via selective fermentation or direct hydrogenation of carbon monoxide.
5. The oxidation of methane from a variety of natural sources to formaldehyde. (The world's atmosphere is gaining in methane content at the rate of 1% a year.)
6. The bulk extraction of hemicelluloses and pentosans from woody biomass and their conversion to furan compounds.
7. The direct fixation of atmospheric nitrogen and its conversion into ammonia, then urea, then melamine.

Some of these are existing –even classical– processes, but they all share a basis of renewable resource derivation. The list could go on. As a common denominator, the output in this research category is specific organic compounds for reaction into the synthetic adhesive polymers we know and use today. It is understood that the prices of chemical compounds derived from these sources will be substantially higher in most cases. However, organic chemical prices in general will be equally higher due to global limitations on access or supply of crude oil and natural gas.

The second category of industry-favored adhesive research involves synthetic resins of recognizable performance based on partial or total replacement of a critical petrochemical constituent such as phenol with a functional organic compound or residue derived from renewable sources. Examples here include:

1. The institution of fractionated or chemically modified lignin for part or all of the phenol in the synthesis of phenol-formaldehyde resins. This would particularly include the newer forms of lignin recovered with minimum structural alteration and also those representing virtually complete depolymerization to phenylpropane units.
2. The substitution of selected and possibly modified carbohydrates for part or all of the phenol in the synthesis of phenol-formaldehyde resins.
3. The reaction of isolated and probably functionalized tannins from natural sources with formaldehyde to yield low temperature-curing thermoset adhesives. These resins may be suitable for use alone or in combination with conventional resorcinol-formaldehyde or phenol-resorcinol-formaldehyde resins.
4. The incorporation of animal or vegetable protein constituents into phenolic resins to form exterior durable adhesives of fast-curing or special properties.
5. The creation of difunctional or multifunctional isocyanate molecules entirely based on renewable resource chemistry.
6. The development of useful adhesive compositions based on the interaction of isocyanate resins with natural polymers such as lignin, proteins, and carbohydrates.